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Carbon-13 Nuclear Magnetic Resonance Studies of Tricyclopropylaluminum, -gallium, and -indium

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^{13}C NMR studies have been carried out on tricyclopropylaluminium, -gallium, and -indium. The concentration and temperature dependence of the NMR spectra of the aluminum derivative have been interpreted in terms of a singlely bridged intramolecular bridge–terminal exchange process with activation parameters of $E_a^\ddagger = 12.4$ (2)kcal/mol, $\Delta H^\ddagger = 11.7$ (2)kcal/mol, and $\Delta S^\ddagger$ −13.1 (1.2) eu. Investigation of the ^{13}C spin–lattice relaxation times at low temperature and calculation of the relative spinning rates, ρ, of the cyclopropyl groups shows that the bridging cyclopropyl groups and the terminal cyclopropyl groups lying on the same side of the Al–C–Al–C rings rotate at the same rate, while the terminal groups on the opposite side rotate at 5–8 times this rate. This confirms the proposal that the low-temperature averaging process observed is a result of the variations in the rotation rate of the bridging cyclopropyl group and not from freezing the terminal cyclopropyl groups in different configurations. The study of the gallium and indium derivatives shows that their ^{13}C chemical shifts are highly dependent on temperature, concentration, and solvent. The measurement of the temperature and concentration dependence of these chemical shifts leads to the conclusion that these species are involved in an equilibrium between monomer and dimer and that the shift in the relative concentration of these two species leads to the observed changes in chemical shift. On this basis, equilibrium constants and enthalpies of dissociation have been calculated. The enthalpies of dissociation obtained for toluene solutions are 5.6 and 4.0 kcal/mol for the gallium and indium compounds, respectively.

Introduction

The mechanisms of group transfer and other reorganization processes in simple organometallic systems have been under investigation for many years. Much of the earlier work has been reviewed,[1-4] and it now seems clear that simple alkylaluminum dimers undergo bridge–terminal exchange via a dissociation process. A second bridge–terminal exchange mechanism involving a monobridged intermediate in which rotation about the bridge bond effects exchange has been suggested as the path in aromatic[5] and in the unsymmetrically bridged system μ-cyclopropyl-μ-methyl-tetramethyldialuminum.[7]

Another type of exchange process which only involves the rotation of a bridging or terminal group without group transfer has been observed with the best studied of these systems, that of the cyclopropylaluminum dimers. Oliver et al.[6-8] have reported that the cyclopropyl bridging group undergoes rotation both in the di-μ-cyclopropyl- and the μ-cyclopropyl-μ-methyl-tetramethyldialuminum molecules as indicated by the nonequivalence of the terminal methyl groups. To account for a similar observation in tricyclopropylaluminum dimer, Olah et al.[9] have proposed a different mechanism with the nonequivalence of terminal groups arising from fixed conformations for them with the assumption that the bridging groups continue to rotate freely. These findings appear to be inconsistent with one another. In order to clarify this inconsistency, to explore the bridge–terminal exchange of the cyclopropyl groups (which had not been previously done because of the complexity of the ^1H NMR spectra), and to extend these studies to the gallium and indium derivatives, we have carried out an extensive ^{13}C NMR study of these systems.

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Experimental Section

All laboratory manipulations involving the synthesis and sample preparation of air-sensitive compounds were performed in an argon-filled drybox or in a high vacuum system (10^{-5} torr or less). The drybox was a Vacuum Atmosphere Drilab equipped with an HE-493 Dritrain. All solvents were dried over $LiAlH_4$ or CaH_2 and degassed on the vacuum system.

Preparation Compounds. Dicyclopropylmercury. Dicyclopropylmercury was synthesized by the method of Reynolds[11] from the cyclopropyl Grignard reagent and mercuric chloride in tetrahydrofuran. Following the normal workup, the dicyclopropylmercury was vacuum distilled with the fraction collected from 96 to 98 °C at ~8 mm (lit. value 110–112 °C at 18 mm) was used. The ^{13}C NMR spectrum of a 20% soluion in benzene-d_6 (v/v) consists of two peaks, each with mercury satellites: 32.1 ppm (d, $^1J(^{13}C–^1H)$ = 153.9 Hz, $^1J(^{13}C–^{199}Hg)$ = 1097.6 Hz), 2.6 ppm (t, $^1J(^{13}C–^1H)$ = 161 Hz, $^2J(^{13}C–^{199}Hg)$ = 19.5 Hz).

Tricyclopropylaluminum Dimer. Tricyclopropylaluminum was synthesized by the direct reaction of aluminum dust (~5-fold excess) with neat dicyclopropylmercury (0.01 mol) by the procedure of Sanders.[6,10,12] The reactants were placed in a tube which was then attached to the vacuum system, evacuated, and sealed. The reaction tube was heated in an oil bath to 75 °C for 1 week. It was then taken to the drybox where it was opened, and the solid transferred to vacuum sublimator and sublimed at 50 °C and 10^{-6} torr; yield 95%. Tricyclopropylaluminum is a white crystalline solid (mp ~60 °C). The ambient-temperature ^{13}C NMR spectrum in toluene-d_8 consists of four peaks at δ_c 12.4, 1.6, –10.7, and –15.2 calculated relative to Me_4Si.

Tricyclopropylgallium. Tricyclopropylgallium was synthesized by metal exchange between gallium metal and dicyclopropylmercury.[12] The reaction was carried out by placing gallium metal (~3-fold excess) in a reaction vessel (simply a long tube with a standard taper joint and a constriction) and then adding the dicyclopropylmercury (0.01 mol) to this vessel. The apparatus was then evacuated, sealed at the constriction, and placed in a 65 °C oil bath for 2 weeks. The sealed vessel was removed and transferred to an argon drybox where it was opened, and the liquid above the gallium amalgam was transferred to an inverted Y-vessel used for distillation. The crude material was distilled at ~70 °C (10^{-6} torr). Tricyclopropyl gallium is a clear, colorless liquid (mp ~15 °C). Yields were essentially quantitative. The ^{13}C NMR spectrum consists of two peaks corresponding to the α- and β-carbon atoms with chemical shifts which show strong concentration, temperature, and solvent dependence as discussed below.

Tricyclopropylindium. Tricyclopropylindium was synthesized in an analogous manner from the reaction of indium metal (3-fold excess) and dicyclopropylmercury (0.01 mol). After 1 week of reaction at 70 °C, the viscous liquid above the indium amalgam was distilled at 80 °C (10^{-6} torr), yield 93%. Tricyclopropylindium forms large clear crystals, mp ~30 °C (lit.[12] value 33–34 °C). The ^{13}C NMR spectrum consists of two peaks with a strong concentration, temperature and solvent dependence as discussed below.

Preparation of NMR Samples. All NMR samples were prepared in the drybox by weight, with the material diluted to the desired concentration in a volumetric glassware with predried solvent. Each sample was transferred to an NMR tube fitted with a standard taper joint, capped with a stopcock, transferred to the vacuum system, and degassed by successive freeze–pump–thaw cycles. The sample was then sealed. All samples made in deuterated solvents were in 10-mm NMR tubes, while 8-mm NMR tubes were used for non-deuterated solvents so that they could be used coaxially in a 10-mm tube containing deuterated solvent.

Determination of NMR Spectra. ^{13}C NMR spectra were determined at 15 MHz on a JEOL FX-60 spectrometer or at 75 MHz on a Nicolet NT-300 spectrometer. Unless otherwise specified, all spectra were broad-band proton decoupled. Chemical shifts were assigned relative to internal solvent peaks as follows: toluene-d_8, 20.4 ppm; cyclopentane, 25.6 ppm.

T_1 measurements were made by using the standard inversion–recovery techniques.[13] For the infinity spectra, t was equal to at least 5 times the T_1 value. The standard deviations quoted are for the least-squares fit of a particular data set. All T_1 values were reproducible within 10%.

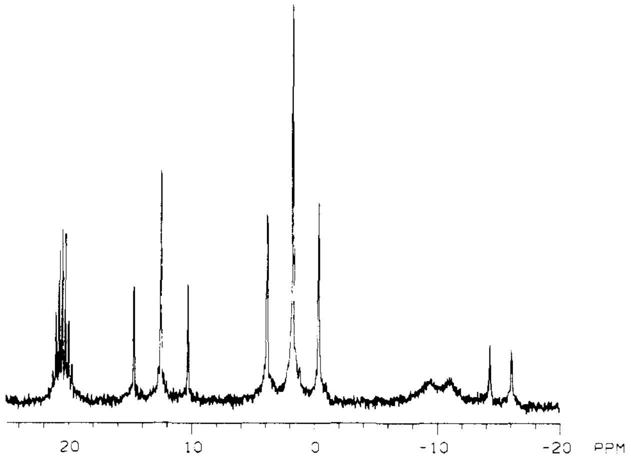

Figure 1. The 75-MHz ^{13}C NMR spectrum of a 0.2 M solution of tricyclopropylaluminum dimer in toluene-d_8 at 30 °C with proton coupling.

Temperature Calibration. FX-60. Temperature control of the sample with the FX-60 was achieved by using the standard JEOL temperature controller. The temperature at the sample was read by using a copper–constantan thermocouple inserted in an NMR tube which was maintained in the probe until a constant reading was achieved, and then the sample was transferred to the probe and allowed to equilibrate for a minimum of 30 min. After the spectrum was run, the temperature was read again. If this temperature was not within 1° of the initial reading, the spectrum was rerun.

NT 300. The Nicolet NT-300 uses the standard Nicolet temperature controller under NIC-1180 software control. Experience with this spectrometer has shown that the actual temperature at the sample is highly reproducible over a wide range of temperatures and nitrogen flow rates. This can be seen very clearly when the spectra of samples containing chemically exchanging systems which are strongly temperature dependent are compared. Spectra run on the sample at the same nominal temperature at exactly reproducible. To estimate the real sample temperature, a solution of Me_4Si/methyl iodide in the ratio of 1:3 was run over the range of +1 to –60 °C. Vidrine and Peterson's relationship[14] was then used to obtain a calibration curve for the sample temperature for the ^{13}C probe.

Determination of Exchange Lifetimes from NMR Spectra. The exchange lifetimes of particular species undergoing chemical exchange were determined by NMR line-shape analysis methods. Theoretical spectra generated from a line-shape equation were compared to the experimental spectra and the parameters alternatively changed until an acceptable fit was achieved.

The solution of the Bloch equation based on the McConnell modification[15] for the uncoupled AB system as derived by Carlson[16] was used. This had previously been adapted by Crotty[17] as a FORTRAN subroutine for use by the nonlinear least-squares fitting routine KINFIT.[18,19] Initial estimates were required for the difference between the two peaks, the rate constant, the equilibrium constant, the center of the peaks, and an experimental scale factor. The lifetimes of the two sites in the absence of exchange were used as parameters, although wide variations in these values had little or no effect on the final values for exchange lifetimes. The nonlinear least-squares program KINFIT was then used to alternately vary the parameters until a fit between the calculated and experimental spectra was achieved.

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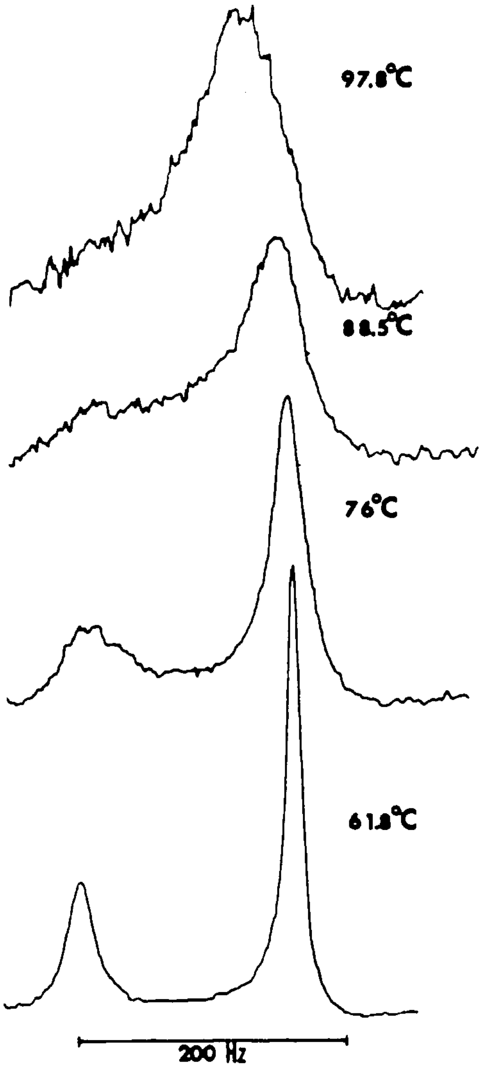


Figure 2. Temperature dependence of the 15-MHz $^{13}C\{^1H\}$ NMR spectrum of tricycloproylaluminum dimer in toluene-d_8. Only the lines associated with the bridging and terminal β-carbon atoms are shown.

Results and Discussion

The ^{13}C NMR spectra of tricyclopropylaluminum dimer with proton coupling is shown in Figure 1. The ambient-temperature spectrum consists of two triplets and two doublets with chemical shifts of δ_c 12.4, 1.6, −10.7, and −15.2, which corresponds to β-bridging, β-terminal, α-terminal, and α-bridging carbon atoms, respectively. The assignments of the α- and β-carbon atoms are unambiguous from the splitting observed. The bridge and terminal assignments are also quite certain from their relative intensities, from their relaxation behavior, and, also, are consistent with the assignments made by Olah et al.[9]

In earlier studies it was established that bridge–terminal exchange occurred, but no quantitative studies were carried out due to the complexity of the proton spectra.[10] The $^{13}C\{^1H\}$ NMR spectra cause no such difficulties and a typical series of spectra, as a function of temperature, for the β-carbon atoms is shown in Figure 2 with coalesence observed at ~88 °C (15 MHz) in toluene. Only the β-carbon atoms were used in this analysis because of their greater signal/noise ratio and to eliminate any possible interference from aluminum quadrupolar interaction which could alter the relaxation times of the α carbon atoms. Coalesence could not be observed below the boiling point of the solvent at 75 MHz as a result of the 5-fold increase in the frequency difference between the lines.

Table I. Tricyclopropylaluminum Dimer Bridge–Terminal Exchange Rates vs. Temperature and Concentration

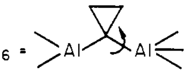
M[a]	temp, °C	rate,[b] s^{-1}
0.49	61.8	75
	76	180
	80	230
	84.5	260
	87	267
	88.5	324
	93.5	377
	97.8	486
0.345	71	100
	81	203
	90	335
	92	350
0.2	73.5	125
	78	172
	81.5	207
	83	217
	87	272
	98.5	434
0.173	71	141
	81	226
	90	310
	92	385
0.12	76	165
	81	188
	86	209
0.034	71	121
	90	262

[a] Based on dimer in toluene-d_8. [b] $1/\tau_b$ is the lifetime of the cyclopropyl group in the bridging site.

Each spectrum, both as a function of temperature and concentration, was analyzed by the procedures described in the Experimental Section with the data collected in Table I. These data show no significant dependence of the lifetime on the concentration which implies a first-order reaction in dimer. This observation is consistent with either of the two mechanisms shown in eq 1 and 2 which

$$Al_2(c\text{-}C_3H_5)_6 = 2Al(c\text{-}C_3H_5)_3 \qquad (1)$$

$Al_2(c\text{-}C_3H_5)_6$ =



(2)

correspond to a dissociative process and to a simple bridge opening with rotation, respectively. Other mechanisms may be postulated but have been previously rejected as improbable for a variety of reasons.[1,2] The difference between the two proposed paths is apparent only in a detailed examination of the rate equations which leads to the expressions for the first-order rate constants of $k_1 = {}^3/_2\tau_b^{-1}$ and $k_1 = 3\tau_b^{-1}$ for the dissociative and bridged intermediate pathways, respectively, and does not permit an experimental test to be made between these two paths. Therefore, distinction between the two possible pathways must be made on the basis of other information and may not lead to a decisive choice.

The activation parameters for the process were obtained from the Arrhenius expression

$$\text{rate} = A \exp(-E_a^{\ddagger}/RT) \qquad (3)$$

and from the Eyring equation

$$\ln (k/T) = \ln (k_B/h) + \Delta S^{\ddagger}/R - (\Delta H^{\ddagger}/RT) \qquad (4)$$

The latter expression leads to slightly different values for the entropy of activation between the two mechanisms as a result of the differences in the rate expressions. The results of these calculations are given in Table II. The values of $E_a^{\ddagger}$ and $\Delta H^{\ddagger}$ are quite low when compared to the

Table II. Activation Parameters for Tricyclopropylaluminum Bridge–Terminal Exchange

M[a]	$E_a^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger\,b}$	$\Delta S^{\ddagger\,c}$
0.49	12.4 ± 0.2	11.6 ± 0.2	−13.1 ± 1.4	−14.5 ± 1.4
0.345	13.9 ± 0.8	13.2 ± 0.8	−9.1 ± 6.6	−10.2 ± 6.6
0.2	11.5 ± 0.5	10.8 ± 0.5	−15.8 ± 4.0	−17.2 ± 4.0
0.173	11.2 ± 0.5	10.6 ± 0.5	−16.2 ± 3.9	−17.6 ± 3.9
0.12	5.8 ± 0.06	5.2	−32	−33
0.034	10.1	9.4	−20	−21
overall	12.4 ± 0.2	11.7 ± 0.2	−13.1 ± 1.2	−14.5 ± 1.2

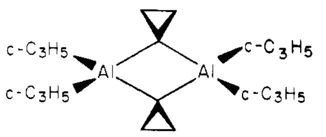
[a] Based on dimer in toluene-d_8. [b] Eu for open-intermediate mechanism. [c] Eu for dissociative mechanism.

simple alkylaluminum derivatives such as Al_2Me_6, while the entropy of activation is reasonably large and negative, in constrast to the generally positive values associated with the dissociative mechanisms.[1,2] These values are consistent with those obtained for the bridge–terminal exchange observed in μ-methyl-μ-(diphenylamino)-tetramethyldialuminum and also are consistent with the parameters obtained from the tolyl-bridged dimers which are thought to proceed through a single-bridged mechanism.[5] In addition, relatively low E_a^{*} and ΔH^{*} values are inconsistent with a full dissociation assuming that the cyclopropyl groups form a more stable Al–C–Al bridge than do simple saturated alkyls.

On the basis of these considerations we, therefore, concluded that the most probable mechanism for the bridge–terminal exchange in tricyclopropylaluminum dimer is that indicated in eq 2, with only a single bridge opened during the course of the reaction. This exchange reaction then constitutes a second example, along with the tolyl-bridged system,[5] where there are identical bridging moieties in which bridge–terminal exchange occurs without complete dissociation.

Tricyclopropylaluminum Dimer Bridge Rotation. In addition to the high-temperature bridge–terminal exchange, there is a second, much faster, averaging process which leads to splitting of the lines associated with both the α- and β-carbon atoms of the terminal groups. This may be seen clearly in Figure 3. This had previously been observed for tricyclopropylaluminum,[6,9,10] for di-μ-cyclopropyl-tetramethyldialuminum[6,8] and for μ-cyclopropyl-μ-methyl-tetramethyldialuminum.

This intramolecular averaging process has been interpreted in two ways. The first interpretation, proposed for the methyl-substituted derivatives, was based on the analysis of temperature-dependent NMR studies and was on the assumption that the bridging cyclopropyl groups were free to rotate at elevated temperatures, but that this rotation slowed at lower temperatures, with these groups ultimately remaining in the syn configuration at very low temperatures as observed in the solid state.[8,20] The structure and views of the two conformations are shown in I–III. The exchange process is consistent with the observed experimental data and is supported by calculations of the barrier to rotation for the bridging group between the syn and anti conformations.[6,8] The second mechanism proposed for this averaging process is based on the assumption that the bridging cyclopropyl groups are free to rotate even at low temperatures while the terminal groups become fixed in a specific conformation under these conditions.[9] This path is consistent with the observations reported for tricyclopropylaluminum dimer, providing that the set of assumptions made is correct but in no case can it account for the nonequivalence of the terminal methyl groups in di-μ-cyclopropyl- or μ-cyclopropyl-μ-methyl-tetramethyldialuminum.



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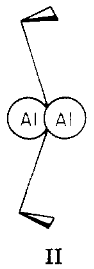

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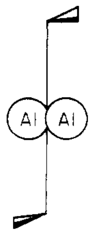

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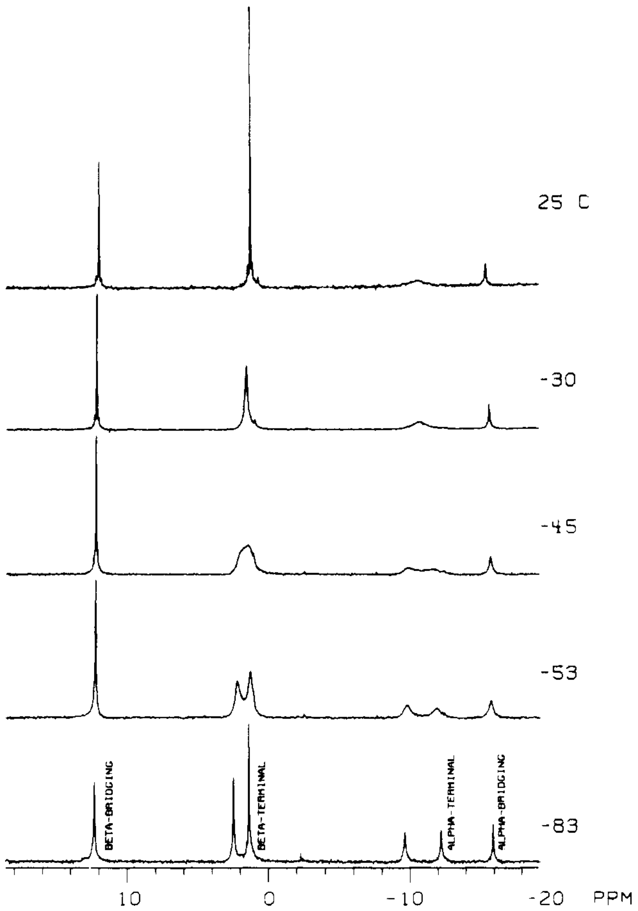

Figure 3. The temperature dependence of the 75-MHz $^{13}C\{^1H\}$ NMR spectrum of a cyclopentane solution of tricyclopropylaluminum dimer. Assignments are given from left to right in the −83 °C spectrum with two lines assigned to the β terminal and α terinal groups.

In an effort to clarify this situation and to determine if there are two different averaging processes occurring, a study of the ^{13}C spin–lattice relaxation times has been carried out, since these relaxation times may be related to the molecular tumbling and internal rotational motion of molecules.[21,22] The relaxation of ^{13}C nuclei may result from a number of mechanisms, but for nuclei directly bonded to protons, ^{13}C–^1H dipole–dipole relaxation is usually predominant. For isotropic tumbling of the molecule, the relaxation time will be a function of a rotational correlation time. If, however, rotational reorientation is anisotropic or if internal motion must be considered, an additional correlation time for the internal

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Table III. ^{13}C Spin-Lattice Relaxation Times for Tricyclopropylaluminum Dimer as a Function of Temperature[a]

temp, °C	T_1 relaxatn times, s (% T_1^{DD})					
	β_b	β_t		α_t		α_b
30	1.78	1.84		*b*		*b*
−42	0.26 (100)	0.39 (96)		0.76 (61)		0.50 (126)
−50	0.16	0.19[c]	0.29[d]	0.34[c]	0.80[d]	0.35
−55	0.16 (89)	0.18[c] (92)	0.32[d] (101)	0.36[c] (89)	0.62[d] (83)	0.30 (83)
−67	0.14	0.16[c]	0.32[d]	0.28[c]	0.66[d]	0.32
−70	0.10	0.12[c]	0.22[d]	0.19[c]	0.50[d]	0.19

[a] At 15MHz. [b] Not measured at this field strength due to low signal/noise for these broad peaks. [c] Downfield peak. [d] Upfield peak.

motion of the group also must be included. This fact permits assignments of relative rotation rates to be made for internal motions in a molecule. The efficiency of a given internal rotation in shortening the overall effective correlation time (and lengthening T_1) for a given carbon is governed by the angle, θ, between the C–H bond vector and the preferred rotational axis.

Allerhand[23] has derived an expression to evaluate T_1^{DD} as a function of three parameters: (1) the overall reorientation correlation time, (2) the internal motion correlation time, and (3) the angle, θ, between the C–H bond vector and the internal rotational axis. Thus, for a given system, if the following two conditions hold, (1) the ^{13}C T_1 relaxation is via the dipole–dipole mechanism and (2) θ can be defined, then the T_1 relaxation times will provide information about molecular tumbling and internal rotation.

For the terminal cyclopropyl rings in tricyclopropylaluminum dimer, the angle between each of the carbon–proton vectors and the α-carbon–aluminum bond (about which rotation would take place) is constant. Each of the carbon–proton vectors will undergo reorientation from two sources: (1) the overall isotropic tumbling of the molecule and (2) the internal rotation of the cyclopropyl group about the carbon–aluminum bond. However, the overall tumbling of the molecule will be constant for all of the nuclei. Therefore, the T_1^{DD} will provide a means of directly comparing the rotations of the various cyclopropyl groups. The ^{13}C T_1 relaxation data are summarized in Table III.

To confirm the assumption that the relaxation is predominantly dipole–dipole, the nuclear Overhauser effect (NOE) was also determined at several temperatures. The percentage of the dipole–dipole mechanisms, where measured, is in parentheses. As is typical of this experiment, there is a large degree of error in these numbers. However, at least for the β-carbon atoms, the dipole–dipole mechanism appears to be nearly the sole relaxation mechanism. For the α-carbon atoms at low temperature the NOE is constant, indicating at least an equivalent contribution from the dipole–dipole mechanism for all of the α-carbon atoms.

Despite possibly large errors in the T_1 values, several observations may be made. First of all the T_1 values obtained for the α- and β-carbon atoms in a given ring from the low temperature data show that the relaxation behavior of the individual groups are in the approximate ratio of 2:1 as predicted from the relative numbers of directly bonded protons at each site with the assumption that there are no differences in the reorientation, either isotropic tumbling or internal rotation, between the α- and β-carbon atoms on a particular cyclopropyl ring. This further supports that the ^{13}C–^1H dipole–dipole mechanism as the predominant mechanism for relaxation of both the α- and β-carbon atoms.

Table IV. Cyclopropyl Ring Rotation Ratios for Tricyclopropylaluminum at Low Temperatures

temp, °C	α_t[b] T_1, s	$T_1(t)/T_1(b)$	ρ[a]	α_t[c] T_1, s	$T_1(t)/T_1(b)$	ρ[a]
−50	0.34	0.97	1	0.80	2.3	6
−55	0.36	1.2	2	0.62	2.1	5
−67	0.28	0.9	1	0.66	2.1	5
−70	0.19	1.0	1	0.50	2.6	8

[a] Ratio of rates of rotation of terminal group to bridging group as calculated from T_1 ratios.[24] [b] Downfield peak. [c] Upfield peak.

Of far more importance, is the fact that the relaxation times for the α- and β-carbon atoms in the bridging and the downfield terminal cyclopropyl groups are approximately the same, whereas these for the upfield cyclopropyl groups are about double these values. This implies that there are significant differences in the rotational rates of the two types of terminal groups and that one class of terminal groups has relaxation behavior similar to that of the bridging units.

In an effort to quantify these relationships, Levy,[24] making use of Allerhand's relationship[23] for evaluation of T_1^{DD}, has calculated the spinning ratio, ρ, as a function of the T_1 ratio for a variety of angles between the C–H vector and the axis of rotation. In the present system, the T_1 ratio between the bridging α-carbon atoms and the downfield terminal α-carbon atom is approximately 1, while the ratio between the bridging and terminal T_1 values for the upfield peak ranges between 2.1 to 2.6 and the angle between the C–H vector and the carbon–aluminum bond for the terminal α-carbons of tricyclopropylaluminum dimer is approximately 60° (60° assuming idealized sp^2 geometry or 56.9° based on the H–C–H angle in cyclopropane[25]). With use of Levy's calculations for 60°, ρ can be estimated as 1 between the bridging and downfield (α-carbon atom) terminal group and in the range of 5–8 for the upfield group (Table IV).

Thus, there is a significant difference in the rates of rotation of the two sets of terminal groups of tricycloaluminum dimer at low temperature with the bridging group rotating at a rate approximately equal to that of the slower group. These observations lead to several conclusions. (1) Olah et al.[9] misinterpreted these data in terms of the process leading to the magnetic nonequivalence of the terminal groups. (2) The predominant form in solution at low temperatures is the syn conformation, similar to that in the solid state. (3) The terminal group which give rise to lines at 2.51 and −9.65 ppm is the group on the same side as the bridging cyclopropyl group and undergoes hindered rotation as a result of this. The group giving rise to lines at 1.39 and −12.47 ppm is on the opposite side of

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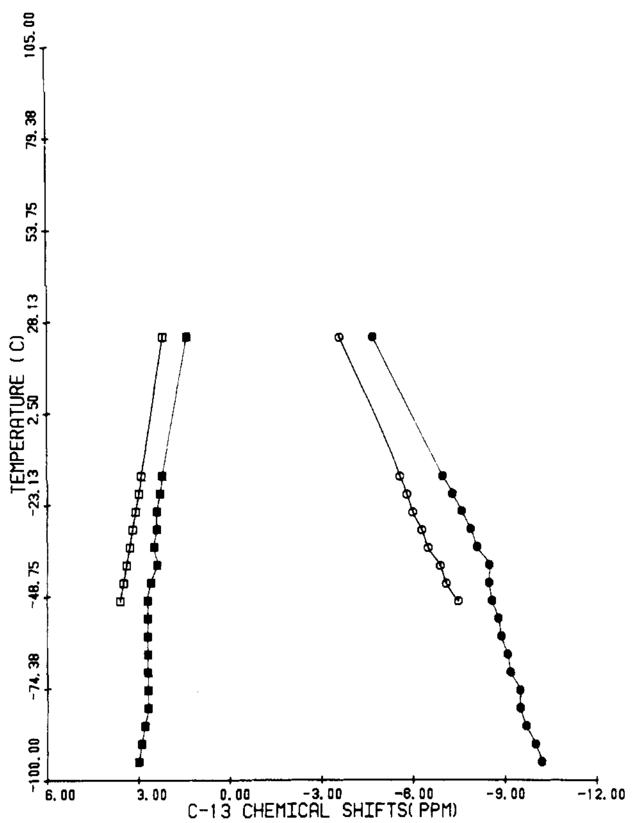

Figure 4. The temperature dependence of the chemical shifts of both the α- and β-carbon atoms of tricyclopropylgallium in cyclopentane and toluene solutions: 1.4 M in cyclopentane, β-carbon atom (■) and α-carbon atom (●); 1.4 M in toluene-d_8, β-carbon atom (□) and α-carbon atom (○).

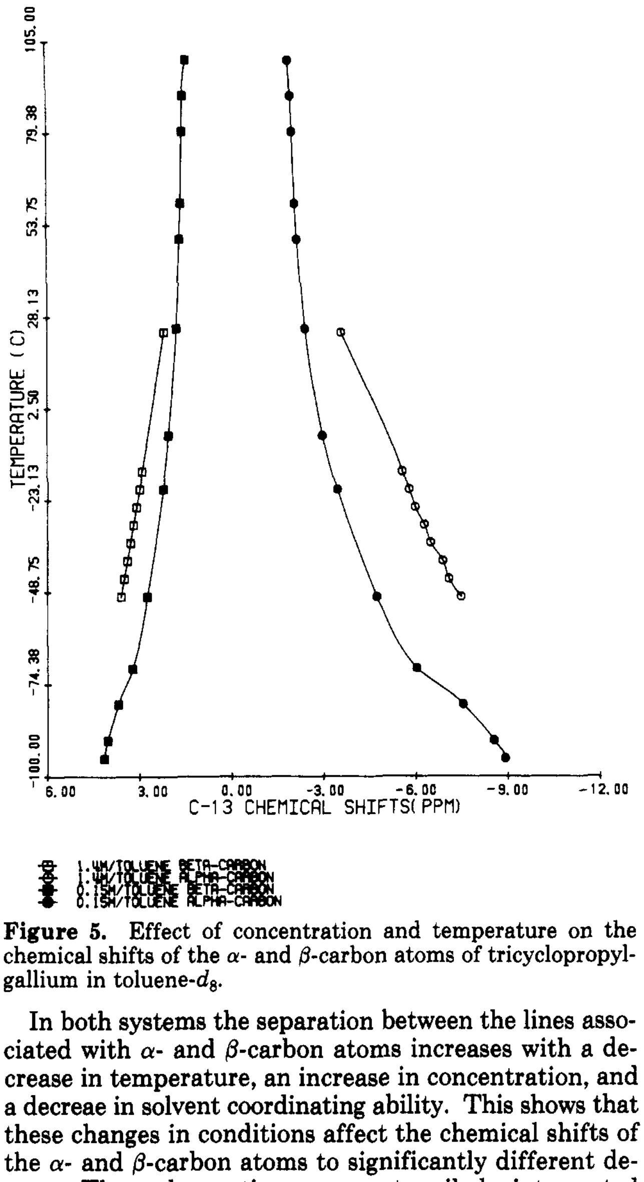

Figure 5. Effect of concentration and temperature on the chemical shifts of the α- and β-carbon atoms of tricyclopropylgallium in toluene-d_8.

the molecule in a less hindered site with the groups rapidly rotating even at low temperature. (5) Despite the steric interactions which lead to differentiation between the rotational rates of the various groups, the cyclopropyl group forms a very stable bridged dimer.

Tricyclopropylgallium and -indium. In general, the heavier group 3 metals have less tendency to form higher aggregation states via electron-deficient bonding than aluminum with the only confirmed dimeric species, trivinylgallium[27,28] and the phenylethynyl derivatives of both gallium[29] and indium.[30] Even the phenyl derivatives of gallium and indium are monomeric in the solid state.[31] Thus, the earlier indication, based on limited cryoscopic data, that the tricyclopropylgallium and -indium derivatives were slightly associated[12] is of particular interest since it would serve as an indication of the stability of the metal–cyclopropyl–metal bridge as compared to other bridging units.

The $^{13}C\{^1H\}$ spectra of both tricyclopropylgallium and -indium consist of only two peaks, corresponding to the α- and β-carbon atoms even at low temperatures. This indicates that either of these derivatives consist only of monomer or of some monomer–dimer mixture with rapid interchange of groups under all conditions studied. Examination of the chemical shifts of both the α- and β-carbon atoms in the gallium and indium derivatives as a function of concentration, temperature, and solvent as seen in Figures 4, 5, and 6 shows each of these factors causes major changes on the chemical shift values.

In both systems the separation between the lines associated with α- and β-carbon atoms increases with a decrease in temperature, an increase in concentration, and a decreae in solvent coordinating ability. This shows that these changes in conditions affect the chemical shifts of the α- and β-carbon atoms to significantly different degrees. These observations can most easily be interpreted in terms of a monomer–dimer equilibrium in which the cyclopropyl groups are undergoing rapid exchange between different metals and different sites.

With the assumption of a monomer–dimer equilibrium, with rapid exchange on the NMR time scale, then the chemical shift of the carbon atoms at any given time will be a weighted average of three sites: monomer (δ_m), dimer bridging (δ_{db}), and dimer terminal (δ_{dt}). If the monomer is similar to the dimer-terminal groups and the terminal and bridging groups behave in the same manner as they do in tricycopropylaluminum dimer, then the observed changes in chemical shift would correspond to increases in dimer concentration with increasing concentration, decreasing temperature, and decreasing interaction.

An alternative explanation for the observed changes in chemical shift might involve some type of specific complex formation between the solvent molecule and the monomer such as that reported for trimethylgallium in benzene, with an enthalpy of formation of the complex of 2.8 (0.15) kcal/mol.[32] This does not, however, appear to explain the results of the present study since similar results were obtained in both cyclopentane and toluene, and the concentration dependence cannot be accounted for through this approach.

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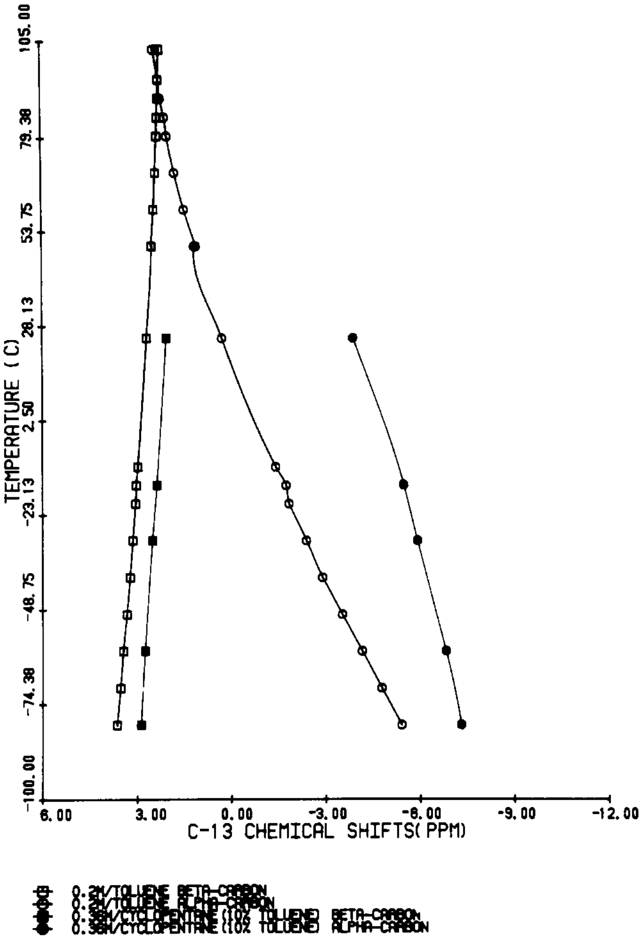

Figure 6. The temperature and solvent dependence of the chemical shifts of the α- and β-carbon atoms of tricyclopropylindium.

Since the tricyclopropylgallium and -indium derivatives represents the first cases in which formally saturated groups appear to provide sufficiently strong bridging units to lead to dimer formation with these metals, we have attempted to provide a more quantitative description of these systems. This has been done by analyzing the change in the chemical shifts as a function of temperature and of concentration.

The change in chemical shift of the cyclopropyl groups with temperature is assumed to result from a change in the relative populations of the groups among different magnetically nonequivalent sites in the monomer–dimer equilibrium. Higher aggregation states such as trimers or tetramers cannot be rigorously excluded, but there is no evidence for these in the group 3 metal–carbon-bridged systems.

The concentration of the dimer [D] and the monomer [M] may be expressed as $[D] = (C - x)$ and $[M] = 2x$ where C is the initial concentration, assuming all dimer, and x is the amount of dimer dissociated. The general expression for the observed chemical shift of a rapidly exchanging system is then given by the mole fractions of the specific sites times their nonexchange chemical shifts.

$$\delta_{\text{obsd}} = (1/6C)[6x(\delta_{\text{m}}) + 4(C - x)(\delta_{\text{dt}}) + 2(C - x)(\delta_{\text{db}})] \tag{5}$$

There are two limiting cases for this expression. As the dissociation, x, goes to zero, i.e., all dimer, then

$$\delta_{\text{obsd}} = \tfrac{2}{3}(\delta_{\text{dt}}) + \tfrac{1}{3}(\delta_{\text{db}}) \tag{6}$$

or as x approaches C, i.e., all monomer, then

$$\delta_{\text{obsd}} = \delta_{\text{m}} \tag{7}$$

Table V. Association Constants vs. Temperature for 0.15 M Tricyclopropylgallium in Toluene

temp, °C	chem shift,[a] ppm	K_{eq}[b]
105	−1.9	4.12×10^{-3}
95	−2.0	4.65×10^{-2}
85	−2.0	4.65×10^{-2}
65	−2.1	9.10×10^{-2}
55	−2.2	1.38×10^{-1}
30	−2.4	2.38×10^{-1}
0	−3.0	6.12×10^{-1}
−15	−3.5	1.03
−45	−4.8	2.91
−65	−6.0	6.94
−75	−7.5	2.43×10
−85	−8.5	7.94×10
−90	−8.9	1.57×10^{2}

[a] α-Carbon. [b] Defined as $K_{\text{eq}} = [\text{dimer}]/[\text{monomer}]^2$; calculated using upper chemical shift limit = −1.89 ppm and lower chemical shift limit = −10.0 ppm.

Table VI. Association Constants for Tricyclopropylgallium and Tricyclopropylindium

concn	solvent	source of data	K_{eq}[a]
	Tricyclopropylgallium		
0.15 M	toluene	β-carbon	0.58
		α-carbon	0.24
1.4 M	cyclopentane	β-carbon	2.1×10^{-3}
		α-carbon	0.12
1.4 M	toluene	β-carbon	0.12
		α-carbon	0.11
	Tricyclopropylindium		
0.2 M	toluene	β-carbon	2.1
		α-carbon	0.88
0.36 M	cyclopentane/ 10% toluene	β-carbon	0.17
		α-carbon	0.27

[a] At 30 °C.

Table VII. Enthalpies of Dissociation for Tricyclopropylgallium and Tricyclopropylindium

concn	solvent	enthalpies of dissociatn, kcal/mol: α-carbon	β-carbon
	Tricyclopropylgallium		
0.15 M[a]	toluene-d_8	5.9 ± 0.4	5.2 ± 0.5
1.4 M	toluene-d_8	5.6 ± 0.2	5.6 ± 0.08
1.4 M	cyclopentane	5.7 ± 0.3	6.3 ± 0.9
	Tricyclopropylindium		
0.2 M	toluene-d_8	4.0 ± 0.1	3.9 ± 0.09
0.36 M	cyclopentane/ 10% toluene	3.9 ± 0.5	6.0 ± 0.6

[a] Based on monomer.

Values for these cases can be estimated from the experimental spectra if two assumptions are made. (1) At low temperature the dissociation approaches zero, making the observed chemical shift equal to that in eq 6. (2) At high temperature the dimer is completely dissociated and the observed shift is that of the monomer. Letting the average chemical shift for the dimer equal δ_{d}, then eq 5 becomes

$$\delta_{\text{obsd}} = [(\chi/c)(\delta_{\text{m}} - \delta_{\text{d}})] + \delta_{\text{d}} \tag{8}$$

Thus, from an estimate of the low- and high-temperature chemical shift limits and from the observed chemical shift at any given temperature, the degree of dissociation and equilibrium constant may be calculated.

If the further assumptions are made that the solution behaves ideally and that the change in enthalpy for the

Table VIII. ^{13}C Chemical Shifts of Triorganoaluminum Compounds with a Comparison to the Parent Hydrocarbon

	^{13}C chem shifts[a]					
	bridging			terminal		
R group	α	β	γ	α	β	γ
methyl[b]	−5.6			−8.2		
	(−3.4)[c]			(−6.0)		
ethyl[d]	0.5	8.2		0.0	9.4	
	(−5.0)	(1.7)		(−5.5)	(3.9)	
n-propyl[d]	13.5	18.4	20.3	12.5	19.5	21.2
	(−2.0)	(2.9)		(−3.0)	(4.0)	
tert-butyl[e]	...	...		26.3	30.5	
				(1.4)	(6.5)	
cyclopropyl[f]	−15.2	12.4		−10.7	1.6	
	(−11.8)	(15.8)		(−7.1)	(5.1)	

[a] Ppm relative to Me_4Si. [b] Reference 9. [c] Values in parentheses are defined as chemical shift of the compound minus the chemical shift of the parent alkane (chemical shifts of the alkanes from ref 22). [d] In toluene: Yamamoto, O.; Hayamiyu, K.; Yanagisawa, M. *J. Organomet. Chem.* **1974**, *73*, 17. [e] In benzene: Muller, H.; Rosch, L.; Erb, W. *Ibid.* **1977**, *140*, C17. [f] In toluene-d_8 (this work).

Table IX. One Bond Carbon-Proton Coupling Constants (Hz) for Group 3 Tricyclopropyl Compounds

	$^1J(^{13}C-^1H)$	
	β-carbon	α-carbon
Tricyclopropylindium[a]		
30 °C	160	148
103 °C	160	150
Tricyclopropylgallium		
30 °C		
1.4 M[b]	162	147
0.15 M[c]	162	148
Tricyclopropylaluminum[d]		
30 °C		
bridging	166	133
terminal	160	126
−78 °C		
bridging	166	133
terminal downfield	159	136
terminal upfield	159	131

[a] 0.2 M in toluene-d_8. [b] For both 1.4 M in toluene-d_8 and 1.4 M in cyclopentane. [c] In toluene-d_8. [d] 0.5 M in toluene-d_8.

dissociation is not a function of temperature, then

$$\ln K_{eq} = -(\Delta H/RT) + \text{constant} \qquad (9)$$

and an analysis of the chemical shift as a function of temperature yields an estimate of the enthalpy of dissociation.

A typical set of equilibrium constants as a function of temperature is shown in Table V for 0.15 M tricyclopropylgallium in toluene. Tables VI and VII give a summary of equilibrium constants for both the gallium and indium compounds and of their enthalpies of dissociation. The agreement obtained between different samples and from the calculations using both the α and β atom chemical shifts is quite good considering the number of assumptions made. This is especially true for the calculations using the β-carbon chemical shift because of the relatively small change in this value which make it particularly sensitive to the estimates used for the chemical shifts of monomer and dimer. Additional support for the values obtained comes from the previous obervation by Sanders[12] that 0.085 M solution of tricyclopropylgallium in cyclohexane at 6 °C was 8 (5%) associated. The present study gives an equilibrium constant of 0.33 at 6 °C or 5% association, clearly within the error limits of the experiment.

An examination of these data permit several conclusions to be drawn. First, the observed dissociation energies of 5.7 kcal/mol for tricyclopropylgallium and of 4.0 kcal/mol for tricyclopropylindium fall into the trend which one would expect with the increasing sizes of the metal atoms. Further, the value for the gallium derivative fits between the estimates made by Matteson,[4] who set an upper limit for the dissociation energy of trimethylgallium dimer of 5 kcal/mol (a compound which is monomer under the condition used in this set of studies) and that estimated by Oliver[33] for trivinylgallium of less than 10 kcal/mol (trivinylgallium is dimeric under these same conditions). Additional support for this range for the dissociation energies comes from examination of the alkylaluminum derivatives with dissociation enthalpies in solution of 16.3 kcal/mol for Al_2Me_6,[34] 12.5 kcal/mol for Al_2Et_6,[34] and 8.1 kcal/mol for $Al_2(i\text{-}Bu)_6$.[35] The first two of the derivatives are predominately dimeric at elevated temperatures, while the latter undergoes significant dissociation at room temperature, much as do tricyclopropylgallium and -indium.

A final point which is of some interest is the fact that no difference was noted between the equilibrium constants or dissociation energies obtained in cyclopentane and toluene solution. This implies that the often invoked solvent interaction in aromatic compounds has a small effect on these parameters which lies within the experimental error with the upper limit set from the studies on the $GaMe_3$–benzene system of ~2 kcal/mol.[32]

^{13}C Chemical Shift Values. The ^{13}C chemical shifts of a number of aluminum derivatives are collected in Table VIII along with the relative chemical shifts of these groups from the parent alkane. These data show that the cyclopropyl group is particularly sensitive to the influence of the aluminum atom, with the α-carbon atoms more deshielded than for any of the other examples. Further, the chemical shift difference between the α- and β-carbon atoms of the bridging group of 27.6 ppm is far greater than that (12.2 ppm) observed between the α- and β-carbons in the terminal group. Whereas for the saturated derivatives the $\Delta\delta$ values between α- and β-carbon atoms on the bridging and terminal groups is far less. For example, in triethylaluminum dimer, the differences are 6.7 and 9.4 ppm and in tri-*n*-propylaluminum dimer these values are 4.9 and 7.0 ppm, respectively. This is what would be anticipated from the interaction of the cyclopropyl ring with the nonbonding orbitals on aluminum leading to the sttabilization of the bridged unit.[6]

This same type of interaction may be implied for the gallium and indium derivatives from the marked chemical shift changes associated with dimer formation. However, quantitative information on this is unavailable since the independent chemical shifts for the bridging and terminal groups could not be obtained because of the rapid exchange processes.

Examination of Table IX which lists the $^{13}C-^1H$ coupling constants for the tricyclopropylmetal derivatives provides some additional information. These data show that C–H coupling constants for the β-carbon–hydrogen pair are essentially uneffected by the metal or by the position of the ring in the dimeric molecules. The α-carbon–proton

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coupling is significantly altered by the metal, decreasing in absolute value with decreasing electronegativity of the element with the $^1J(^{13}C-^1H)$ values in the order In > Ga > Al.

There is essentially no difference observed between the coupling constants for the bridging and terminal cyclopropyl groups in dimeric tricyclopropylaluminum. Thus, further supporting the proposed mode of stabilization of the bridge bond in these tricyclopropylmetal derivatives through the interaction of the nonbonding metal orbitals with the p orbitals of the α-carbon atom. These interactions would leave the s orbitals essentially unperturbed should not effect the $^{13}C-^1H$ coupling to any great extent.

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Metal Carbonyl Anion Generation Using Potassium Fluoride or Tetrabutylammonium Fluoride

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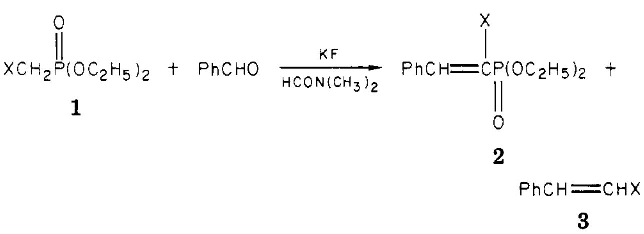
Received September 14, 1981

Triiron dodecacarbonyl reacts with dry potassium fluoride and commercial 18-crown-6, in tetrahydrofuran, to give the hydridoundecacarbonyltriferrate anion. The latter is also efficiently produced from $Fe_3(CO)_{12}$ and a 1 M solution of tetrabutylammonium fluoride. The quarternary ammonium fluoride can catalyze the reduction of nitrobenzenes to anilines by either $Fe_3(CO)_{12}$ or $Mn_2(CO)_{10}$. While $Co_2(CO)_8$ and $Co(CO)_3NO$ react with tetrabutylammonium fluoride, the resulting species are incapable of reducing nitrobenzene but can carbonylate 2-(bromomethyl)naphthalene.

Numerous publications have appeared in recent years on the utilization of fluoride ion as a base[2] and as a nucleophile[3] in organic synthesis. The fluoride used in these reactions is usually in the form of potassium fluoride or tetraalkylammonium fluorides.

There are many examples illustrating the ability of 18-crown-6 to solubilize potassium fluoride in relatively nonpolar solvents, thereby generating so-called "naked" fluoride ion. However, the exceedingly hygroscopic nature of potassium fluoride, tetraalkylammonium fluorides, and crown ethers cannot be overemphasized. The presence of water can have a major influence on the course of a variety of reactions involving fluoride ion. An example is the reaction of a phosphonate (1, X = CN, $COOC_2H_5$) with benzaldehyde in *N,N*-dimethylformamide. In the presence of a small amount of "dry" potassium fluoride, the Knoevenagel product (**2**) is the major product with little of the Wittig–Horner adduct (**3**) being obtained. Crown ether can accelerate this reaction. The proportion of **3** increases when some (but not too much) water is present, with the highest yield of **3** being attained with $KF{\cdot}2H_2O$.[4]


$$XCH_2P(O)(OC_2H_5)_2 + PhCHO \xrightarrow[HCON(CH_3)_2]{KF} PhCH{=}C(X)P(O)(OC_2H_5)_2 + PhCH{=}CHX$$

1 **2** **3**

Liquid–liquid and solid–liquid phase-transfer catalysis is a useful technique in organometallic as well as in organic chemistry.[5] Crown ethers have been employed as catalysts for certain organometallic phase transfer processes, including the synthesis of ferrocenes[6] and bridging hydroxo complexes of platinum,[7] as well as the iron carbonyl induced reduction of nitroarenes to anilines.[8]

This paper describes the reactions of potassium fluoride and tetrabutylammonium fluoride with triiron dodecacarbonyl, dimanganese decacarbonyl, and several other metal carbonyls. Water plays a significant role in all of these reactions, with the facile generation of metal carbonyl hydrides being important in certain cases.

Results and Discussion

When triiron dodecacarbonyl was treated with an approximately equimolar amount of potassium fluoride and 0.25 equiv of "dry" 18-crown-6 in tetrahydrofuran, the solution remained intense green [$Fe_3(CO)_{12}$] after being stirred at room temperature for 1 day. If, however, "wet" (i.e., commercial) 18-crown-6 was used instead, the reaction mixture turned deep red in less than 30 min. Under the latter conditions, the hydridoundecacarbonyltriferrate anion was generated and could be isolated as the bis(triphenylphosphin)iminium salt on addition of bis(triphenylphosphin)iminium chloride. The hydride was characterized on the basis of elemental analysis and the occurrence of an absorption maximum (methanol) at

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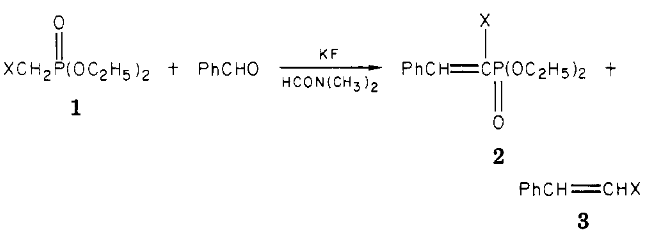

$$\underset{\mathbf{1}}{\mathrm{XCH_2\overset{\overset{O}{\|}}{P}(OC_2H_5)_2}} + \mathrm{PhCHO} \xrightarrow[\mathrm{HCON(CH_3)_2}]{\mathrm{KF}} \underset{\mathbf{2}}{\mathrm{PhCH{=}\overset{\overset{X}{|}}{\underset{\underset{O}{\|}}{C}}P(OC_2H_5)_2}} + \underset{\mathbf{3}}{\mathrm{PhCH{=}CHX}}$$

1

2

3

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This paper describes the reactions of potassium fluoride and tetrabutylammonium fluoride with triiron dodecacarbonyl, dimanganese decacarbonyl, and several other metal carbonyls. Water plays a significant role in all of these reactions, with the facile generation of metal carbonyl hydrides being important in certain cases.

Results and Discussion

When triiron dodecacarbonyl was treated with an approximately equimolar amount of potassium fluoride and 0.25 equiv of "dry" 18-crown-6 in tetrahydrofuran, the solution remained intense green [$Fe_3(CO)_{12}$] after being stirred at room temperature for 1 day. If, however, "wet" (i.e., commercial) 18-crown-6 was used instead, the reaction mixture turned deep red in less than 30 min. Under the latter conditions, the hydridoundecacarbonyltriferrate anion was generated and could be isolated as the bis(triphenylphosphin)iminium salt on addition of bis(triphenylphosphin)iminium chloride. The hydride was characterized on the basis of elemental analysis and the occurrence of an absorption maximum (methanol) at

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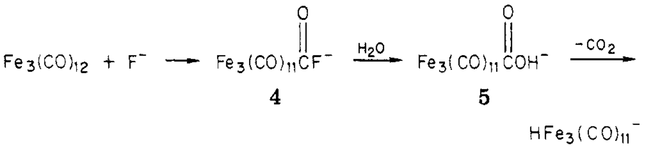
Table I. Yields of Anilines Obtained from the Reaction of Nitroarenes with $Fe_3(CO)_{12}$, $(C_4H_9)_4NF$, and Water

p-$RC_6H_4NO_2$(6), R, mmol	$Fe_3(CO)_{12}$, mmol	$(C_4H_9)_4NF$ (1 M), mmol	H_2O, mmol	p-$RC_6H_4NH_2$-(7),[a] %
CH_3, 9.92	5.95	0.18	28.0	37
CH_3, 10.2	6.12	0.60	6.5	21
CH_3, 10.3	6.15	0.60	27.0	45
CH_3, 10.2	6.10	0.60	32.0	48
CH_3, 9.91	5.94	0.80	23.0	66
CH_3O, 10.3	6.17	0.60	26.0	63
Cl, 10.2	6.09	0.60	27.0	71
COPh, 10.4	6.22	0.60	29.0	94

[a] Anilines were identified by comparison of physical data with those for authentic materials.

540–545 mm.[9] In addition, the red solution was capable of reducing p-nitrotoluene to p-toluidine. Such an $HFe_3(CO)_{11}^-$ mediated reduction of nitro compounds has previously been reported by using crown ether[8] and quaternary ammonium ion[10] catalysis, both under basic conditions.

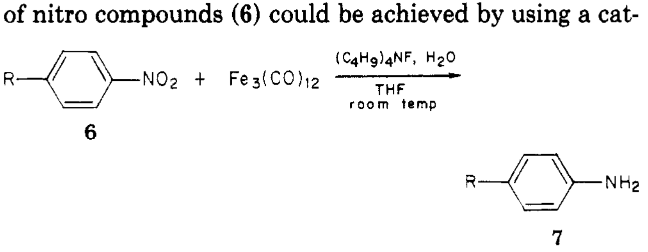
Being a solid, dibenzo-18-crown-6 proved easier to obtain in an anhydrous form than 18-crown-6. When the dry dibenzo derivative was used for the reaction of $Fe_3(CO)_{12}$ with potassium fluoride in anhydrous tetrahydrofuran, no reaction occurred after 18 h at room temperature. However, if the reaction mixture was heated to reflux for only 10 min, clean conversion to the hydride took place which, on addition of p-nitrotoluene, forms p-toluidine. What may be occurring at elevated temperatures is the attack of fluoride ion on $Fe_3(CO)_{12}$ to give **4**. Small amounts of



water (possibly from "dry" KF) can convert *4* to the hydroxycarbonyl anion **5** which, on subsequent elimination of carbon dioxide, would generate the trinuclear iron hydride. Alternatively, fluoride ion can convert water to hydroxide ion, the latter reacting with $Fe_3(CO)_{12}$ to give **5**.

The $HFe_3(CO)_{11}^-$ ion also is formed rapidly (less than 5 min) when $Fe_3(CO)_{12}$ in tetrahydrofuran was treated with a 1 M solution of tetrabutylammonium fluoride at room temperature. When the reaction was run in the presence of p-nitrotoluene (6.7/8.0/11.2 mmol ratio of $Fe_3(CO)_{12}$/$(C_4H_9)_4NF$/p-nitrotoluene), there was complete reduction to p-toluidine in 5 min. No reaction was observed when p-nitrotoluene was exposed to tetrabutylammonium fluoride (1 M) for 72 h.

Of greater potential was the finding that the reduction of nitro compounds (**6**) could be achieved by using a catalytic amount of the tetraalkylammonium fluoride and a small quantity of added water. Good yields of amine (**7**) were realized by using the relative millimole quantities of $Fe_3(CO)_{12}$/**6**/H_2O/10% $(C_4H_9)_4NF$ (1 M) of 6/10/27/0.6 (approximate ratio-exact values are listed in Table I). The use of too little (6.5 mmol) or too much (99 mmol) water affords lower product yields, as does the use of less fluoride. In addition, allowing the solutions to stir overnight has little effect on the yield of the aromatic amine.



When dimanganese decacarbonyl was treated with either 1M $(C_4H_9)_4NF$ or the hydrated fluoride, $(C_4H_9)_4NF{\cdot}3H_2O$, in THF (under nitrogen or carbon monoxide), the manganese pentacarbonyl anion was formed. The reaction mixture displayed terminal metal carbonyl stretching bands at 1895 and 1860 cm^{-1} (THF) and addition of iodine/methylene chloride resulted in bleaching of the solution. Both of these observations are consistent with the presence of $Mn(CO)_5^-$.[11] *No* other metal carbonyl bands were observed in the infrared region. Interestingly, nitro compounds (**6**) were reduced to anilines (**7**) by $Mn_2(CO)_{10}$, added water, and a catalytic amount of tetrabutylammonium fluoride. Obviously, a catalytic quantity of a species which functions as a hydrogen source (e.g., metal carbonyl hydride) must be present, since $Mn(CO)_5^-$ will not convert **6** to **7** (Table II). The use of *cis*-$HMn(CO)_4PPh_3$ for the reduction of halides has been described in the literature.[12]

The reactions of several other metal carbonyls with tetrabutylammonium fluoride was also examined. Treatment of dicobalt octacarbonyl with hydrated tetrabutylammonium fluoride in THF afforded the cobalt tetracarbonyl anion (ν_{CO} = 1885 cm^{-1}).[11] However, these solutions do *not* reduce nitro compounds to amines. A nonreducing solution was also obtained from the reaction of cobalt tricarbonyl nitrosyl with $(C_4H_9)_4NF$. That solution, which also displayed a carbonyl stretching band at 1885 cm^{-1}, could be used for carbonylating 2-(bromomethyl)naphthalene to (2-naphthyl)acetic acid.[13] Cyclopentadienylcobalt dicarbonyl failed to react with fluoride ion. Iron pentacarbonyl affords the $HFe_3(CO)_{11}^-$ ion on exposure to 1 M $(C_4H_9)_4NF$.

In conclusion, potassium fluoride and tetrabutylammonium fluoride can induce the facile conversion of $Fe_3(CO)_{12}$ to $HFe_3(CO)_{11}^-$ and of $Mn_2(CO)_{10}$ to $Mn(CO)_5^-$. Tetrabutylammonium fluoride is an effective catalyst for reducing nitro compounds to amines by $Fe_3(CO)_{12}$ or $Mn_2(CO)_{10}$ under mild conditions.

Experimental Section

General Data. Infrared spectra were recorded on a Unicam SP-1100 spectrometer, equipped with a calibration standard. Nuclear magnetic resonance and mass spectral determinations were made by using Varian T60 and MS9 instruments, respectively.

Triiron dodecacarbonyl, dimanganese decacarbonyl, cobalt carbonyl, cobalt tricarbonyl nitrosyl, and cyclopentadienylcobalt

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Table II. Yields of Anilines Obtained from the Reaction of Nitroarenes with $Mn_2(CO)_{10}$, $(C_4H_9)_4NF$, and Water

p-$RC_6H_4NO_2$(6), R, mmol	$Mn_2(CO)_{10}$, mmol	$(C_4H_9)_4NF$ (1 M), mmol	H_2O, mmol	*p*-$RC_6H_4NH_2$-(7), %
CH_3, 9.96	5.94	0.60	33.5	52
CH_3, 5.54	2.85	7.40		58
OCH_3, 10.2	6.12	0.60	31.0	73
COPh, 10.6	6.20	0.60	29.5	88

dicarbonyl were purchased from Strem Chemicals, Inc., and were used as received. Iron pentacarbonyl was obtained from Pressure Chemical Co. The nitro compounds were purchased from Aldrich Chemical Co. or Fisher Scientific Co. The 1 M $(C_4H_9)_4NF$ solution and the crown ethers were obtained from Aldrich Chemical Co., while "dry" potassium fluoride was purchased from Alfa/Venton. 18-Crown-6 was dried by dissolving in methylene chloride, and the solution was left standing over magnesium sulfate (dry box). After filtration and removal of solvent, colorless powder was obtained.

Tetrahydrofuran was dried by distillation from sodium or potassium benzophenone ketyl. All reactions were run under a dry atmosphere of nitrogen (or carbon monoxide in isolated cases).

Reaction of $Fe_3(CO)_{12}$ with KF and Dry 18-Crown-6. Triiron dodecacarbonyl (0.91 g, 1.80 mmol) was dissolved in tetrahydrofuran (30–35 mL). The crown ether (0.12 g) was added, followed by potassium fluoride (0.10 g). The reaction mixture was stirred for 1 day at room temperature. The intense green-black color of $Fe_3(CO)_{12}$ remained, and thin-layer chromatography indicated no reaction. Addition of 0.10 g of *p*-nitrotoluene gave no reduction.

Reaction of $Fe_3(CO)_{12}$ with KF and Wet 18-Crown-6. To $Fe_3(CO)_{12}$ (2.09 g, 4.15 mmol) in THF or 1,2-dimethoxyethane (30 mL) was added 18-crown-6 (0.49 g) and then KF (0.24 g, 4.15 mmol). After the solution was stirred for 30 min at room temperature, bis(triphenylphosphin)iminium chloride was added to the deep red solution. When the mixture was left standing, $[(Ph_3P)_2N][HFe_3(CO)_{11}]$ precipitated: visible (CH_3OH) λ 545 nm;[9] yield 84%.

Anal. Calcd for $C_{47}H_{31}NO_{11}P_2$: C, 55.60; H, 3.08; N, 1.40. Found: C, 55.46; H, 3.21; N, 1.57.

Reaction of $Fe_3(CO)_{12}$ with KF and Dibenzo-18-crown-6. A mixture of $Fe_3(CO)_{12}$ (0.97 g, 1.93 mmol), KF (0.112 g, 1.93 mmol), and dibenzo-18-crown-6 (0.126 g) in THF (40 mL) was stirred for 18 h at room temperature. No reaction occurred. The reaction mixture was heated to reflux, *p*-nitrotoluene (0.091 g, 1.32 mmol) was added, and the solution was refluxed for 10 min. The solution was cooled to room temperature and filtered, and the filtrate was concentrated by rotary evaporation. Chromatograpy of the oily residue (silica gel) gave *p*-toluidine in 65% yield.

Reaction of $Fe_3(CO)_{12}$ with Tetrabutylammonium Fluoride. To $Fe_3(CO)_{12}$ (1.02 g, 2.03 mmol) in THF (30 mL) was added 2.0 mL of a 1 M THF solution of tetrabutylammonium fluoride. The solution turned deep red in 2–3 min and, after being concentrated, gave a UV absorption maximum at 540–545 mm, characteristic of $[(C_4H_9)_4N][HFe_3(CO)_{11}]$, yield 67%.

Reaction of $Fe_3(CO)_{12}$ with $(C_4H_9)_4NF$ and *p*-Nitrotoluene. *p*-Nitrotoluene (1.53 g, 11.1 mmol) was added to a THF (40 mL) solution containing $Fe_3(CO)_{12}$ (3.36 g, 6.68 mmol) and $(C_4H_9)_4NF$ (8.0 mL of a 1 M solution). A highly exothermic reaction took place, and after filtration and concentration of the filtrate, workup by column chromatography (1:1 ether–hexane) afforded pure *p*-toluidine in 95% yield.

Representative Procedure for the $(C_4H_9)_4NF$-Catalyzed Reaction of Nitroarenes (6) with $Fe_3(CO)_{12}$. To a mixture of $Fe_3(CO)_{12}$ (2.99 g, 5.94 mmol), $(C_4H_9)_4NF$ (0.80 mL), and *p*-nitrotoluene (1.36 g, 9.91 mmol) was added, after 20 min, water (0.408 g, 23 mmol). The reaction mixture was stirred overnight, filtered, and concentrated. Pure *p*-toluidine was isolated in 66% yield by chromatography on silica gel using 1:1 ether–hexane.

Reaction of $Mn_2(CO)_{10}$ with Hydrated $(C_4H_9)_4NF$. A mixture of $Mn_2(CO)_{10}$ (0.499 g, 1.28 mmol) and $(C_4H_9)_4NF{\cdot}3H_2O$ (0.816 g, 1.30 mmol) in THF (50 mL) was stirred overnight at room temperature. An infrared spectrum showed carbonyl stretching absorptions at 1895 and 1860 cm^{-1}. Then 0.088 g (1.28 mmol) of *p*-nitrotoluene was added, and the solution was stirred for 2 days at the end of which an IR spectrum revealed bands due to $Mn(CO)_5^-$ but not $Mn_2(CO)_{10}$.

Representative Procedure for the $[C_4H_9]_4NF$-Catalyzed Reaction of Nitroarenes (6) with $Mn_2(CO)_{10}$. To a mixture of dimanganese decacarbonyl (2.39 g, 6.12 mmol), $(C_4H_9)_4NF$ (0.6 mL of a 1 M THF solution) in THF (50 mL) was added *p*-nitroanisole (1.56 g, 10.2 mmol) followed by water (0.56 g). The reaction mixture was stirred for 3 days and then filtered. Rotary evaporation of the filtrate gave a semisolid which was chromatographed on silica gel. Elution with 5:1 hexane–ethyl acetate gave pure *p*-anisidine in 73% yield.

Reaction of $Co_2(CO)_8$ with Hydrated Tetrabutylammonium Fluoride. A mixture of $Co_2(CO)_8$ (0.493 g, 1.44 mmol) and $(C_4H_9)_4NF{\cdot}3H_2O$ (0.907 g, 1.44 mmol) in THF (50 mL) was stirred for 16 h at room temperature. The solution became much lighter in color, and a absorption maximum occurred in the infrared region at 1885 cm^{-1}. If *p*-nitrotoluene (0.100 g, 1.44 mmol) was added, no reduction of the nitro compound took place.

Reaction of $Co(CO)_3NO$ with $(C_4H_9)_4NF$. A mixture of $Co(CO)_3NO$ (0.93 g, 5.39 mmol) and $(C_4H_9)_4NF$ (6.6 mmol) in THF (50 mL) was stirred under a carbon monoxide atmosphere for 17 h. Addition of 2-(bromomethyl)naphthalene resulted in carbonylation to (2-naphthyl)acetic acid in 48% yield, mp 141–142 °C. The melting point was not depressed on admixture with authentic (2-naphthyl)acetic acid.

Reaction of Iron Pentacarbonyl with 1 M $(C_4H_9)_4NF$. To a THF (50 mL) solution containing iron pentacarbonyl (2.08 g, 10.6 mmol) was added 10.6 mL of a 1 M $(C_4H_9)_4NF$ solution. The solution turned deep red, and after 2–3 days, the $HFe_3(CO)_{11}^-$ ion could be isolated as the $(PPh_3)_2N^+$ salt as for $Fe_3(CO)_{12}$.

Acknowledgment. We are greatful to NSERC and NATO for support of this research.

Registry No. 6, R = CH_3, 99-99-0; 6, R = CH_3O, 100-17-4; 6, R = Cl, 100-00-5; 6, R = COPh, 1144-74-7; 7, R = CH_3, 106-49-0; 7, R = CH_3O, 104-94-9; 7, R = Cl, 106-47-8; 7, R = COPh, 1137-41-3; $[(Ph_3P)_2N][HFe_3(CO)_{11}]$, 23254-21-9; $[(C_4H_9)_4N][HFe_3(CO)_{11}]$, 80146-07-2; $[HFe_3(CO)_{11}]^-$, 55188-22-2; $[Mn(CO)_5]^-$, 14971-26-7; $Fe_3(CO)_{12}$, 17685-52-8; $Mn_2(CO)_{10}$, 10170-69-1; $Co_2(CO)_8$, 10210-68-1; $Co(CO)_3NO$, 14096-82-3; iron pentacarbonyl, 13463-40-6; fluoride, 16984-48-8; cobalt tetracarbonyl anion, 14971-27-8.

Organotransition-Metal Complexes of Very Basic Ketones. The Synthesis of Dicarbonylcyclopentadienyliron Complexes of Diphenylcyclopropenone, Tropone, and Phenalenone. The Crystal and Molecular Structure of Dicarbonylcyclopentadienyliron Tropone Tetrafluoroborate

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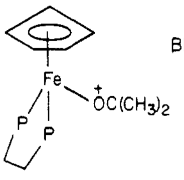
The synthesis and properties of three new ketone complexes of dicarbonylcyclopentadienyliron tetrafluoroborate are described. Diphenylcyclopropenone, tropone, and phenalenone were studied because of their high basicity and potential for extensive delocalization of charge. The structure of the tropone complex ($FeC_{14}H_{11}BF_4$) was determined confirming oxygen to iron σ bonding and that there is no signficant reduction in C–C bond alternation in the tropone ring upon coordination. The complex crystallizes in space group $P2_1/c$ with $Z = 4$ and lattice constants of $a = 7.408$ (4), $b = 16.69$ (1), $c = 12.466$ (9) Å, and $\beta = 92.86$ (4)°.

Introduction

Metal complexes of ketones in the form of simple adducts such as $MgBr_2{\cdot}3(CH_3)_2CO$ and $FeCl_3{\cdot}(C_6H_5)_2CO$ have been known for over 70 years, and this class of compounds is highly populated.[1] In all of these cases, the oxygen is presumed to be σ bound to the metal ion.

In the last decade an interest in complexes of the carbonyl function with organotransition-metal groups has developed. In 1971 Silverthorn reported the iron complex **1**, a novel species so labile that the acetone ligand was displaced by N_2.[2] Later, Williams and Lalor isolated the more stable $Fp(acetone)^+PF_6^-$ salt (**2**) ($Fp = CpFe(CO)_2$).[3] Recently, Rosenblum and co-workers prepared a variety of $Fp(carbonyl)^+$ complexes that included simple and conjugated ketones, aldehydes, esters, and amides, as part of an effort to enhance the reactivity of the carbonyl group.[4] Shortly after this paper was published, Schmidt and Thiel described the synthesis of similar complexes[5] and we reported the isolation of a Fp^+ complex of diphenylcyclopropenone.[6]



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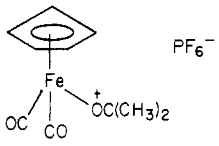

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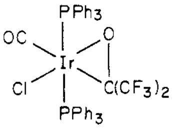
Spectral data indicate that oxygen is σ bound to the iron in these complexes and the crystal structure of one of them, $Fp(3\text{-methylcyclohexenone})^+PF_6^-$ supports that assignment.[4] However, while σ bonding is the dominant type of interaction in all metal carbonyl complexes, side or π bonding has been observed occasionally in complexes such as **3**[7] and **4**[8] in which the ketones are electron deficient.



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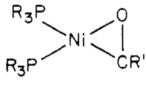
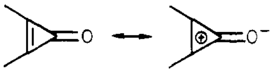


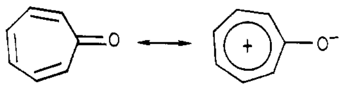
4a, $R = C_6H_5$, $R' = CF_3$
b, $R = C_2H_5$, $R' = C_6H_5$

Apparently the role of the metal is significant, because, in contrast to the side attachment of nickel in **4b**, when the Fp^+ group is used to complex benzophenone the iron is coordinated through the oxygen only.[5]

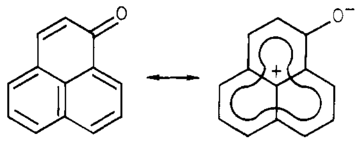
Before publication of the more recent papers on $Fp(carbonyl)^+$ complexes,[4,5] we had investigated the reactions of diphenylcyclopropenone (DPCPO), **5**, tropone (TROPO), **6**, and phenalenone (PNLNO), **7**, with Fp^+ reagents. We envisioned that the highly polar nature of the carbon–oxygen bonds and the resulting increased donor capabilities of the oxygen atoms, due to a significant degree to the contributions of resonance forms **5′**, **6′**, and **7′**, would favor rapid formation of very stable oxygen–iron bonds. Moreover, we wished to examine the effect of coordination of oxygen to iron on the C–C bond lengths in the ketone to see if bond alternation were significantly reduced as a result of charge delocalization in the ring.



5 **5′**



6 **6′**



7 **7′**

Prior to this work no organotransition-metal complexes of **5** and **7** were well characterized although Lewis acid

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Table I. Bond Distances (Å)

Fe-O_1	1.983 (5)	C_4-C_5	1.311 (13)
Fe-C_{13}	1.796 (7)	C_6-O_1	1.238 (8)
Fe-C_{14}	1.796 (7)	C_6-C_7	1.431 (10)
Fe-C_1	2.089 (8)	C_6-C_{12}	1.441 (9)
Fe-C_2	2.096 (8)	C_7-C_8	1.359 (10)
Fe-C_3	2.065 (7)	C_8-C_9	1.400 (13)
Fe-C_4	2.048 (8)	C_9-C_{10}	1.351 (14)
Fe-C_5	2.068 (8)	C_{10}-C_{11}	1.380 (14)
C_1-C_2	1.434 (16)	C_{11}-C_{12}	1.340 (11)
C_1-C_5	1.375 (16)	C_{13}-O_2	1.117 (8)
C_2-C_3	1.412 (15)	C_{14}-O_3	1.135 (9)
C_3-C_4	1.330 (13)		

Table II. Selected Bond Angles (Deg)

O_1FeC_{13}	97.9 (2)	$C_7C_6C_{12}$	122.8 (6)
O_1FeC_{14}	97.3 (3)	$C_6C_7C_8$	129.2 (7)
$C_{13}FeC_{14}$	95.9 (3)	$C_7C_8C_9$	131.4 (8)
FeO_1C_6	136.9 (4)	$C_8C_9C_{10}$	126.7 (8)
$FeC_{13}O_2$	175.8 (7)	$C_9C_{10}C_{11}$	128.7 (7)
$FeC_{14}O_3$	173.8 (7)	$C_{10}C_{11}C_{12}$	130.4 (8)
		$C_{11}C_{12}C_6$	130.7 (8)

adducts of these ketones employing simple metal halides σ bound to the oxygen have been reported.[9,10] Similar adducts of tropone (**6**) have also been prepared[11] as well as some organotransition complexes in which the metal is π complexed to the ring system as in tropone tricarbonylchromium.[12] Attempts to synthesize organotransition-metal complexes of diphenylcyclopropenone (**5**), first prompted by suggestions that they may be involved in carbonylation reactions of acetylenes,[13] met with limited success because the reagents either opened the ring or formed species too unstable to permit characterization.[14-17] In this paper we report the synthesis and characterization of organoiron complexes of **5**, **6**, and **7** including the crystal and molecular structure of one of them, dicarbonylcyclopentadienyliron tropone tetrafluoroborate.

Results and Discussion

Molecular Structure of Fp(TROPO)BF_4. An ORTEP[18] diagram of the Fp(TROPO) cation as it exists in crystals of its BF_4^- salt is given in Figure 1. The structural features most relevant to this study are that the iron atom is σ bound to the tropone oxygen and that the tropone ring shows no significant reduction in bond alternation from that observed in free tropone at −60 °C.[19] Pertinent bond distances and angles are given in Tables I and II.[20]

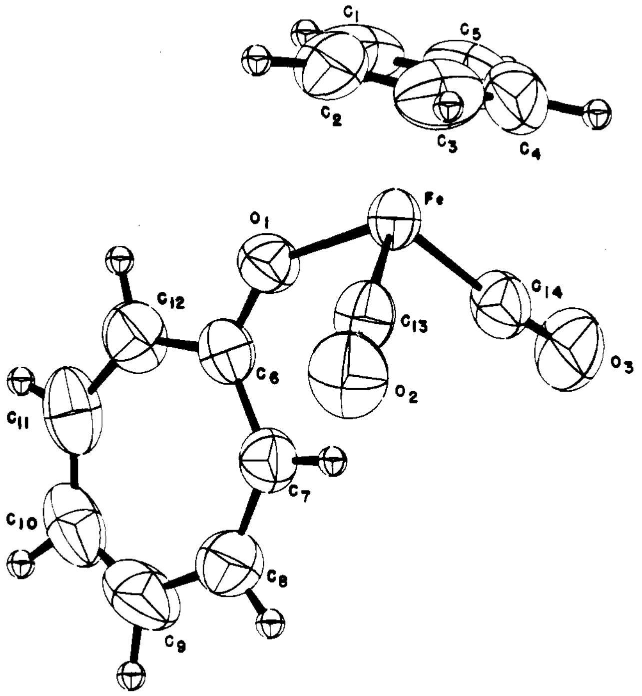

Figure 1. An ORTEP drawing of the $[CpFe(CO)_2C_7H_6O]^+$ cation as it exists in crystals of its BF_4^- salt. Anisotropic ellipsoids are drawn at 50% probability, and the hydrogen atoms have been deliberately reduced in size for clarity.

Bond parameters in the tropone ring display the same trend as that observed in the free tropone at −60 °C.[19] Relatively short C–C distances occur at C_7–C_8, C_9–C_{10}, and C_{11}–C_{12}. Carbon atoms of the tropone ring are planar, with the maximum deviation being 0.014 (10) Å and the average deviation being 0.008 (9) Å. The oxygen atom (O_1), however, is displaced 0.05 Å out of this plane toward the iron atom. The observed ketonic C–O bond length of 1.238 (8) Å is the same as that observed for the π-complexed tropone in tricarbonyl(tropone)chromium of 1.23 Å.[12] The plane of the tropone ligand is rotated slightly, by 1.9°, from the plane defined by Fe, O_1, and C_6. The cyclopentadienyl ligand is approximately perpendicular to this plane, the angle being 89.5°.

The Fe–O_1 distance of 1.983 (5) Å is the same as the corresponding distance in the (3-methylcyclohexenone)Fp cation of 1.980 (6) Å, which is considered a single bond.[4] However, the Fe–O_1–C_6 angle of 136.9 (4) is ~3° larger than in the cyclohexenone complex.[4] The cyclopentadienyl ring is planar, and the average C–C distance is 1.373 (16) Å while the average internal ring angle is 108.0 (9)°. The iron atom is 1.71 Å from the cyclopentadienyl plane, and the average Fe-C_{cp} distance of 2.073 (8) Å is the same as that reported for tricarbonylcyclopentadienyliron hexafluorophosphate.[21]

The shortest nonbonded contacts occur between fluorines and hydrogens. The shortest of these is the $F_1 \cdots H_4^I$ distance of 2.3 Å, where I = 1 − x, 1 − y, and 1 − z. This contact would be 0.10 Å shorter if H_4 were placed at its true internuclear distance from C_4. Unfortunately, the excessive values for the thermal parameters of the fluorines

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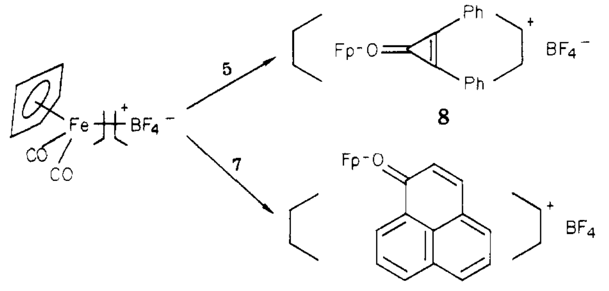
Table III. Comparison of Solvolytic Stabilities of Fp(ketone)$^+$ Complexes with pK_a's of Protonated Ketones

complex	$t_{1/2}$,[a] min	pK_a
Fp(TROPO)$^+$ (**10**)	120	−0.60[23]
Fp(DPCPO)$^+$ (**8**)	45	−3.20[23]
Fp(PNLNO)$^+$ (**9**)	30	−1.40[24]

[a] Rate of displacement measured by NMR at 20 °C in CD_3CN.

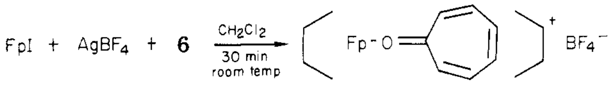
precludes any detailed analysis and the calculated contacts are not necessarily a reliable estimate of the average internuclear separations.

Synthesis and Properties. The Fp$^+$ complexes of ketones **5** and **7** were prepared in good yields by treating an excess of the free ketone with Fp(isobutylene)$^+BF_4^-$ for 10 min at 65–70 °C in dichloroethane.



9

Our attempts to prepare the tropone complex **10** by the



10

same reaction failed. However, using the method recently developed by Reger,[22] in which the Fp$^+$ intermediate is generated from FpI and $AgBF_4$ in CH_2Cl_2, we were able to prepare Fp(TROPO)$^+BF_4^-$ (**10**) in modest yield (18%).

Complexes **9** and **10** are bright red solids and **8** is orange-red. All are air stable. Fp(DPCPO)BF_4 (**8**) and Fp(PNLNO)BF_4 (**9**) are microcrystalline materials whereas Fp(TROPO)BF_4 (**10**) can be isolated as long needles. Only **10** produced crystals suitable for analysis by X-ray diffraction. Complexes **8**, **9**, and **10** are the most soluble adducts of these ketones. While numerous simple metal halide adducts of **5**,[9] **6**,[11] and **7**,[10] all presumably σ bound to oxygen have been prepared they are characterized by very low solubility. In contrast, **8**, **9**, and **10** dissolve readily in acetonitrile and nitromethane. Dichloromethane will solubilize **8** and **10** but not **9**. None of the three dissolve in solvents such as ether, benzene, or hexane.

Decomplexation of ketone by solvent occurs in each case but the relative stabilities do not parallel the basicities of the free ketones as expected (Table III). Steric factors appear to dominate since the largest ligand, PNLNO, is most readily displaced, and the smallest, TROPO, is most tightly bound. TROPO is also the strongest base but the relative importance of nonbonded interactions was clearly indicated when we tried unsuccessfully to prepare the Fp$^+$ complex of 2-methyltropone. These observations parallel those made on Fp(olefin)$^+$ complexes which exhibit destabilization of the metal–olefin bond with increasing alkyl substitution.[25]

Table IV. Comparison of Carbonyl Stretching Frequencies

ketone, νCO (cm^{-1})	$\Delta\nu$	
	R_2CO-Fp	R_2CO-MX_n
tropone, 1583	75[a]	~55[b,11]
diphenylcyclopropenone, 1640	85[a]	~60[c,9]
phenalenone, 1641	151[a]	120-160[b,10]

[a] Spectra obtained in perfluorokerosene mulls. [b] KBr pellets. [c] Nujol mulls. M = Li, Ca, B, Ga, Sn, Ti, Zn, Cd, Cu, Co, Mn, Ni; X = Cl, Br, F.

Table V. Comparison of Ultraviolet Spectra

	λ_{max}, nm (log ϵ), in CH_3CN
DPCPO	227 (4.32), 285 (4.41), 297 (4.46), 310 (sh)
Fp(DPCPO)BF_4	226 (4.77), 286 (4.72), 296 (4.73), 312 (sh)
TROPO	224 (4.26), 228 (4.24), 231 (4.21), 303 (3.78), 314 (sh)
Fp(TROPO)BF_4	224 (4.53), 228 (4.52), 231 (4.51), 331 (4.03)
PNLNO	313 (3.54), 356 (4.01), 377 (3.94)
Fp(PNLNO)BF_4	337 (3.64), 376 (3.73), 445 (3.80)
F_3B(PNLNO)[a]	347, 3.93 (4.20), 4.42 (4.04)

[a] Spectrum recorded on ether solution of adduct.[10]

Spectral Properties. Comparison of the infrared spectra of the complexed and free ketones showed the reduction in the carbonyl stretching frequency expected for attachment of the metal to the oxygen. The magnitudes of the $\Delta\nu$(CO)'s parallel closely those observed for simple metal halide adducts of these ketones (Table IV).

The ultraviolet spectra of Fp(TROPO)BF_4 and Fp(DPCPO)BF_4 resemble those of the free ketones with one exception: the long wavelength absorption at 303 nm in the free tropone is shifted to lower energy ($\Delta\nu$ = 28 nm) upon complexation (Table V). The Fp(PNLNO)BF_4 complex shows significant differences in the UV spectrum in that all three absorptions above 300 nm in the free ketone experience a bathochromic shift. These shifts are similar to those reported for gallium trichloride and boron trifluoride adducts of PNLNO.[10] While absorption data above 500 nm were recorded for similar Lewis acid adducts of TROPO[11] and DPCPO,[9] no absorptions in the 300–500-nm region were reported to permit a comparison with our Fp$^+$ complexes.

Experimental Section

X-ray Structure. Red needle shaped crystals of **10** were cut under a microscope and wedged inside 0.30-mm glass capillaries. The crystal used for data collection was a parallellpiped with dimensions of 0.87 × 0.33 × 0.33 mm. A photographic examination followed by an examination of the reciprocal lattice net with the diffractometer indicated the space group was $P2_1/c$ (No. 14).[26] The corresponding lattice constants obtained from the centering of 12 reflections (λ = 0.70926 Å) were a = 7.408 (4) Å, b = 16.69 (1) Å, c = 12.466 (9) Å, and β = 92.86 (4)°. This unit cell containing four molecules of $[(C_5H_5)(C_7H_6O)(CO)_2Fe]BF_4$ yields as

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Table VI. Atomic Coordinates[a]

atom	10^4x	10^4y	10^4z
Fe	3517.4 (10)	3826.8 (5)	3274.8 (6)
C_1	3837 (23)	2603 (5)	2986 (7)
C_2	5496 (13)	2932 (6)	3435 (10)
C_3	5041 (12)	3224 (5)	4449 (7)
C_4	3296 (12)	3084 (6)	4569 (7)
C_5	2549 (13)	2721 (6)	3727 (9)
C_6	2895 (8)	4478 (4)	1036 (5)
C_7	2551 (9)	5282 (4)	1365 (5)
C_8	2217 (11)	5944 (5)	751 (7)
C_9	2094 (13)	6048 (6)	−364 (9)
C_{10}	2244 (11)	5474 (7)	−1118 (7)
C_{11}	2588 (11)	4667 (6)	−977 (6)
C_{12}	2871 (12)	4238 (5)	−75 (6)
C_{13}	4901 (8)	4695 (4)	3538 (5)
C_{14}	1420 (9)	4294 (5)	3581 (6)
O_1	3245 (7)	3934 (3)	1691 (3)
O_2	5808 (8)	5211 (4)	3754 (5)
O_3	38 (8)	4521 (5)	3792 (6)
B	863 (11)	6783 (6)	3558 (7)
F_1	2329 (9)	6287 (5)	3527 (6)
F_2	−673 (9)	6385 (4)	3184 (6)
F_3	713 (7)	7035 (4)	4577 (4)
F_4	1098 (9)	7424 (4)	2893 (5)
H_1	1314	2566	3642
H_2	3659	2351	2304
H_3	6638	2947	3121
H_4	5844	3478	4960
H_5	2669	3229	5187
H_7	2558	5366	2119
H_8	2033	6419	1150
H_9	1881	6579	−619
H_{10}	2095	5648	−1842
H_{11}	2630	4367	−1623
H_{12}	3093	3684	−187

[a] Estimated standard deviations are given in parentheses for the least significant digit.

a calculated density of 1.595 g/mL. The experimental density, by flotation, was 1.60 (2) g/mL.

Intensity data were collected as described previously[27] at ambient room temperature (22 ± 2 °C). Background counts were of 10-s duration and the standard reflections remained statistically constant during the collection of $h,k,\pm l$ data to a limiting 2θ of 52.87°. From the entire data set, two reflections (the 104 and 106) appeared as double peaks which were not the result of overlap with a β peak from higher angle data and thus remain unexplained. Both were included in the processed data; however, the 106 had $I < 3\sigma(I)$ and was therefore judged unobserved. Standard deviations were calculated according to

$$\sigma(F) = [C + k^2B + (0.01I)^2/4|F_o|^2Lp^2]^{1/2}$$

where C and B are the counts of the scan and sum of the background, respectively, k is the ratio of scan time to background counting time, and I is the net intensity of the peak. Of the 3183 unique data measured, a total of 2188 with $I < 3\sigma(I)$ were taken as observed. The solution and refinement of the structure were also done as described previously.[27] However, final cycles utilized full matrix[28] refinement and were done as a two-step process, varying all nonhydrogen parameters except for the four fluorines in the first step followed by a cycle varying all nonhydrogen parameters except the oxygens and two carbonyl carbons. Theoretical coordinates for all hydrogen atoms were derived at a distance of 0.95 Å from the respective carbon atoms and thermal parameters were taken as 7 Å^2. All hydrogen parameters were fixed in further refinement which converted with $R = 8.2\%$ and $R_w = 11.1\%$. The error of fit was 1.31 and residual electron density from a final difference synthesis ranged from 0.99 e/Å^{-3} in the region of the metal to −0.76 e/Å^3. The resulting atomic coordinates are listed in Table VI.

Syntheses. Fp(isobutylene)$^+BF_4^-$ was prepared by treating Fp(isobutylene) with HBF_4.[29] We found that it was essential to remove excess HBF_4 for successful isolation of the intermediate. FpI[30] was purified according to Reger's procedure.[22] $AgBF_4$ was obtained from Ozark–Mahoning and used only in a dry glovebag filled with nitrogen. Methylene chloride and 1,2-dichloroethane were refluxed over P_2O_5 and distilled immediately before use. PMR spectra were recorded on a Varian EM 390 spectrometer using Me_4Si as an internal standard. IR spectra were recorded on a Perkin-Elmer 137 spectrophotometer, and UV data were obtained from a Beckman DK-2A spectrophotometer.

Dicarbonylcyclopentadienyliron Tropone Tetrafluoroborate (10). A 100-mL Schlenk flask that had been oven dried and purged with nitrogen was charged with FpI (0.82 g, 2.69 mmol), $AgBF_4$ (0.57 g, 2.92 mmol), and CH_2Cl_2 (50 mL) and stirred for 30 min at room temperature. The reaction mixture was then filtered under nitrogen using a Schlenck filter funnel and filter aid (Celite) into a three-neck 100-mL round-bottomed flask. To this solution was added tropone[31] (0.85 g, 8.02 mmol), and the resulting solution was stirred for 15 min. Filtration, followed by the addition of 400 mL of dry ether to the filtrate, gave a turbid mixture. Storage at 5 °C for 3 days produced 0.17 g of bright red crystals which were isolated by filtration. The filtrate contained a brown oily layer that also gave red crystals when mixed with CH_2Cl_2 and ether and chilled to 5 °C. The following procedure, repeated twice, gave analytically pure **10**. The red crystals were dissolved in a minimum of CH_2Cl_2 and filtered in a pipette containing a small piece of microwipe. Enough ether was added to the filtrate to make it turbid. Cooling to 5 °C overnight gave crystalline product. Application of this procedure to the brown oil also gave analytically pure **10**. From these steps 0.18 g (0.49 mmol, 18% yield) was obtained: ^1H NMR (CD_3CN, 0 °C) δ 7.95–6.70 (m, 6 H), 5.40 (s, 5 H); IR ν(C≡O) (CH_3CN solution) 2061, 2016 cm^{-1}, (C═O) (perfluorokerosene mull) 1508 cm^{-1}. Anal. Calcd for $FeC_{14}H_{11}BF_4$: Fe, 15.14; C, 45.41; H, 2.97. Found: Fe, 14.97; C, 45.38; H, 3.08.

Dicarbonylcyclopentadienyliron Phenalenone Tetrafluoroborate (9). Fp(isobutylene)BF_4 (1.00 g, 3.13 mmol) and phenalenone[32] (1.00 g, 5.55 mmol) in 40 mL of 1,2-dichloroethane were stirred at ~65 °C for 10 min. After being cooled to room temperature, the reaction mixture was filtered and ether was added to the filtrate which precipitated a red solid. The solid was collected and washed with benzene until the washings were colorless, leaving 0.9 g (65% yield) of crude product. The following procedure was repeated three times to obtain analytically pure **9**. The red solid (0.2 g) was dissolved in 5 mL of CH_3CN at 0 °C under nitrogen and filtered through a pipette containing a small piece of microwipe. Ether was then added to precipitate the product: ^1H NMR (CD_3CN, 0 °C) δ 8.68–7.88 (m, 7 H), 7.00 (d, 1 H), 5.51 (s, 5 H); IR ν(C≡O) (CH_3CN solution) 2061, 2016 cm^{-1}, ν(C═O) (perfluorokerosene mull) 1490 cm^{-1}. Anal. Calcd for $FeC_{20}H_{13}O_3BF_4$: Fe, 12.42; C, 54.05; H, 2.93. Found: Fe, 12.42; C, 54.06; H, 3.00.

Dicarbonylcyclopentadienyliron Diphenylcyclopropenone Tetrafluoroborate (8). The procedure described above was followed by using 0.5 g (1.56 mmol) of Fp(isobutylene)BF_4 and 0.96 g (4.68 mmol) of diphenylcyclopropenone[33] and 20 mL of dichloroethane producing 0.39 g (0.83 mmol, 53% yield) of crude **10**. Analytically pure sample was obtained by recrystallizing 3 times from CH_2Cl_2–ether at room temperature: ^1H NMR (CD_3CN, 0 °C) δ 8.37–8.03 (m, 4 H), 8.03–7.63 (m, 6 H); 5.50 (s, 5 H); IR (perfluorokerosene mull) ν(C≡O) 2053, 2004, ν(C═O) 1555 cm^{-1}. Anal. Calcd for $FeC_{22}H_{15}O_3BF_4$: Fe, 11.91; C, 56.17; H, 3.19. Found: Fe, 12.02; C, 55.96; H, 3.32.

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Registry No. 5, 886-38-4; **6**, 539-80-0; **7**, 548-39-0; **8**, 77097-10-0; **9**, 80485-05-8; **10**, 80485-07-0; FpI, 12078-28-3; Fp(isobutylene)BF_4, 41707-16-8.

Supplementary Material Available: A listing of the anisotropic thermal parameters and structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

Kinetics of the Protodestannylation of Vinyltrialkyltins and Substituted Vinyltrialkyltins

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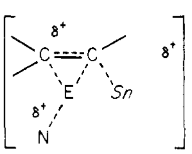
Results of a kinetic study of the protodestannylation of a number of vinyltrialkyltins and substituted vinyltrialkyltins by hydrogen chloride in methanol–water are reported. The relative rate constants are consistent with a steric sequence and open transition state. Substitution of a methyl group or phenyl group on the β-carbon leads to rate enhancement but in lesser magnitude than in the iodostannylation reaction. The effect of the concentration of water in methanol has been studied. Triphenylvinyltin underwent reaction with 2,4-dinitrobenzenesulfenyl chloride with the result that a tin–phenyl bond was cleaved.

Introduction

Electrophilic substitution involving cleavage of a carbon–metal bond has been studied in a number of systems. The favorite metal leaving groups have been those of group 4 and mercury while the carbon substrates have included alkyl, aryl, allyl, allenyl, and vinyl. Electrophilic agents have been bromine, iodine, mercuric halides, and the proton.[1] The order of substrate reactivity when the metal is tin has been shown to be allyl > allenyl > phenyl > vinyl > alkyl.[2,3]

Mechanistically the reaction can be described as S_E2 (S_E2' when the substrate is allyl[2] or a combination when the substrate is allenyl[3]), and the major point of discussion is the structure of the transition state. Since each electrophile carries with it one or more atoms with unshared pairs of electrons, the possibility exists for these atoms to provide nucleophilic assistance to the departing metal. Concomitant is the question of where the transition state lies on the reaction coordinate. An early transition state would presumably not involve significant nucleophilic assistance since not much charge is localized on the metal while a later transition state could involve nucleophilic assistance provided either by the attacking agent or by the solvent. Baekelmans et al.[4] and Abraham et al.[5] have described the two limiting cases as an open transition state (I) and a closed transition state (II). It should be noted that the open transition state (I) does not preclude nucleophilic assistance from an appropriate solvent.[2]



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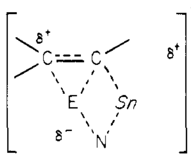

II

In vinylmetallic, allylmetallic, and allenylmetallic systems, the situation is more complicated in that the electrophile probably attacks the π electrons of the double bond. This suggests that the β-carbon of the vinylmetallic system will develop some positive charge in the transition state as the bond to the α-carbon is being formed.[6] Thus the electrophile may be coordinated to both carbons of the vinyl group. In studies of this system, Nesmeyanov et al.[7] and Beletskaya and Reutov[8] favor closed three-center and four-center transition states to account for retention of configuration in halo- and protodemercuration of vinylmercurials in dioxane, methanol, and DMF. Baekelmans et al.[4] suggests an open transition state for iododemetalation of a series of vinyltin compounds in methanol. Their conclusion was based primarily on a large positive salt effect. Also Gupta and Majee[9] report quantum mechanical calculations by the Del Re method which

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[6] This transition state may lead to an intermediate with a tetrahedral carbon at the site of substitution and a full positive charge on the β-carbon. See ref 10.

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[8] Beletskaya, I. P.; Karpov, V. I.; Reutov, O. A. *Dokl. Akad. Nauk SSSR* **1965**, *161*, 286.

[9] Gupta, R.; Majee, B. *J. Organomet. Chem.* **1973**, *49*, 191.

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Registry No. 5, 886-38-4; **6**, 539-80-0; **7**, 548-39-0; **8**, 77097-10-0; **9**, 80485-05-8; **10**, 80485-07-0; FpI, 12078-28-3; Fp(isobutylene)BF_4, 41707-16-8.

Supplementary Material Available: A listing of the anisotropic thermal parameters and structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

Kinetics of the Protodestannylation of Vinyltrialkyltins and Substituted Vinyltrialkyltins

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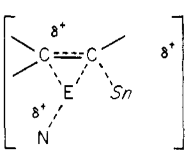
Results of a kinetic study of the protodestannylation of a number of vinyltrialkyltins and substituted vinyltrialkyltins by hydrogen chloride in methanol–water are reported. The relative rate constants are consistent with a steric sequence and open transition state. Substitution of a methyl group or phenyl group on the β-carbon leads to rate enhancement but in lesser magnitude than in the iodostannylation reaction. The effect of the concentration of water in methanol has been studied. Triphenylvinyltin underwent reaction with 2,4-dinitrobenzenesulfenyl chloride with the result that a tin–phenyl bond was cleaved.

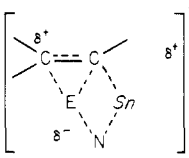
Introduction

Electrophilic substitution involving cleavage of a carbon–metal bond has been studied in a number of systems. The favorite metal leaving groups have been those of group 4 and mercury while the carbon substrates have included alkyl, aryl, allyl, allenyl, and vinyl. Electrophilic agents have been bromine, iodine, mercuric halides, and the proton.[1] The order of substrate reactivity when the metal is tin has been shown to be allyl > allenyl > phenyl > vinyl > alkyl.[2,3]

Mechanistically the reaction can be described as S_E2 (S_E2' when the substrate is allyl[2] or a combination when the substrate is allenyl[3]), and the major point of discussion is the structure of the transition state. Since each electrophile carries with it one or more atoms with unshared pairs of electrons, the possibility exists for these atoms to provide nucleophilic assistance to the departing metal. Concomitant is the question of where the transition state lies on the reaction coordinate. An early transition state would presumably not involve significant nucleophilic assistance since not much charge is localized on the metal while a later transition state could involve nucleophilic assistance provided either by the attacking agent or by the solvent. Baekelmans et al.[4] and Abraham et al.[5] have described the two limiting cases as an open transition state (I) and a closed transition state (II). It should be noted that the open transition state (I) does not preclude nucleophilic assistance from an appropriate solvent.[2]



I



II

In vinylmetallic, allylmetallic, and allenylmetallic systems, the situation is more complicated in that the electrophile probably attacks the π electrons of the double bond. This suggests that the β-carbon of the vinylmetallic system will develop some positive charge in the transition state as the bond to the α-carbon is being formed.[6] Thus the electrophile may be coordinated to both carbons of the vinyl group. In studies of this system, Nesmeyanov et al.[7] and Beletskaya and Reutov[8] favor closed three-center and four-center transition states to account for retention of configuration in halo- and protodemercuration of vinylmercurials in dioxane, methanol, and DMF. Baekelmans et al.[4] suggests an open transition state for iododemetalation of a series of vinyltin compounds in methanol. Their conclusion was based primarily on a large positive salt effect. Also Gupta and Majee[9] report quantum mechanical calculations by the Del Re method which

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(1) For a review see: Matteson, D. S. "Organometallic Reaction Mechanisms of the Nontransition Elements"; Academic Press: New York, 1974; Chapters 2, 3, and 4.

(2) Mangravite, J. A.; Verdone, J. A.; Kuivila, H. G. *J. Organomet. Chem.* **1976**, *104*, 303.

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(4) Baekelmans, P.; Gielen, M.; Malfroid, P.; Nasielski, J. *Bull. Soc. Chim. Belg.* **1976**, *77*, 25.

(5) Abraham, M. H.; Spalding, T. R. *J. Chem. Soc. A* **1969**, 784.

(6) This transition state may lead to an intermediate with a tetrahedral carbon at the site of substitution and a full positive charge on the β-carbon. See ref 10.

(7) Nesmeyanov, A. N.; Borisov, A. E. *Tetrahedron* **1957**, *1*, 158.

(8) Beletskaya, I. P.; Karpov, V. I.; Reutov, O. A. *Dokl. Akad. Nauk SSSR* **1965**, *161*, 286.

(9) Gupta, R.; Majee, B. *J. Organomet. Chem.* **1973**, *49*, 191.

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Table I. Second-Order Rate Constants and Activation Parameters for the Protodestannylation of Vinyltins and Substituted Vinyltins

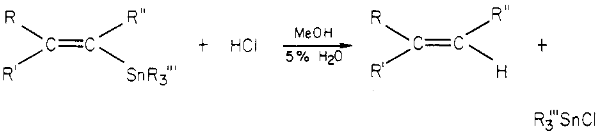
compds	k_2,[a] $M^{-1}\ s^{-1}$ 25.0 ± 0.1 °C	35.0 ± 0.1 °C	45.0 ± 0.1 °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal mol^{-1} deg
1, $CH_2{=}CHSnMe_3$	0.005 26	0.0118	0.0234	12.9	−26.0
2, $CH_2{=}CHSnEt_3$	0.003 53	0.008 04	0.0163	13.2	−25.6
3, $CH_2{=}CHSn$-*n*-Pr_3	0.001 48	0.003 39	0.008 23	14.9	−21.6
4, $CH_2{=}CHSn$-*n*-Bu_3	0.001 48	0.003 57	0.008 38	15.1	−21.0
5, (*E*)-$CH_3CH{=}CHSnMe_3$	0.152	0.302		11.8	−22.9
6, (*Z*)-$CH_3CH{=}CHSnMe_3$	0.108	0.222	0.368	10.5	−27.8
7, $CH_2{=}C(CH_3)SnMe_3$	0.003 13				
8, (*E*)-$C_6H_5CH{=}CHSn$-*n*-Bu_3	0.0861	0.211	0.327	11.5	−25.0
9,[b] $(CH_2{=}CH)_2Sn$-*n*-Bu_2	0.000 640	0.001 53	0.004 56	17.2	−15.8
10,[b] $(CH_2{=}CH)_4Sn$		0.000 440	0.001 10	15.9	−22.6

[a] Values for k_2 are the mean of at least three determinations which agree to within ±3%. [Sn] = 1.00×10^{-3} M; [HCl] = 50.0×10^{-3} M; [H_2O] = 5% in MeOH. [b] Experimental rate constants for **9** and **10** reduced by 2 and 4, respectively, to account for the statistical factor.

suggest an open transition state based on the substituent effects found by Baekelmans.[4]

In a recent report, Eaborn and co-workers[10] propose a two-step mechanism for the protodestannylation of a series of (β-styryl)trimethyltins. The initial rate determining step involves addition of a proton at the carbon bearing the tin group to give a carbenium ion which then goes on in a second step to lose the tin group. The intermediacy of the carbenium ion is based on the correlation with σ^+ constants although the ρ value was quite small (−1.1).

We report the protodestannylation of a series of vinyltin compounds in methanol–5% water. The reaction, as shown below, was studied kinetically, and activation parameters were obtained from the rate data at 25, 35, and 45 °C. The stereochemistry of the reaction was shown to be retention of configuration for one substrate, and the effect of the concentration of water on the rate was determined (eq 1).



(1)

Results

The compounds included in this study were synthesized by reaction of the appropriate olefinic Grignard reagent or lithium reagent with a trialkyltin chloride or by addition of trialkyltin hydride to a substituted acetylene. The stereochemistry of the (*Z*)- and (*E*)-propenyltrimethyltins and the (*E*)-(β-styryl)tributyltin was determined by IR and NMR spectroscopy, and the spectra corresponded to those previously reported by Seyferth et al.[11]

The kinetic studies were carried out by taking advantage of the ultraviolet spectra of the unsaturated tin compounds. All of the compounds possessed a broad and intense absorption at about 190–200 nm which is associated with the C═C—Sn system. Beer–Lambert law plots showed the concentration dependency of this absorption. When the diminution of this absorption on the shoulder at 225 nm was observed, as a function of time, satisfactory second-order and pseudo-first-order (excess electrophile) rate plots were obtained through at least 3 half-lives for the reaction. The rate constants agreed to ±3%. The concentration of tin compound was approximately 10^{-3} M, and for most compounds the concentration of HCl was varied from stoichiometric to 50-fold excess. The composition of the solvent system, methanol–water, had a significant effect on the value of the second-order rate constant and will be discussed below. Rate constants were obtained at three temperatures (25, 35, and 45 °C) for most compounds and enthalpies and entropies of activation calculated by computer least-squares techniques. The errors in the values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were no greater than 10 percent as indicated by the standard deviation of the slopes of the lines. The products of the reactions were determined by sweeping reaction mixtures with nitrogen and collecting the products in a liquid-nitrogen trap. Ethylene and propylene were characterized by IR spectroscopy. In the case of styryltributyltin, sodium fluoride was added to the system after reaction and the tributyltin fluoride filtered and characterized by melting point.

Table I lists the second-order rate constants at each of three temperatures and the corresponding activation parameters. Comparison of the k_2 value for **1** with second-order rate constants for the reaction of **1** with iodine in methanol (306 $M^{-1}\ s^{-1}$)[4] and mercuric chloride in methanol (660 $M^{-1}\ s^{-1}$)[12] shows that the HCl–methanol system is much less reactive. A similar decrease in reactivity for allyltins with HCl in methanol[2] compared to I_2 or mercuric chloride in methanol[12] has been reported. A qualitative explanation for the decreased reactivity of the solvated proton as an electrophile in these systems is that the proton is a "hard" acid while iodine and mercuric chloride are "soft" acids. The electrophile attacks the "soft" electrons of the olefinic tin compounds and allyltin compounds.

The rate constants for **1**–**4** show the effect of alkyl substitution on tin. The order of reactivity is Me > Et > *n*-Pr ≈ *n*-Bu, which is characteristic of the steric sequence of Abraham and Hill.[13] However, it should be noted that this steric sequence is somewhat compressed compared to the reported tetralkyltin sequences, Me (100), Et (67.1), *n*-Pr (28.1), *n*-Bu (28.1) compared to Me (100), Et (12), *n*-Pr (1.5), Bu (0.6), *i*-Pr (0.06)[14,15] and Me (100), Et (0.81), *n*-Pr (0.13), *n*-Bu (0.14), *i*-Pr (10^{-5}),[16] and also somewhat different from that reported by Baekelmans et al,[4] Me (100), Et (109), *n*-Pr (53.6), *i*-Pr (16.0).

Focusing on the rate constants for **1**, **4**, and **5**–**8** the effect of substitution on the vinyl skeleton can be seen. At 25

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(12) Kashin, A. N.; Beletskaya, I. P.; Malkhasyan, A. T.; Reutov, O. A. *Zh. Org. Khim.* **1974**, *10*, 677.

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(16) Abraham, M. H.; Spalding, T. R. *J. Chem. Soc. A* **1969**, 399.

Table II. Effect of Water Concentration on the Rate of Protodestannylation of Tributylvinyltin

$[H_2O]$ in MeOH, mol/L	k_2, M^{-1} s^{-1} (at 25.0 °C)	$[H_2O]$ in MeOH, mol/L	k_2, M^{-1} s^{-1} (at 25.0 °C)
0.55	0.004 25	2.78[a]	0.001 48
1.10	0.002 68	3.33	0.001 41
1.67	0.002 07	3.89	0.001 39
2.22	0.001 77		

[a] This concentration corresponds to 5% water and is the solvent used in kinetic studies.

°C substitution of a methyl group on the β-carbon increases the reactivity by a factor of about 30 when the methyl group is trans to the tin and by about 20 when the methyl group is cis to the tin.[17] Substitution of a phenyl group is even more effective in increasing the reactivity (×60) when it is β and trans to the tin and the leaving group is tributyltin (entries 4 and 7). Finally, the substitution of a methyl group on the α-carbon decreases the reactivity by a factor of about 2. Baekelmans et al.[4,18] report similar effects for the iododestannylation of substituted vinyltins. However, as with the relative reactivities of the steric sequence discussed above, the difference in reactivity is not as large when the solvated proton is the electrophile.

Finally, the rate constants for compounds **4**, **9**, and **10** at 35 °C show the decrease in reactivity caused by substitution of vinyl groups for butyl groups on tin. One substitution decreases the reactivity by a factor of 2 while complete substitution leads to an eightfold decrease. The latter change is very similar to that reported by Baekelmans.[4]

The stereochemistry of the reaction was investigated for one substrate by carrying out the reaction of (*E*)-(β-styryl)trimethyltin (**11**) with DCl in CD_3OD in an NMR tube. The spectrum of the product showed only 18-Hz coupling expected for trans protons in (*E*)-2-phenylethene-*1-d*,[19] indicating that the electrophilic substitution in this case took place with retention of configuration. The product was checked for isomerization stability under the reaction conditions. Also if isomerization did take place, it would not be expected to yield pure *E* isomer but rather a mixture containing substantial amounts of the *Z* isomer. This work further substantiates the previous reports that bimolecular electrophilic substitution for tin at a vinylic carbon takes place with retention of configuration.[4,20]

Verdone et al.[21] have reported that variations in the concentration of water in methanol lead to large changes in the second-order rate constants for the protodestannylation of allyltins. They interpret the phenomenon on the basis of the greater ability of the methyloxonium ion as a proton-transfer agent than the hydronium ion. An increase in the concentration of water shifts the equilibrium in eq 2 toward the less reactive electrophile.

$$MeOH_2^+ + H_2O \rightleftarrows MeOH + H_3O^+ \qquad (2)$$

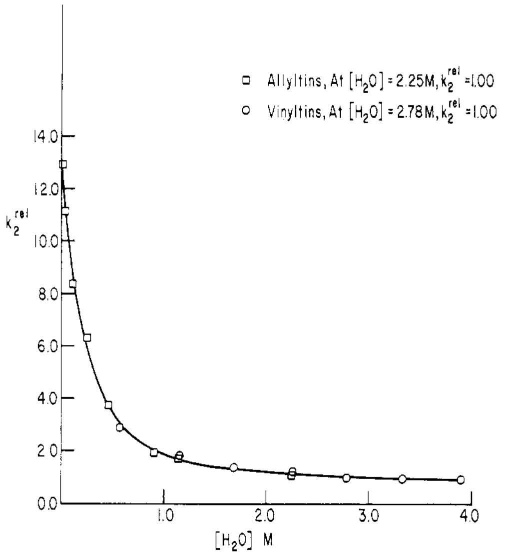
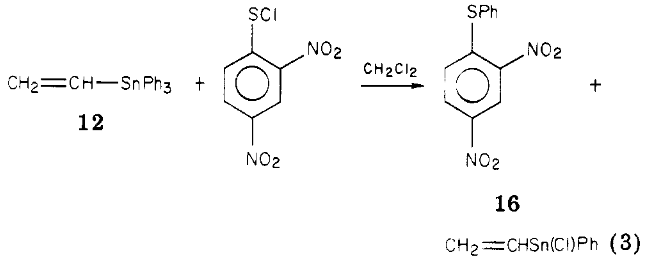


Figure 1. Effect of molar concentration of water on the relative rates of protodestannylation.

We have studied the effect of changes in the concentration of water on the rate of protodestannylation of tributylvinyltin (**4**) and find a similar effect on the magnitude of the second-order rate constant. The data are given in Table II, and Figure 1 shows a plot of relative rate constants for allyltrimethyltin and **4** as a function of water concentration.

2,4-Dinitrobenzenesulfenyl chloride has not been used extensively as an electrophile for the cleavage of carbon-metal bonds. Its utility, however, lies in the fact that the organic group cleaved from the metal is easily characterized as the corresponding thioether. It has been reported that changes in the nature of the electrophile or changes in the solvent[11] can alter the order of reactivity of groups attached to the metal. The reaction, shown in eq 3, between triphenylvinyltin (**12**), indicates that a phenyl group is more reactive than a vinyl group with this electrophile. The diaryl sulfide was the only dinitrophenylthio product found and was characterized by melting point and IR spectroscopy.



12 **16** (3)

Three additional vinyltin compounds were studied: divinyltin dichloride (**13**), vinyltin trichloride (**14**), and perfluorovinyltributyltin (**15**). Each of the compounds exhibited the intense absorption at about 200 nm, and thus we employed the usual diminution in absorbance technique to follow the cleavage reaction with HCl in MeOH–5% H_2O at 25 °C. No change in absorbance was observed over periods of 66 h for **13**, 18 h for **14**, and 90 h for **15**. This suggests that the olefinic carbon–tin bond remains unbroken under these conditions. In the case of **15**, this result is surprising in view of the reactivity of perfluorovinyltins with gaseous hydrogen bromide and other electrophiles.[22]

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(17) The greater reactivity in electrophilic substitution of trans isomers compared to cis isomers has been noted previously. See ref 4 for reference to previously reported examples.

(18) This work confirms the assumption by Baekelmans et al.[4] that an α-methyl group decreases the reactivity about the same as an α-ethyl group. See ref 4, footnote *a*, to Table II.

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(20) Bullpitt, M. H.; Kitching, W. *J. Organomet. Chem.* **1972**, *34*, 321.

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To further explore the low reactivity, bromine in methanol and also in acetonitrile was allowed to react with **14**. Although no products were isolated, the NMR spectrum of the reaction mixture indicated only addition of bromine to the double bond.

$$CH_2{=}CHSnCl_3 + Br_2 \xrightarrow[\text{or } CH_3CN]{MeOH} CH_2Br{-}CHBrSnCl_3 \tag{4}$$

Discussion

The results presented above suggest that protodestannylation at an olefinic carbon passes through an open type transition state of the type proposed by Baekelmans et al.[4] A major difference between the transition state of this system and that of iododestannylation seems to be the amount of positive charge located on the β-carbon. Rate enhancement due to stabilization of β-methyl groups is not as evident in these reactions (*trans*-CH_3, ×30, *cis*-CH_3, ×20 vs. *trans*-CH_3, ×340, *cis*-CH_3, ×110). Even more conclusive is the fact that a *trans*-β-phenyl group is only twice as activating as the methyl group. If there was a substantial positive charge on the β-carbon, the phenyl group should exert a far greater effect.

It follows that if the magnitude of positive charge on the β-carbon is diminished, then more positive charge must be stabilized on tin. This stabilization can arise from electron donation from the solvent or an extended solvated electrophile. The effect of water on the rate constants noted above suggests that at 5% water, the proton is solvated primarily by water rather than methanol.

The activation parameters provide evidence for solvent participation in the transition state. As noted for protodestannylation of a series of trialkylallyltins in which the size of the alkyl groups increased, the effect on the rate was a small decrease as size increased.[2] The similarity in rates was due to compensating increases in enthalpy and entropy of activation. A similar compensating effect in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ is seen here although the differences, especially in $\Delta S^\ddagger$, are even smaller. An increase in electron-donating ability by the alkyl groups on tin decreases both the need for and space for stabilization of the transition state by the solvent acting as a Lewis base. The activation parameters for compounds **1**–**4** fall into two groups instead of showing a continuous change. The electron-donating ability of propyl in compound **3** should not be much different from ethyl in compound **2**, but the increased size becomes significant.

The same phenomenon can be seen in comparing the activation parameters for compounds **4**, **9**, and **10**. Substitution of vinyl groups for butyl groups decreases the extent of electron donation such that the major contribution to the decreased reactivity is in the enthalpy term.

Experimental Section

Syntheses. Compounds **1**–**4**, **11**, **12**, **14**, and **15** were synthesized from the vinyl Grignard reagent and the appropriate trialkyltin halide.[22-24] They were purified by distillation and checked for purity by gas chromatography. Structures were verified by boiling point and IR and NMR spectroscopy. Compounds **5**, **6**, and **7** were prepared from the appropriate propenyllithium compound and trimethyltin chloride.[11a] *Z* and *E* isomers (**5** and **6**) were separated by gas chromatography on a 9-ft, 17% XF-1150 on Chromosorb P column. Compounds **8** and **11** were prepared by the addition of the appropriate trialkyltin hydride to phenylacetylene.[25] Compound **14** was prepared by symmetrization of dichlorodivinyltin and tin tetrachloride.[26] Compounds **9**, **10**, and **13** were gifts from M & T Corp. They were redistilled, checked for purity by gas chromatography, and characterized by IR and NMR before use. Table III lists boiling point and ^1H NMR data for the substrates.

Table III. Physical and ^1H NMR Data[a] for Vinyltin Substrates

compd	bp °C	^1H NMR (neat, ppm, Me_4Si)	*J*, Hz
1	97–99	0.11 (9 H) 5.29–6.70 (3 H)	$^{117/119}Sn$-CH 53/55
2	66–68 (14 torr)	0.51–1.44 (15 H) 5.39–6.73 (3 H)	
3	101 (19 torr)	0.67–1.87 (21 H) 5.34–6.73 (3 H)	
4	82 (0.4 torr)	0.57–1.71 (27 H) 5.28–6.66 (3 H)	
5	124–126[b]	0.04 (9 H) 1.80 (3 H) 5.92 (2 H)	$^{117/119}Sn$-CH 54/56
6	124–126[b]	0.15 (9 H) 1.76 (3 H) 5.75 (1 H) 6.50 (1 H)	$^{117/119}Sn$-CH 52/54 CH_3-CH 6.5 CH_3-C=CH 1.0 CH=CH 12
7	115–117	0.05 (9 H) 1.12 (3 H) 4.94 (1 H) 5.47 (1 H)	$^{117/119}Sn$-CH 53/55 CH_2=C <1
8	160–164 (0.5 torr)[c]	0.3–1.7 (27 H) 6.7 (2 H) 7.1–7.5 (5 H)	 CH=CH <1
9	114–116 (15 torr)	0.71–1.85 (18 H) 5.46–6.73 (6 H)	
10	61–62 (20 torr)	5.54–6.77	
11	125–131 (12 torr)[c]	0.14 (9 H) 6.75 (2 H) 7.0–7.5 (5 H)	$^{117/119}Sn$-CH 53/55 CH=CH <1
12	36.5–38[d]	5.64–6.80 (3 H)[e] 7.03–7.68 (15 H)	
13	81–83 (15 torr)	5.94–7.00	
14	61–63.5 (17 torr)	6.13–7.02	
15	91–92 (0.8 torr)		

[a] ^1H NMR recorded on Perkin-Elmer R-24 or Varian A60 spectrometers. [b] See Experimental Section for separation of **5** and **6**. [c] Separated from the *Z* isomer by preparative GLC on 10-ft, 10%, SE-30 on Chromosorb W column. [d] Melting point (uncorrected). [e] ^1H NMR spectrum run in CCl_4.

Kinetic Procedure. All glassware was thoroughly cleaned by soaking overnight in concentrated nitric acid, rinsed ten times with distilled water and three times with methanol, and dried in an oven at 60 °C. Solutions of tin compounds in methanol,

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standardized hydrochloric acid in methanol, and methanol-deionized water (to bring the final water concentration to 5%) were thermostated prior to mixing. After the reaction solution was mixed, it was transferred to a cuvette and the absorbance read as a function of time in a Beckman DU-Gilford with a thermostated cell compartment. Most substrates were run under second-order conditions (nearly equal concentrations of tin compound and acid in the range of 10^{-3} M) at least at one temperature and also under pseudo-first-order conditions with a 50-fold excess of acid. Second-order rate constants and activation parameters were obtained from a standard least-squares plot.

Reaction of Triphenylvinyltin (12) with 2,4-Dinitrobenzenesulfenyl Chloride. A solution of 0.620 g (2.65×10^{-3} mol) of 2,4-dinitrobenzenesulfenyl chloride in 5 mL of methylene chloride was added dropwise with stirring to 1.00 g (2.65×10^{-3} mol) of triphenylvinyltin (12) in 5 mL of methylene chloride. The reaction mixture was allowed to stir overnight. The solution was washed twice with water, dried over magnesium sulfate, and evaporated to dryness. The residue was dissolved in hot ethanol. On cooling, 0.49 g (67%) of yellow crystals was formed. A second recrystallization gave crystals of 2,4-dinitrophenyl phenyl sulfide **16**, mp 118–119 °C [lit.[27] 119.5–120.5 °C]. The NMR spectrum showed only aromatic protons.

Acknowledgment. We wish to thank Professor H.G. Kuivila for helpful discussions during the preparation of this paper. The research was supported by several grants from the Colgate University Research Council which are gratefully acknowledged. Also we wish to thank M & T Chemicals for their gift of chemicals and Norwich Pharmical for recording some of the NMR spectra.

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The Diethynylcyclobutadiene Rearrangement: A Degenerate Ligand Reorganization in the Coordination Sphere of (η^5-Cyclopentadienyl)cobalt[1]

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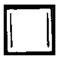
Reaction of CpCo(CO)$_2$ with bis(trimethylsilyl)butadiyne leads to small amounts of silylated 1,2- and 1,3-diethynylcyclobutadiene complexes **13** and **18** among other products. Alternatively, cocyclization of bis(trimethylsilyl)hexatriyne with bis(trimethylsilyl)acetylene furnishes **13** in 64.2% yield. These compounds may be protodesilylated with alcoholic KOH or fluoride. Flash vacuum thermolysis of the 1,2-diethynylcyclobutadiene complexes **9**, **19**, and **49** induces a clean rearrangement in which the four sp carbons of the ethynyl groups cyclize to form a new cyclobutadiene ring and the original cyclobutadiene ring retrocyclizes to generate two new alkyne groups. In this way **9** undergoes a degenerate rearrangement, whereas **19** converts to **30**, and **49** equilibrates with **50**. Mechanistic speculation is offered which suggests a CpCo-complexed cycloocta-3,7-diene-1,5-diyne (**11**) or cycloocta-1,2,3,5,6,7-hexaene (**12**) as a likely intermediate. A topologically equivalent alternative, (η^4-tricyclo[4.2.0.0^{2,5}]octa-1,3,5,7-tetraene)(η^5-cyclopentadienyl)cobalt (**10**), appears less favored on theoretical grounds.

Polycyclic benzenoid hydrocarbons have played an important part in the development of the theory of π-electronic cycles. They have received renewed recent attention in connection with diverse areas such as those concerned with the mechanism of carcinogenicity induced by environmentally abundant polycyclic benzenoids[4] and the conversion of coal to liquid and gaseous fuels.[5] These compounds are conceptually derived by linear and angular fusion of benzene rings, the latter constituting the prototype aromatic molecule.[6] One might conceive of nonbenzenoid analogs of the benzenoid aromatics formed by fusion of the prototype "antiaromatic"[7] molecule: cyclobutadiene.[8] The first three members of such a series (which can only be linear) are cyclobutadiene (1), butalene (bicyclo[2.2.0]hexa-1,3,5-triene) (2), and tricyclo[4.2.0.0^{2,5}]octa-1,3,5,7-tetraene (3), for which in analogy with the trivial naming of biphenylene, the name bicyclobutadienylene may be proposed. Interestingly, and in contrast to the benzenoid series, only the first member, cyclobutadiene, has been studied relatively thoroughly.[8] Compound 2 has been invoked as a reactive intermediate,[9]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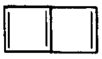
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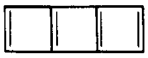
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[8] S. Masamune, F. A. Souto-Bachiller, T. Machiguchi, and J. E. Bertie, *J. Am. Chem. Soc.*, **100**, 4889 (1978); D. W. Whitman and B. K. Carpenter, *ibid.*, **102**, 4272 (1980), and the references therein.

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standardized hydrochloric acid in methanol, and methanol-deionized water (to bring the final water concentration to 5%) were thermostated prior to mixing. After the reaction solution was mixed, it was transferred to a cuvette and the absorbance read as a function of time in a Beckman DU-Gilford with a thermostated cell compartment. Most substrates were run under second-order conditions (nearly equal concentrations of tin compound and acid in the range of 10^{-3} M) at least at one temperature and also under pseudo-first-order conditions with a 50-fold excess of acid. Second-order rate constants and activation parameters were obtained from a standard least-squares plot.

Reaction of Triphenylvinyltin (12) with 2,4-Dinitrobenzenesulfenyl Chloride. A solution of 0.620 g (2.65×10^{-3} mol) of 2,4-dinitrobenzenesulfenyl chloride in 5 mL of methylene chloride was added dropwise with stirring to 1.00 g (2.65×10^{-3} mol) of triphenylvinyltin (**12**) in 5 mL of methylene chloride. The reaction mixture was allowed to stir overnight. The solution was washed twice with water, dried over magnesium sulfate, and evaporated to dryness. The residue was dissolved in hot ethanol. On cooling, 0.49 g (67%) of yellow crystals was formed. A second recrystallization gave crystals of 2,4-dinitrophenyl phenyl sulfide **16**, mp 118–119 °C [lit.[27] 119.5–120.5 °C]. The NMR spectrum showed only aromatic protons.

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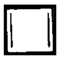
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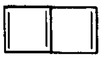
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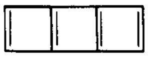
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(bicyclo[2.2.0]hexa-1,3,5-triene) (2), and tricyclo-[4.2.0.0^{2,5}]octa-1,3,5,7-tetraene (3), for which in analogy with the trivial naming of biphenylene, the name bicyclobutadienylene may be proposed. Interestingly, and in contrast to the benzenoid series, only the first member, cyclobutadiene, has been studied relatively thoroughly.[8] Compound 2 has been invoked as a reactive intermediate,[9]

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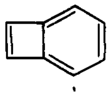
and one of its interesting features is its potential to exist as the isomeric cyclic bisallene or *p*-benzyne biradical.[10] The 8π-system **3** has similar and additional structural possibilities which it might be inclined to adopt in an effort to alleviate strain related and electronically induced destabilizing features. These are shown in **4**–**8**.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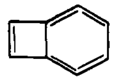
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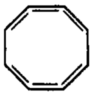
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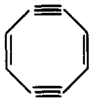
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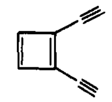
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The literature reveals that some theoretical thought has been devoted to **3**.[10] This is of interest particularly with respect to estimates of its relative stability in comparison with **1** and **2**. In most treatments the stability of **3** is calculated to lie inbetween that of **1** and **2**,[10c] all three compounds being destabilized by conjugation ("antiaromatic"). For example, a structure–resonance theory approach suggests negative resonance energies (REs) of −0.65, −0.31, and −0.52 eV for **1**, **2**, and **3**.[10c] A perturbational molecular orbital estimate[10b] similarly places the stability of **3** (RE = 2.45 β) lower than that of **2** (RE = 2.83 β). A graph theoretical approach to this problem is particularly instructive because it is based on the enumeration of so-called conjugated circuits related to the presence and relative importance of classical Kekulé structures.[11] Thus, in the five possible resonance structures of **3**, one may detect four benzene-like circuits, but ten cyclobutadiene and two cyclooctatetraene circuits. The resulting calculated resonance energy value is in accord with the other treatments portraying **3** to be more antiaromatic (AA = −65.88%) than **2** (AA = −57.24%).

Inspection of **6** and **7** and comparison with **3** suggests the interesting possibility that all of these molecules might be resonance structures. This suggestion is deemed unlikely on the basis of the results of ab initio SCF LCAO-MO calculations revealing distinct energy minima on the D_{2h} C_8H_4 potential energy surface.[12]

Intuitively, **7** might be deemed the lowest energy isomer in the series. It also constitutes an attractive synthetic target since it would represent the first unsubstituted planar cyclooctatetraene derivative, a molecule of considerable current theoretical interest.[18] The anticipated strain in such a system, although appreciable, should not be prohibitive, on the basis of literature analogies,[18,19] particularly the remarkable stability of cycloocta-1,5-diyne.[19a]

The equally interesting cycloocta-1,2,3,5,6,7-hexaene (**6**) is similar to **7** in that it also contains a planar, monocyclic eight π-electron system. 1,2,4,5,7-Cyclooctapentaene, a dihydro derivative of **6**, has been suggested as an intermediate in the thermal rearrangement of *cis*,*cis*-octa-3,5-diene-1,7-diyne to benzocyclobutadiene.[20]

Potential synthetic approaches to the C_8H_4 manifold symbolized by structures **3**–**7** will have to take into account the likely lability and sensitivity of any of the target molecules. Transition metals have frequently been used as stabilizing appendages to otherwise reactive or thermally labile π systems.[21] It occurred to us that this might be applicable also in this case. In particular, rather than attempting to trap one of the reactive species **3**, **6**, and **7** by using an added metal complex, a strategy we considered fraught with experimental difficulties, we felt that incorporating the metal into a suitable precursor from which one of the theoretically interesting ligands might be accessible by unimolecular rearrangement was a more promising proposition.

Stabilization of cyclobutadienes by complexation to a transition metal has been firmly established experimentally[22] after having been predicted theoretically.[23] In particular, (η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt complexes are air-stable and, in the absence of reactive substituents, can be heated in condensed phases to well

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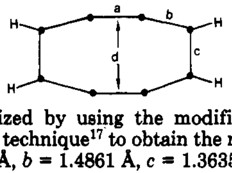
[10] (a) H. E. Simmons and A. G. Anastassiou in M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds", Academic Press, New York, 1967, p 396. (b) M. J. S. Dewar, M. C. Kohn, and N. Trinajstić, *J. Am. Chem. Soc.*, **93**, 3437 (1971); (c) W. C. Herndon and M. L. Ellzey, *ibid.*, **96**, 6631 (1974); (d) C. F. Wilcox, Jr., *Tetrahedron Lett.*, 795 (1968).

[11] M. Randić, *J. Am. Chem. Soc.*, **99**, 444 (1977); *Tetrahedron*, **23**, 1905 (1977); see also J. A. N. F. Gomes, *Croat. Chem. Acta*, **53**, 561 (1980).

[12] Single-determinant SCF LCAO-MO Hartree–Fock calculations[13] were performed with the Gaussian 70 computer program series[14] using the minimal STO-3G basis set and the recommended standard exponents.[15] The only C_8H_4 geometries considered were those that have D_{2h} configurations. In each geometry, the hydrogen atoms were positioned such that the C–H bond lengths were their standard value[16] of 1.08 Å and such that all eight C–C–H bond angles were equal. Starting with the geometry for **3** in which all ten C–C bond lengths were set to their standard value[16] of 1.4 Å, the dimensions *a*, *b*, *c*, and *d* shown were



simultaneously optimized by using the modified Davidon–Fletcher–Powell gradient search technique[17] to obtain the minimum-energy geometry for **3**: a = 1.3464 Å, b = 1.4861 Å, c = 1.3635 Å, d = 1.5014 Å; total energy = −301.091 062 hartrees. Successive increases in parameter *d* from the optimized geometry for **3** suggested the presence of a second energy minimum in the D_{2h} C_8H_4 potential surface. Simultaneous optimization[17] of dimensions *a*, *b*, *c*, and *d* then gave the minimum-energy geometry for **7**: a = 1.1800 Å, b = 1.4719 Å, c = 1.3340 Å, d = 2.5863 Å; total energy = −301.284 705 hartrees. An attempt to find the transition state for a possible **3** ⇄ **7** rearrangement led to the discovery of a third energy minimum. After simultaneous optimization[17] of parameters *a*, *b*, *c*, and *d*, the minimum-energy geometry for **6** resulted: a = 1.3081 Å, b = 1.3764 Å, c = 1.4053 Å, d = 2.0226 Å; total energy = −300.990 194 hartrees. Although we do not have much confidence in the quantitative accuracy of the method or even the relative energy ordering when applied to our system, we do attach some significance to the theoretical distinction between **3**, **6**, and **7**.

[13] C. C. J. Roothan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[14] W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.

[15] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

[16] J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).

[17] J. B. Collins, P. von R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, **64**, 5142 (1976).

[18] For some benzoderivatives, see: C. F. Wilcox, Jr., J. P. Uetrecht, G. D. Grantham, and K. G. Grohmann, *J. Am. Chem. Soc.*, **97**, 1914 (1975); H. N. C. Wong, P. J. Garratt, and F. Sondheimer, *ibid.* **96**, 5604 (1974); H. N. C. Wong and F. Sondheimer, *Angew. Chem.*, **88**, 126 (1976); *Angew. Chem., Int. Ed. Engl.*, **15**, 117 (1976); F. Gerson, W. B. Martin, G. Plattner, F. Sondheimer, and H. N. C. Wong, *Helv. Chim. Acta*, **59**, 2038 (1976); R. Destro, T. Pilati, and M. Simonetta, *Acta Crystallogr., Sect. B*, **B33**, 447 (1977); T.-L. Chan, Y.-S. Lam, and T. C. W. Mak, *ibid.*, **B35**, 218 (1979); M.-K. Au, T.-W. Siu, T. C. W. Mak, and T.-L. Chan, *Tetrahedron Lett.*, 4269 (1978); H. N. C. Wong and F. Sondheimer, *ibid.*, 983 (1980); *J. Org. Chem.*, **45**, 2438 (1980); H. Gugel and H. Meier, *Chem. Ber.*, **113**, 1431 (1980); R. A. G. de Graaff, S. Gorter, C. Romers, H. N. C. Wong, and F. Sondheimer, *J. Chem. Soc., Perkin Trans. 2*, 478 (1981). A planar perfluorotetrakis(cyclobutacyclooctatetraene) has recently been reported: F. W. B. Einstein, A. C. Willis, W. R. Cullen, and R. L. Soulen, *J. Chem. Soc., Chem. Commun.*, 526 (1981).

[19] For some less unsaturated derivatives, see: (a) E. Kloster-Jensen and J. Wirz, *Helv. Chim. Acta*, **58**, 162 (1975); (b) H. Maier and H. Petersen, *Synthesis*, 596 (1978); H. Petersen, H. Kolshorn, and H. Meier, *Angew. Chem.*, **90**, 483 (1978); *Angew. Chem., Int. Ed. Engl.*, **17**, 461 (1978); W. Leupin and J. Wirz, *Helv. Chim. Acta*, **61**, 1663 (1978); H. Petersen and H. Meier, *Chem. Ber.*, **113**, 2383 (1980); H. Meier, H. Petersen, and H. Kolshorn, *ibid.*, **113**, 2398 (1980).

[20] G. H. Mitchell and F. Sondheimer, *J. Am. Chem. Soc.*, **91**, 7520 (1969).

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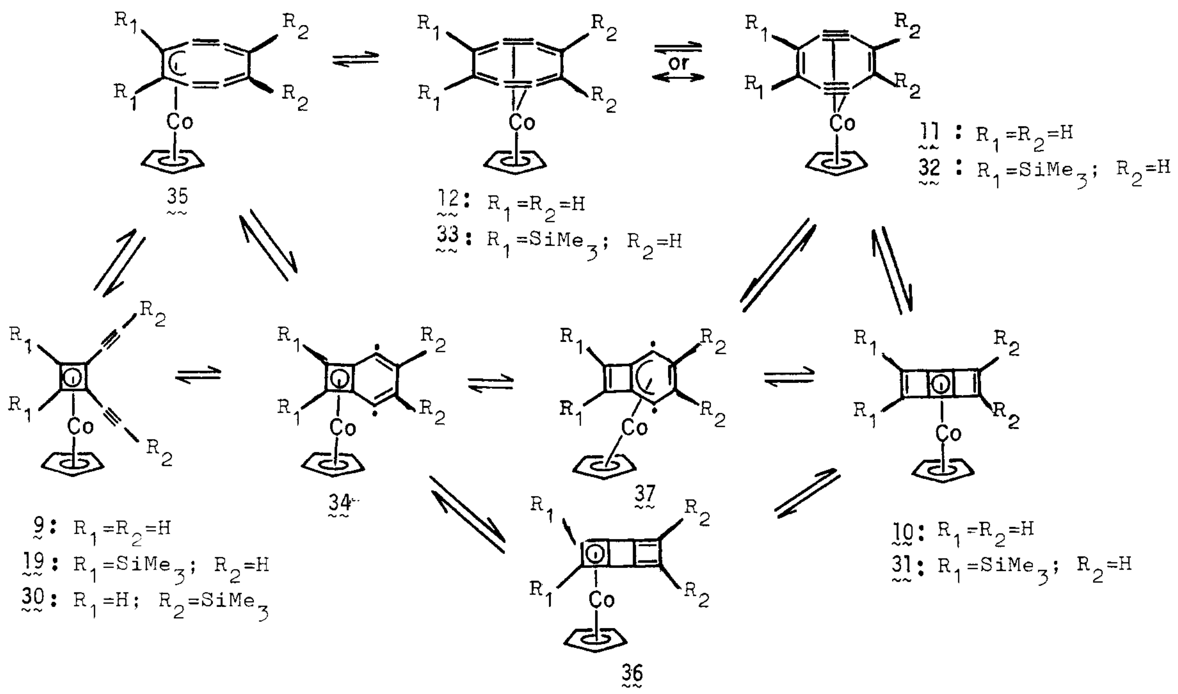
[22] (a) A. Efraty, *Chem. Rev.*, **77**, 691 (1977), and the references therein; (b) P. M. Maitlis and K. W. Eberius, "Nonbenzenoid Aromatics", J. P. Synder, Ed., Academic Press, New York, 1971, Chapter 6.

[23] H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

Scheme I



over 200 °C without detectable decomposition.[22] Given these considerations, a practical approach to the synthesis of at least liganded **3**, **6**, or **7** might be to start with (η^4-1,2-diethynylcyclobutadiene)(η^5-cyclopentadienyl)cobalt (CpCo) (**9**), which should be sufficiently stable to be isolated, characterized, and exposed to thermal rearrangement conditions. (η^4-cyclobutadiene)CpCo complexes can often be prepared by direct reaction of $CpCo(CO)_2$ with the corresponding alkynes.[22,24] Thermolysis or photolysis of **9** would then hopefully generate **10**, **11**, or **12**, the CpCo complexes of **3**, **7**, and **6**, respectively (Scheme I).

It is not clear to what extent complexation will change the order of thermodynamic stability of **3**, **6**, and **7**. However, one might anticipate the electronically most destabilized ligand to be the most strongly bound.[25] If **10**, **11**, or **12** resulted from rearrangement of **9**, the corresponding free ligands might be obtained by oxidative[22] or ligand displacement[26] techniques.

CpCo complex **9** has an important advantage over other possible metal complexes of **8** (for example, the iron tricarbonyl complex). The (η^5-cyclopentadienyl)cobalt bond strength, 64 kcal mol^{-1} (from cobaltocene), is substantially greater than the ligand–metal bond energies for carbon monoxide, phosphine, isocyanide, olefin, alkyl, and butadiene ligands.[27] Consequently, the cyclopentadienyl moiety is expected to serve as a relatively inert blocking group for the three cobalt coordination sites not occupied by the respective ligands **3**, **6**, **7**, and **8**. The potential reactivity of other ligands that might be used to complete the metal's coordination shell could result in undesired reactions that would obscure or prevent the desired rearrangement of ligand **8**. The following is a full account of the preparation of 1,2-diethynylcyclobutadiene complexes of the type **9** and their thermal and other chemistry which has led to the discovery of a novel transformation in the coordination sphere of cobalt, the 1,2-diethynylcyclobutadiene rearrangement.[28]

Results and Discussion

Preparation of (Diethynyl-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt Complexes. The 1,2-diethynylcyclobutadiene ligand of CpCo complex **9** can be conceptually dissected into component alkynes in two different ways. One dissection gives two molecules of butadiyne; the other dissection yields acetylene and hexatriyne. Reaction of either pair of component alkynes with $CpCo(CO)_2$ could, in principle, provide **9**.[22,24]

However, butadiyne[29] and hexatriyne[30] polymerize at temperatures much lower than those required for the cyclization reaction. This problem might be circumvented by using either bis(trimethylsilyl)butadiyne[34] or bis(trimethylsilyl)acetylene and bis(trimethylsilyl)hexatriyne[33] to prepare **13** (Scheme II). Protodesilylation would then yield the desired **9**. Alcoholic KOH is known to protodesilylate ethynyl trimethylsilyl groups,[31] and removal of aromatic trimethylsilyl substituents has been achieved with fluoride ion,[32] under conditions which might be effective on the cyclobutadiene nucleus.

Unfortunately, reaction of $CpCo(CO)_2$ with 2 equiv of bis(trimethylsilyl)butadiyne in refluxing *n*-octane followed by chromatographic separation of the products on silica

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(24) (a) R. L. Hillard and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **99**, 4058 (1977); (b) J. R. Fritch and K. P. C. Vollhardt, *Angew. Chem.*, **91**, 439 (1979); *Angew Chem., Int. Ed. Engl.*, **18**, 409 (1979); (c) R. I. Duclos, K. P. C. Vollhardt, and L. S. Yee, *J. Organomet. Chem.*, **174**, 109 (1979); (d) J. R. Fritch, K. P. C. Vollhardt, M. R. Thompson, and V. W. Day, *J. Am. Chem. Soc.*, **101**, 2768 (1979); (e) E. R. F. Gesing and K. P. C. Vollhardt, *J. Organomet. Chem.*, **217**, 105 (1981); (f) G. Ville, K. P. C. Vollhardt, and M. J. Winter, *J. Am. Chem. Soc.*, **103**, 5267 (1981).

(25) M. J. S. Dewar, *Angew. Chem.*, **83**, 859 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).

(26) A. Krebs, H. Kimling, and R. Kemper, *Justus Liebigs Ann. Chem.*, 431 (1978).

(27) J. A. Connor, *Top. Curr. Chem.*, **71**, 71 (1977); V. I. Tel'noi and I. B. Rabinovich, *Russ. Chem. Rev.* (*Engl. Transl.*) **46**, 689 (1977); J. R. Chipperfield, J. C. R. Sneyd, and D. E. Webster, *J. Organomet. Chem.*, **178**, 177 (1979).

(28) A preliminary report has been published: J. R. Fritch and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **100**, 3643 (1978).

(29) J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 44 (1951).

(30) J. B. Armitage, C. L. Cook, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 2010 (1952).

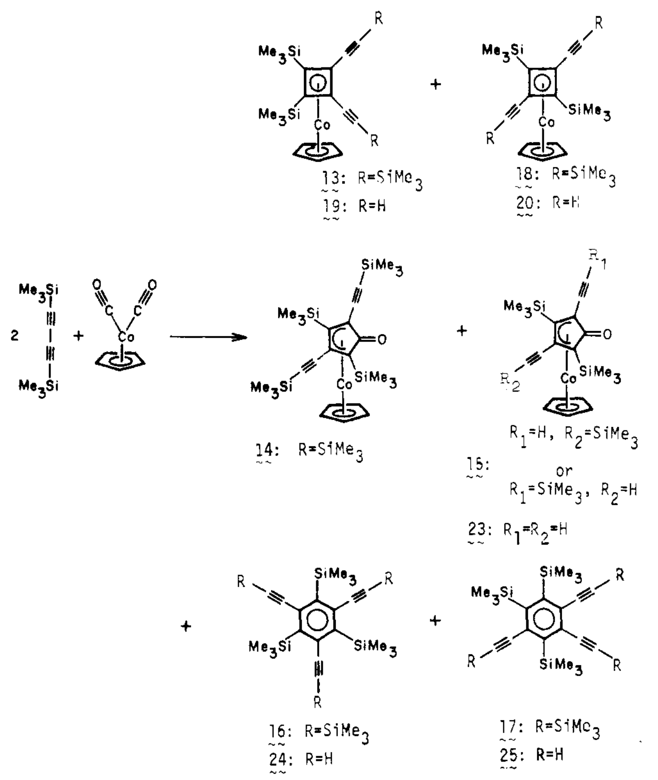
(31) D. A. Ben-Efrain "The Chemistry of the Carbon-Carbon Triple Bond", S. Patai, Ed., Part 2, Wiley, New York, 1978, Chapter 18.

(32) (a) N. Ishikawa and K. Isobe, *Chem. Lett.*, 435 (1972); (b) R. F. Cunico and E. M. Dexheimer, *J. Organomet. Chem.*, **59**, 153 (1973).

(33) H. Bock and H. Seidl, *J. Chem. Soc. B*, 1158 (1968).

(34) D. R. M. Walton and F. Waugh, *J. Organomet. Chem.*, **37**, 45 (1972).

Scheme II



gel afforded primarily the (2,4-diethynyl-η^4-cyclopentadienone)CpCo complexes **14** (24% yield) and **15** (27%), smaller amounts of diyne cyclotrimers **16** (6.4%) and **17** (4.0%), and only trace amounts of the (diethynyl-η^4-cyclobutadiene)CpCo complexes **13** (0.5%) and **18** (0.8%) (Scheme II). Formation of substituted (η^4-cyclopentadienone)CpCo complexes from the reaction of $CpCo(CO)_2$ and alkynes is well-known.[35] Triethynylbenzenes **16** and **17** were previously reported as products from the $Hg[Co(CO)_4]_2$-catalyzed trimerization of bis(trimethylsilyl)butadiyne.[36]

Complex **15**, which was obtained as a single, pure isomer having one of the two possible structures shown in Scheme II, probably resulted from protodesilylation of **14** during chromatography on silica gel. In fact, silica gel chromatography frequently converted a substantial fraction of all trimethylsilylethynyl groups, including those of **13** and **18**, into terminal ethynyl or acetyl groups. Consequently, silica gel chromatography of mixtures containing trimethylsilylethynyl groups was avoided whenever possible.

Alcoholic KOH protodesilylated the ethynyl positions of complex **13** to provide the thermally unstable complex **19** in 94% yield. Similarly, complex **18** was converted to **20**. The trimethylsilyl substituents on the cyclobutadiene rings of **19** and **20** are evidently inert to alcoholic KOH, even though the carbon to which they are bound is between sp^1 and sp^2 hybridized[37] constituting a potentially good leaving group.

The cyclobutadiene ring positions can also be protodesilylated but only with a stronger desilylating agent such as fluoride ion. For example, (1,3-diethynyl-η^4-cyclobutadiene)CpCo (**21**) resulted in 94% yield from **20**, or in 100% yield from **18**, by reaction with tetramethylammonium fluoride and H_2O in Me_2SO.

Treatment of a THF solution of **21** with 2 equiv of *n*-butyllithium followed by 2 equiv of chlorotrimethylsilane provided (1,3-bis((trimethylsilyl)ethynyl)-η^4-cyclobutadiene)CpCo (**22**) in 97% yield. The synthesis of **22** was required in order to establish the identity of the products obtained from the flash vacuum pyrolyses discussed later.

It was found that the yield of **19** could be increased by slow syringe pump addition of the reactants to nitrogen-flushed, refluxing *n*-decane (bp 174 °C), removal of solvent, and protodesilylation of the resulting residue with alcoholic KOH. The latter treatment greatly improved the chromatographic separation of products. In this way, **19** (2% yield), **20** (51%), **24** (11%), **25** (2%), and **23** (7%), in addition to a new complex **26** (4%), (2,4-diethynyl-5-(trimethylsilyl)-η^4-cyclopentadienone)CpCo, were isolated after chromatography on neutral alumina. The structures of all new compounds are in accord with their spectral and analytical characteristics (see Experimental Section). The relative assignment of the 1,2- vs. the 1,3-diethynyl substitution pattern in the cyclobutadiene complexes is based on the characteristic mass spectral fragmentation patterns[39] with prominent molecular ion peaks due to retro [2 + 2] cyclization of the four-ring, ^{13}C satellite NMR spectra (vide infra), chemical correlations (vide infra), and ultimately an unambiguous synthesis of **13** (vide infra). The substitution pattern in **26** was established by spectral comparison with model compounds.[40]

The observed product distribution in Scheme II is clearly indicative of preferential oxidative coupling of two complexed diynes to furnish a 2,4-bis trimethylsilylated cobaltacyclopentadiene.[14] This is surprising since the trimethylsilyl group ordinarily prefers the α-position in cobaltacycles of this type.[24a,40,41,42] Bis(trimethylsilyl)butadiyne and other 1,3-diynes react with iron carbonyls to form metallacycles and cyclopentadienone complexes in which the ethynyl groups are located in all possible positions.[43]

In larger scale preparations of **13** and **18**, particularly when using a large excess of bis(trimethylsilyl)butadiyne, a small quantity of a new compound, **27**, was isolated which gave spectral data consistent with 1,2,4,5-tetrakis((trimethylsilyl)ethynyl)-3,6-bis(trimethylsilyl)benzene (**27**). This structural assignment was subsequently ascertained by conversion to the known[44] 1,2,4,5-tetraethylbenzene by protodesilylation (KOH, ethanol) to give 1,2,4,5-tetraethynyl-3,6-bis(trimethylsilyl)benzene (**28**), hydrogenation (Wilkinson's catalyst) to 1,2,4,5-tetraethyl-3,6-bis(trimethylsilyl)benzene (**29**), and protodesilylation (CF_3CO-OH) to give 1,2,4,5-tetraethylbenzene, identical with an authentic sample and distinct from the independently prepared other two isomers.[44] Compound **27** is formally the product of a cocyclization of two bis(trimethylsilyl)butadiyne units with one bis(trimethylsilyl)hexatriyne

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(35) R. S. Dickson and P. J. Fraser, *Adv. Organomet. Chem.*, **14**, 245 (1974).

(36) W. Hübel and R. Merényi, *Chem. Ber.*, **96**, 930 (1963).

(37) $J_{^{13}\mathrm{C-H}}$ for the cyclobutadiene protons in **30** is 190.7 Hz, possibly implying hybridization of sp ~1.6 for the corresponding carbon orbitals.[38]

(38) J. B. Stothers, "Carbon-13 NMR-Spectroscopy", Academic Press, New York, 1972.

(39) M. D. Rausch, I. Bernal, B. R. Davies, A. Siegel, F. A. Higbie, and G. F. Westover, *J. Coord. Chem.*, **3**, 149 (1973).

(40) E. R. F. Gesing, J. P. Tane, and K. P. C. Vollhardt, *Angew. Chem.*, **92**, 1057 (1980); *Angew. Chem., Int. Ed. Engl.*, **19**, 1023 (1980).

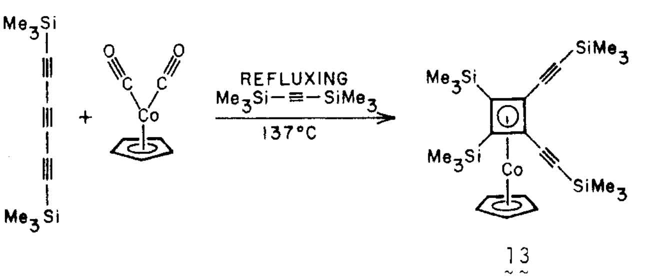
(41) K. P. C. Vollhardt, *Acc. Chem. Res.*, **10**, 1 (1977).

(42) C. Chang, J. A. King, and K. P. C. Vollhardt, *J. Chem. Soc., Chem. Commun.*, 53 (1981). See also: A. Stockis and R. Hoffmann, *J. Am. Chem. Soc.*, **102**, 2952 (1980).

(43) G. G. Cash and R. C. Pettersen, *Inorg. Chem.*, **17**, 650 (1978); F. R. Young, D. H. O'Brien, R. C. Pettersen, R. A. Levenson, and D. L. von Minden, *J. Organomet. Chem.*, **114**, 157 (1976); K. H. Pannell and G. M. Crawford, *J. Coord. Chem.*, **2**, 251 (1973); W. Hübel and R. G. Merényi, *Chem. Ber.*, **96**, 930 (1963).

(44) L. I. Smith and C. O. Guss, *J. Am. Chem. Soc.*, **62**, 2625, 2631 (1940).

Scheme III



molecule. Indeed, the latter was subsequently detected by GC–mass spectroscopy as a 3% impurity in our bis(trimethylsilyl)butadiyne. This suggested that the triyne might function as an efficient cocyclizing agent with bis(trimethylsilyl)acetylene (BTMSA)[41] to provide an alternative and selective route to **13**.

Bis(trimethylsilyl)hexatriyne was prepared by a modification of the literature procedure[33,45] (see Experimental Section) in improved yield. Gratifyingly, syringe pump addition of CpCo(CO)$_2$ and 1 equiv of bis(trimethylsilyl)hexatriyne to refluxing, nitrogen-flushed BTMSA provided the desired **13** in 64.2% yield (Scheme III). Several other compounds were formed in small amounts including a mixture of isomeric bis(cyclobutadiene) complexes derived by further cocyclization of one of the ethynyl groups in **13**, cyclobutadiene complexes generated by cocyclization of 1-(trimethylsilyl)-3-methylbut-1-yn-3-ol, an impurity in commercial BTMSA, and tetrakis(trimethylsilyl)butatriene[24d] (see Experimental Section).

The Diethynylcyclobutadiene Rearrangement. The rearrangement of (1,2-diethynyl-η^4-cyclobutadiene)CpCo (**9**) to **10**, **11**, or **12** (Scheme I) was attempted by flash vacuum pyrolysis (FVP). Although as a result of the very short contact times, the temperature required for a FVP reaction is several hundred degrees centigrade higher than that required for the same reaction carried out in solution, the exclusion of intermolecular gas phase collisions permits thermal unimolecular rearrangements (or fragmentations) to be performed without interfering bimolecular reactions of reactive intermediates with starting material, final products, solvents, or oxygen.[46] Consequently, FVP has proven to be an extremely valuable tool for the preparation and chemical investigation of unstable species[46] and, although uncommon with organometallic compounds, appears to be the method of choice for attempting the rearrangement of **9**, or its derivatives, such as **19**.

Surprisingly, sublimation of **19** through a hot quartz tube at 525 °C (10^{-4} torr) resulted in the unprecedented clean rearrangement to its isomer **30**! The isolated yield was 63%, but since **30** was the only compound detected in the pyrolysate and since the FVP left no trace of any decomposition products inside the quartz FVP tube, the yield of **30** based on **19** that actually sublimed was probably quantitative.[56] A small amount of intractable material was left unsublimed due to decomposition of the sensitive **19**. Protodesilylation of the ethynyl positions of the rearrangement product **30** was effected with alcoholic KOH to produce (1,2-diethynyl-η^4-cyclobutadiene)CpCo (**9**) quantitatively. The spectral data for **30** and its reaction with alcoholic KOH confirmed the presence of two (trimethylsilyl)ethynyl groups. The close similarity (but nonequivalence) of the spectral data for **30** and **22** and of the spectral data for **9** and **21** then provided convincing evidence for the structural assignments. The ^{13}C-satellite peaks in the ^{1}H NMR spectrum of **30** showed that the coupling constant between the two cyclobutadiene hydrogens is less than 0.35 Hz, which is also consistent with 1,2 but not 1,3 substitution of the cyclobutadiene ring. For (η^4-cyclobutadiene)iron tricarbonyl, the coupling constant between 1,2 hydrogens was found to be zero and that between 1,3- hydrogens was 8.9 Hz.[47]

Complex **30** is evidently thermodynamically more stable than **19**. This may be ascribed to two factors. First, the steric strain between the two trimethylsilyl groups of **19** is not present in **30**. Second, the electropositive trimethylsilyl group has a likely electronic preference for the more electronegative sp-hybridized ethynyl carbons over the less electronegative, formally sp^2-hybridized cyclobutadiene ring carbons, and this preference is probably greater than that of a hydrogen atom.[48]

There are several mechanisms which may be formulated in order to explain the observed rearrangement. Scheme I outlines the mechanistic possibilities that have as key intermediates the (η^4-tricyclo[4.2.0.0^{2,5}]octa-1,3,5,7-tetraene)CpCo complex **31**, the (η^4-cycloocta-1,5-diene-3,7-diyne)CpCo complex **32**, or the (η^4-cycloocta-1,2,3,5,6,7-hexaene)CpCo complex **33**. All of these species have the symmetry appropriate of a molecule which would provide the mechanistic connection between **19** and **30**. These intermediates may be kinetically accessible in a variety of ways. For example, *cis*-hex-3-ene-1,5-diyne rearranges to benzene-1,4-diyl (*p*-benzyne) with an activation free energy of 32 kcal mol^{-1}.[9] This might indicate that the rearrangement of **19** is initiated by a similar ring closure to generate (η^4-benzocyclobutadiene-3,6-diyl)CpCo complex **34**. The antisymmetric combination of the two formally singly occupied, nonbonded sp^2-hybridized carbon orbitals of **34** mixes with the antibonding σ molecular orbital between the bridgehead carbons. Although this "through-bond" interaction stabilizes the antisymmetric combination of the two nonbonded, sp^2-hybridized carbon orbitals and also lowers the total energy of diradical **34**, it does so only by populating the antibonding σ molecular orbital between the bridgehead carbons.[49]

Cleavage of the weakened bond would provide (η^4-cycloocta-1,2,3,5,6,7-hexaene)CpCo complex **35**. Alternatively, **35** could be formed directly from **19** by a Cope-type process. Migration of CpCo to the center position of the cycloocta-1,2,3,5,6,7-hexaene ligand would then give complex **33**, which presumably is separated from (η^4-cycloocta-1,5-diene-3,7-diyne)CpCo complex **32** by only a very small activation barrier, if any.

An alternative pathway involves radical coupling of **34** to generate complex **36**. Migration of CpCo to the center cyclobutadiene ring would then yield tricyclooctatetraene complex **31**. If migration were to precede coupling, **37** would become an intermediate which might collapse to **31** or directly open to **32**. The observed rearrangement product would then result from **31**, **32**, or **33** by a corresponding set of reverse transformations.

CpCo participates only passively in the carbon skeleton rearrangements shown in Scheme I. Migration of CpCo between the cyclobutadiene rings of a tricyclo[4.2.0.0^{2,5}]octa-1,3,5,7-tetraene ligand (e.g., **36** → **31**) is predicted to be thermally "forbidden" by orbital symmetry considerations,[50] increasing the likelihood that one of the other

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(45) F. Bohlmann, *Chem. Ber.*, **84**, 785 (1951).

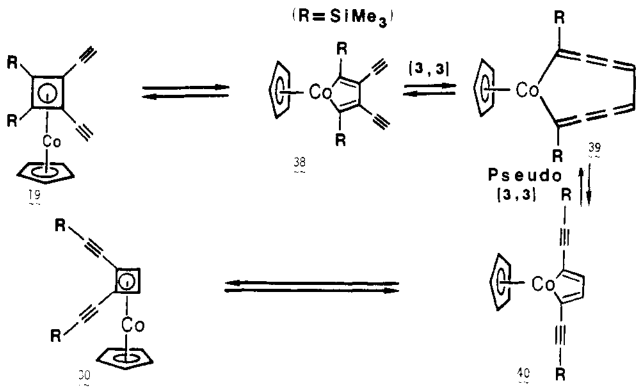
(46) G. Seybold, *Angew. Chem.*, **89**, 377 (1977); *Angew. Chem., Int. Ed. Engl.*, **16**, 365 (1977).

(47) H. A. Brune, H. P. Wolff, and H. Hüther, *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.*, **23B**, 1184 (1968).

(48) L. H. Sommer, "Stereochemistry, Mechanism and Silicon", McGraw-Hill, New York, 1965.

(49) R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971).

Scheme IV



intermediates in Scheme I is present. Intramolecular migration of a transition metal between two rings of a coordinated bi- or tricyclic π system has been well established experimentally.[51]

Scheme IV shows an alternative mechanism for the diethynylcyclobutadiene rearrangement, one in which cobalt participates actively. Oxidative insertion of cobalt into the most sterically strained σ bond of the cyclobutadiene ring of **19** would yield cobaltacyclopentadiene complex **38**. This proposed transformation is essentially the reverse process of the well-known thermal conversion of (triphenylphosphine)(η^5-cyclopentadienyl)cobaltacyclopentadiene complexes into their corresponding CpCo(cyclobutadiene) complexes.[24f,52] Subsequent expansion of the cobaltacyclopentadiene ring by a [3,3] sigmatropic shift would provide cobaltacyclonona-2,3,4,6,7,8-hexaene complex **39**. Complex **40** could then conveivably result via a "pseudo [3,3] sigmatropic shift". This rearrangement would be interesting because it would involve apparently simultaneous [1,3] shifts of two cobalt–carbon bonds; sequential [1,3] shifts would require an intermediate that probably would be prohibitively strained. Consequently, the proposed pseudo [3,3] sigmatropic shift would differ from a normal [3,3] sigmatropic shift only by insertion of a cobalt atom into the migrating bond. Finally, reductive coupling would afford the observed rearrangement product **30**. This mechanism is topologically equivalent to those depicted in Scheme I and is not distinguishable from it by any labeling experiments (unless the cobalt configuration in **38**–**40** is invertible[24f]).

Scheme V outlines yet another possible mechanism for the diethynylcyclobutadiene rearrangement. Retrocyclization of the cyclobutadiene ligand of complex **19** could generate bis(diacetylene)CpCo complex **41**, presumably (but not necessarily)[24f] via the intermediacy of a cobaltacyclopentadiene complex. We have observed such retrocyclizations in specifically (1,2-bis(silyl)-3-alkyl-)-substituted cyclobutadiene–CpCo systems, albeit occurring much more slowly.[24f] Nevertheless, the rather special substitution pattern in **19** makes consideration of this alternative advisable. Once formed, bis(diacetylene)CpCo complexes such as **41** might rearrange by "diacetylene shifts", i.e., migration of CpCo between the two triple bonds of a diacetylene ligand. For example, two such diacetylene shifts would provide bis(diacetylene)CpCo complex **42** from **41**. The observed rearrangement product would then result from subsequent recyclization of the diacetylene ligands.[24f] However, as the scheme indicates, random alkyne rotations and recyclizations should compete with the **19** → **30** transformation, generating product mixtures. Although such rotations may be slow in some complexes,[53] they appear to be fast for CpCo systems (with the exception of bulky ligands).[24b,f] Thus, complexes **43** and **44** should be accessible from **41** and **42**, respectively. The former pair would then be interconverted by two diacetylene shifts, and recyclization would yield **20** and **22**, respectively. Alternatively, a single diacetylene shift of either **43** or **44** could generate **45**, which would subsequently provide either **46** by recyclization or complex **47** by ligand rotation. The latter could also result directly from either **41** or **42** by a single diacetylene shift without the intervention of any alkyne ligand rotations. Recyclization of **47** would then afford complex **48**.

The failure to observe any of the complexes **20**, **22**, **46**, and **48** in the rearrangement of **19** might be ascribed to the greater thermodynamic stability of the observed product, **30**. This would lead to the prediction that exposure of any of the other isomers to the pyrolysis conditions would also convert them to **30**. However, this is not the case. Complexes **20** and **22** are inert at temperatures up to 600 °C. Above that limit one observes retrocyclization of the four-ring complex and mainly extrusion of the resulting (trimethylsilyl)butadiyne ligands, in addition to small amounts of ligand rotation–recyclization products, but no alkyne shifts.[24b]

To rigorously exclude the mechanism depicted in Scheme V, a deuterium-labeling experiment was performed employing **49** as the substrate in the rearrangement. Scheme V predicts the formation of **49**, **51**, and **50** in a statistical (1:2:1) ratio on pyrolysis. Scheme I, on the other hand, should give only pairwise deuterium exchange and avoid the formation of **51**.

Deuteriodesilylation of **30** with a CH_3OD solution of CH_3OK followed by D_2O workup afforded **49** containing deuterium in the ethynyl positions (Scheme VI). Subsequent 520 °C (1×10^{-4} torr) FVP yielded a 1:1 mixture of **49** and **50**. The absence of **51** in the pyrolysate was ascertained by exchanging all acetylenic deuterium in the mixture for proton (methanolic KOH). ^1H NMR and IR spectra of the resulting mixture showed equal amounts of **9** and **50**. Furthermore, the mass spectrum showed peaks of equal intensity at m/e 224 and 226 (corresponding to **9** and **50**, respectively) and the absence of m/e 225 (corresponding to **52**) in any significant amount exceeding that calculated on the basis of the fragmentation of **50**, natural abundance isotope concentrations, and the degree of deuterium incorporation in the pyrolysis mixture. Thus,

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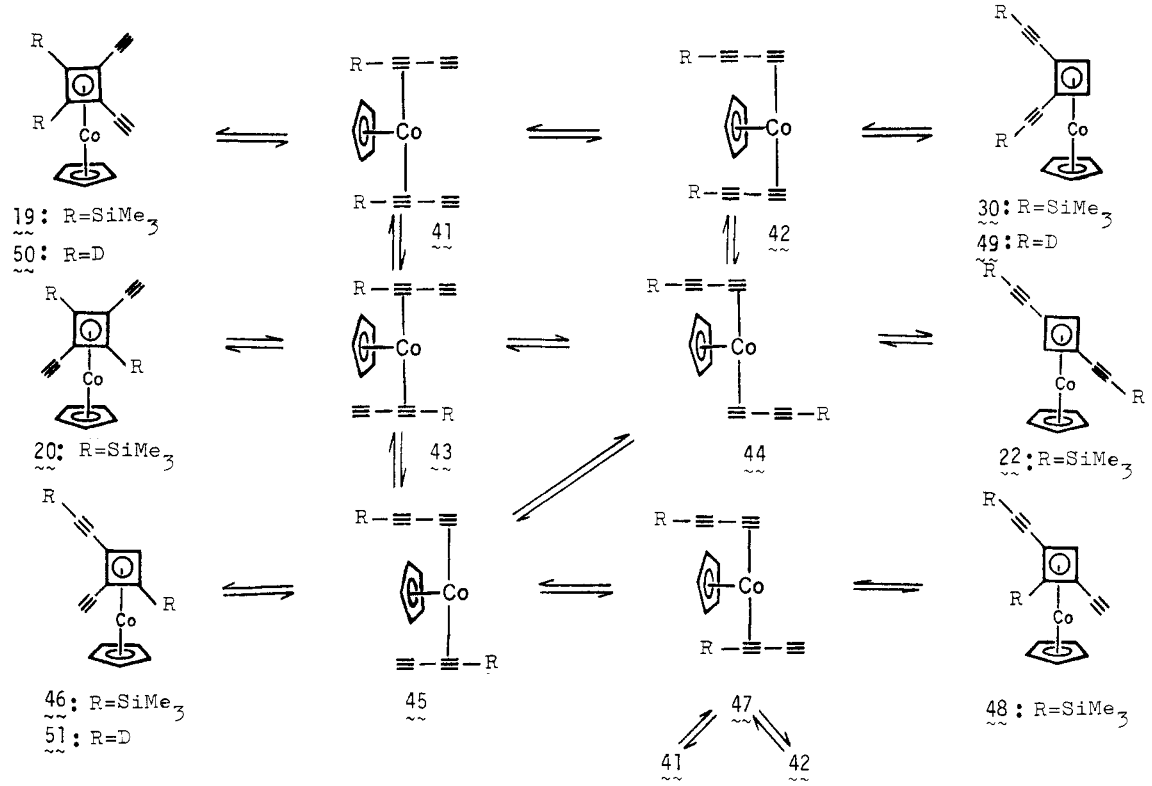
(50) P. Hofmann and T. A. Albright, *Angew. Chem.*, **92**, 747 (1980); *Angew. Chem., Int. Ed. Engl.*, **19**, 728 (1980).

(51) C. C. Lee, R. G. Sutherland, and B. J. Thomson, *J. Chem. Soc., Chem. Commun.*, 1071 (1971); P. M. Treichel and J. W. Johnson, *J. Organomet. Chem.*, **88**, 207 (1975); K. M. Nicholas, R. C. Kerber, and E. I. Stiefel, *Inorg. Chem.*, **10**, 1519 (1971); A. N. Nesmeyanov, N. A. Ustynyuk, L. G. Makarova, and S. Andre, *J. Organomet. Chem.*, **154**, 45 (1978); A. N. Nesmeyanov, N. A. Ustynyuk, L. N. Novikova, T. N. Rybina, Yu. A. Ustynyuk, Yu. F. Oprunenko, and O. I. Trifonova, *ibid.*, **184**, 63 (1980); N. A. Ustynyuk, B. V. Lokshin, Yu. F. Oprunenko, V. A. Roznyatovsky, Yu. N. Luzikov, and Yu. A. Ustynyuk, *ibid.*, **202**, 279 (1980); C. White, S. J. Thompson, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1654 (1977); J. W. Johnson and P. M. Treichel, *J. Chem. Soc., Chem. Commun.*, 688 (1976); P. M. Treichel and J. W. Johnson, *Inorg. Chem.*, **16**, 749 (1977); J. W. Johnson and P. M. Treichel, *J. Am. Chem. Soc.*, **99**, 1427 (1977); M. Magon and G. Schröder, *Liebigs Ann. Chem.*, 1379 (1978); J. Müller, P. Göser, and M. Elian, *Angew. Chem.*, **81**, 332 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 374 (1969).

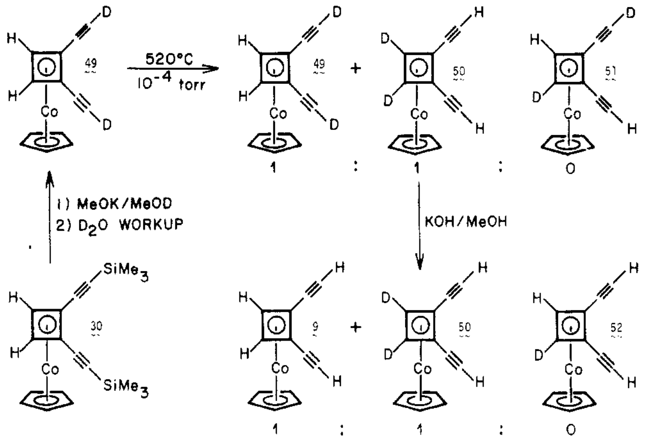
(52) H. Yamazaki and Y. Wakatsuki, *J. Organomet. Chem.*, **149**, 377 (1978); H. Yamazaki and N. Hagihara, *ibid.*, **21**, 431 (1970).

(53) For unhindered rotation in CpM (alkyne) complexes: B. E. Schilling, R. Hoffmann, and D. Lichtenberger, *J. Am. Chem. Soc.*, **101**, 585 (1979); J. L. Davidson, M. Green, J. Z. Nyathi, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 2246 (1977); M. Bottrill and M. Green, *ibid.*, 2365 (1977); B. C. Ward and J. L. Templeton, *J. Am. Chem. Soc.*, **102**, 1532 (1980); D. L. Reger and C. J. Coleman, *Inorg. Chem.*, **18**, 3270 (1979); M. L. H. Green. J. Knight, and J. Segal, *J. Chem. Soc., Dalton Trans.*, 2189 (1977), and the references therein.

Scheme V



Scheme VI



51 is not formed within experimental error in the FVP of **49**. This rules out Scheme V as a likely mechanistic rationale for the 1,2-diethynylcyclobutadiene rearrangement.

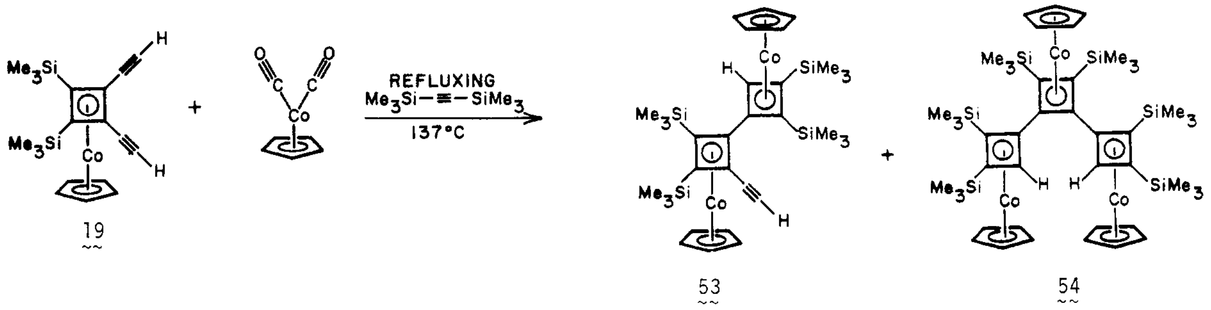
To demonstrate the feasibility of one of the pathways outlined in Scheme I, we considered trapping one of the proposed intermediates. For example, evidence for the diradical character of benzene-1,4-diyl was obtained by radical trapping experiments.[9] Similarly, formation of the known (η^4-1,2-bis(trimethylsilyl)benzocyclobutadiene)(η^5-cyclopentadienyl)cobalt[24c] from thermolysis of complex **19** in alkane solvent would constitute evidence for the intermediacy of diradical **34** in the diethynylcyclobutadiene rearrangement of **19** to **30**. However, thermolysis of **19** in refluxing 2,6,10,14-tetramethylpentadecane (pristane, bp 300 °C) provided only **30** (in 12% yield), in addition to (1-(trimethylsilyl)ethynyl-2-ethynyl-η^4-cyclobutadiene)CpCo (in about 10% yield), probably resulting by protomonodesilylation of **30** due to adventitious moisture.

An attempt to observe any of the intermediates or products in Scheme I by irradiation (Pyrex) of **9** and **50** led only to recovered starting material.

Finally, an additional strategy was attempted in an effort to stabilize one of the suggested intermediates in Scheme I. This was based on the anticipation that the two alkyne units in **19** might be induced to close to a cyclobutadiene in the coordination sphere of added cobalt. However, slow syringe pump addition of an equimolar mixture of **19** and $CpCo(CO)_2$ to refluxing, nitrogen-flushed cyclooctane (bp 151 °C) yielded only intractable products.

When an equimolar mixture of **19** and $CpCo(CO)_2$ was added slowly by syringe pump to refluxing, nitrogen-

Scheme VII



flushed BTMSA, the resulting reaction proceeded along an entirely different course (Scheme VII). After removal of the unreacted BTMSA, alumina chromatography of the resulting nonvolatile residue separated the two possible diastereomers of **53** (57% and 4.6% yields based on starting **19**), the two possible meso diastereomers of **54** (2.5% and 0.28%, three Me_3Si resonances), and also the only other possible diastereomer of **54** (0.44%, six Me_3Si resonances). No evidence could be found for any cocyclotrimerized derivatives.

The preparation of **53** and **54** indicates that either one or both of the ethynyl groups of **19** can individually cocyclize with BTMSA and $CpCo(CO)_2$ to produce either one or two new CpCo-complexed cyclobutadiene rings. The metallacycle precursor to **53** is evidently incapable of incorporating the appended second alkyne group. Interestingly, since the two diastereomers of **53** were isolated in 12:1 ratio, the stereospecificity of this cocyclization is high (about 92%). Even if all of the isolated **54** had resulted from completely stereoselective cocyclization of only the minor diastereomer of **53**, the stereospecificity of the first cocyclization would still be 88%.

In conclusion, we have observed a novel degenerate rearrangement in the coordination sphere of (η^5-cyclopentadienyl)cobalt, termed the 1,2-diethynylcyclobutadiene rearrangement, which most likely proceeds through the intermediacy of a theoretically interesting metal complexed C_8H_4 isomer such as **11** or **12**. Attempts to prove its presence have failed so far. Current investigations are directed at the independent synthesis of complexes of the type **11** or **12**. Their thermal chemistry should prove interesting in connection with our current mechanistic thinking.

Experimental Section

General Considerations and Procedures. $CpCo(CO)_2$, (trimethylsilyl)acetylene,[54] bis(trimethylsilyl)butadiyne,[34] and 1,6-dichlorohexa-2,4-diyne[55] were prepared according to previously published procedures. Other starting materials were purchased from commercial sources. BTMSA is available from PCR Research Chemicals. High boiling hydrocarbons were purified by two concentrated H_2SO_4 washings followed by distillation from CaH_2. Diethyl ether and tetrahydrofuran (THF) were distilled from $LiAlH_4$, *o*-xylene and hexane from CaH_2, methylene chloride from P_2O_5, and 1-heptene from sodium metal, all under N_2. Dimethyl sulfoxide (Me_2SO) was distilled at 75 °C from CaH_2 under 10 torr of N_2. The distilled solvents were stored over 3A molecular sieves under a positive pressure of nitrogen.

Solvents and solutions were degassed either by bubbling a stream of nitrogen through the (preferably refluxing) liquid or by subjecting the liquid to several freeze–evacuation–thaw cycles on a vacuum line.

All column chromatography was performed either on 70-230 mesh silica gel (E.M. Reagents) or on 70-290 mesh neutral alumina (Woelm) activity II. Preparative thin-layer chromatography (TLC) was carried out on plates prepared from silica gel (E.M. Reagents PF-254) containing $CaSO_4$ binder and a fluorescent indicator. Melting points and decomposition points are uncorrected and were determined with a Thomas Hoover Uni-Melt apparatus. Unless indicated otherwise, melting points and decomposition points were obtained from samples that had been sealed inside capillary tubes under nitrogen.

Analytical gas chromatography was carried out with a Hewlett-Packard Model 5710A gas chromatograph equipped with a flame ionization detector (FID). A nitrogen carrier gas flow rate of 60 mL·min^{-1} through a $^1/_4$-in. o.d. × 10-ft length stainless-steel column containing 20% UCW 98 on 60-80 mesh Chromosorb W-DMCS-AW was used to analyze for components having retention times comparable to or less than that of bis(trimethylsilyl)hexatriyne. A nitrogen carrier gas flow rate of 20 mL·min^{-1} through a $^1/_8$-in. o.d. × 20-in. length stainless-steel column containing 10% UCW 98 on 80-100 mesh Chromosorb WAW-DMCB was used to analyze for components having retention times comparable to or greater than that of bis(trimethylsilyl)hexatriyne. After the sample had been injected, the column temperature was held constant at 60 °C for 2 min and was then increased to 270 °C at 4 °C·min^{-1}. These FID GC conditions permitted quantitative analysis of the mononuclear CpCo(cyclobutadiene) complexes.

GC/mass spectral analyses were carried out on a Finnigan Model 4023 GC/mass spectrometer. A helium carrier gas flow rate of 20 mL·min^{-1} through a 2-mm i.d. × 2-m length glass column containing 3% OV 225 on 100-120 mesh Chromosorb WHP was used to analyze the flash vacuum pyrolysates of the CpCo(cyclobutadiene) complexes. The other samples were analyzed with a SP 2100-coated glass capillary column that was temperature-programmed from 40 to 280 °C at 4 °C·min^{-1}.

^{1}H NMR spectra were recorded on Varian T-60 and EM-390 spectrometers and a home-built 180-MHz pulsed-Fourier transform instrument. ^{13}C NMR spectra were obtained on a Nicolet TT-23 25.14 MHz pulsed-Fourier transform instrument and, unless indicated otherwise, were proton decoupled. Data are reported in the following format: (solvent/internal chemical shift reference compound, if not $SiMe_4$) chemical shift in parts per million (ppm) downfield from internal tetramethylsilane (multiplicity, coupling constant(s); number of protons or relative peak height). Standard abbreviations are used. The following ^{1}H NMR chemical shifts (in ppm downfield from internal tetramethylsilane) were measured and then used to reference those ^{1}H NMR spectra that did not use tetramethylsilane as the internal standard: benzene-d_5 in benzene-d_6, 7.093; benzene in CCl_4, 7.20; benzene in CS_2, 7.16; $CHCl_3$ in $CDCl_3$, 7.19. The following ^{13}C NMR chemical shifts (in ppm downfield from internal tetramethylsilane) were used to reference those ^{13}C NMR spectra that did not use tetramethylsilane as the internal standard: center peak of solvent benzene-d_6 triplet, 128.35; center peak of solvent $CDCl_3$ triplet, 77.10. Whenever chromium tris(acetylacetonate) [$Cr(acac)_3$] was used as a spin relaxation agent in ^{13}C NMR samples, its concentration was about 6 mg·mL^{-1}.

Infrared absorption spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer and were referenced to polystyrene absorptions (usually 1601.4 and 1028.0 cm^{-1}). Only selected IR data are presented in the following format: (solvent) ν_{max} in cm^{-1}.

Satisfactory mass spectra and elemental analyses for all new compounds were provided by the Analytical Laboratory of the Chemistry Department of the University of California, Berkeley. The complete mass spectral, infrared, and analytical data, including occasional high-resolution masses, are given in the supplementary material.

Flash Vacuum Pyrolysis (FVP) Apparatus and Procedure. The flash vacuum pyrolyses were performed by subliming the starting materials at low pressure (~10^{-4} torr, measured at a point outside the reactor system) into one end of a hot (350–1000 °C) quartz tube while collecting the resulting FVP products in a liquid-nitrogen-cooled trap connected to the other end of the hot quartz tube. The residence (or contact) times of individual molecules inside the hot zone were estimated to lie between 1 and 20 ms and were typically about 5 ms.[46,56]

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(54) M. Krüerke, *J. Organomet. Chem.*, **21**, 83 (1970).

(55) J. B. Armitage and M. C. Whiting, *J. Chem. Soc.*, 2005 (1952).

(56) FVP of **19** at 451 °C gave a mixture of **30** and **19** in a 7:3 ratio. An approximate E_a for the reaction (36 kcal mol^{-1}) may be calculated from this figure and an estimate of the contact time of the molecule.[46] The latter was obtained empirically by calibrating to tube parameters using known unimolecular reactions (cyclopentadiene from its dimer, cyclopentadiene from norbornene, toluene from cycloheptatriene).[57] This approach may not be valid since at the measured pressures the clearly unimolecular character of these processes is doubtful.[58] This "fall off" effect may be calculated according to the RRK theory[59] and was found appreciable. However, the pressure in the pyrolysis zone is likely to be considerably higher than measured (10^{-4} torr) at a point beyond the product trap. Thus, the above figure provides at least a rough estimate of the barrier of activation.

(57) S. W. Benson, "Kinetic Data on Gas Phase Unimolecular Reactions", United States Department of Commerce, 1970.

(58) K. J. Laidler, "Chemical Kinetics", 2nd ed., McGraw-Hill, New York, 1965.

The cold trap consisted essentially of a 1.5-cm o.d. Pyrex tube bent into the shape of a "V". One end of the V-shaped cold trap was connected to the quartz FVP tube with an outer 14/20 ground glass joint and was also connected to a solvent reservoir through a vacuum stopcock. The other end of the V-shaped cold trap was connected through vacuum stopcocks to a diffusion pump and to a nitrogen line vented to atmospheric pressure through a mercury bubbler. An NMR tube was attached to the bottom of the V-shaped cold trap. The quartz FVP tube was heated with a Hoskins Type FD303A electric furnace. A pentane solution of the starting material was evaporated under aspirator vacuum on a rotary evaporator to a thin crystalline film coating the inside surface of a 25-mL round-bottom flask. The flask was then attached to one end of a quartz FVP tube that consisted of a 1.8-cm o.d. × 36.5-cm length quartz section connected to two inner 14/20 standard taper ground quartz joints, one at each end. (The joints and their stems brought the total length of the quartz FVP tube to 52 cm.) To be sublimed at a sufficiently rapid rate, the starting material usually had to be warmed. This was accomplished by enclosing the 25-mL flask containing the starting material inside a metal can lined with an electrically heated cord. After the sublimation was complete, the products were washed into the attached NMR tube with solvent that had been vacuum transferred into the system.

The Reaction of CpCo(CO)$_2$ with Bis(trimethylsilyl)butadiyne. CpCo(CO)$_2$ (0.864 g, 4.80 mmol) was added by syringe in one portion over 1 min to a degassed, magnetically stirred solution of bis(trimethylsilyl)butadiyne (1.944 g, 10.00 mmol) in *n*-octane (100 mL) refluxing under nitrogen. After 11 h of continued refluxing, the initially reddish orange reaction mixture had turned brown, 97% of the starting bis(trimethylsilyl)butadiyne had been consumed (GC), and the reaction mixture was cooled to room temperature. The solvent was vacuum transferred off the reaction mixture at room temperature (10^{-3} torr), and the resulting nonvolatile dark brown solid residue was chromatographed on silica gel. The first colorless band was eluted from the column with pentane to yield a small amount of unreacted bis(trimethylsilyl)butadiyne.

A second colorless band was then collected with pentane eluent to provide 1,3,5-tris((trimethylsilyl)ethynyl)-2,4,6-tris(trimethylsilyl)benzene[36] (**16**, 125 mg, 0.21 mmol, 6.4% yield). Recrystallization from diethyl ether/methanol and sublimation (95 °C (1×10^{-3} torr)) gave colorless crystals: mp 117.5–118.5 °C; *m/e* (relative intensity) 582 (M$^+$, 39.37), 568 (63.85), 73 (100); NMR (CCl$_4$) δ 0.47 (s, 27 H), 0.22 (s, 27 H); IR (CHCl$_3$) 2146 (C$\equiv$C), 1248 (SiMe$_3$) cm^{-1}.

A third colorless band was then eluted off the column with pentane to afford 1,2,4-tris((trimethylsilyl)ethynyl)-3,5,6-tris(trimethylsilyl)benzene[36] (**17**, 78 mg, 0.13 mmol, 4.0% yield). Recrystallization from diethyl ether/methanol and sublimation (120 °C (1×10^{-3} torr)) gave colorless crystals: mp 124–124.5 °C; *m/e* (relative intensity) 582 (M$^+$, 18.67), 73 (100); NMR (CCl$_4$) δ 0.48 (s, 9 H), 0.44 (s, 9 H), 0.40 (s, 9 H), 0.245 (s, 27 H); IR (CHCl$_3$) 2146 (C$\equiv$C), 1248 (SiMe$_3$) cm^{-1}.

A first yellow band was then eluted off the column with pentane to yield (1,3-bis((trimethylsilyl)ethynyl)-2,4-bis(trimethylsilyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (**18**, 20 mg, 39 μmol, 0.81% yield). Sublimation (90–95 °C (2×10^{-3} torr)) gave yellow-orange crystals: mp 96.5–98.5 °C; *m/e* (relative intensity) 512 (M$^+$, 75.04), 318 (100), 73 (85.93); NMR (CCl$_4$) δ 4.78 (s, 5 H), 0.27 (s, 18 H), 0.15 (s, 18 H); IR (CHCl$_3$) 2135 (C$\equiv$C), 1247 (SiMe$_3$) cm^{-1}.

A second yellow band was then eluted off the column with pentane to provide (1,2-bis((trimethylsilyl)ethynyl)-3,4-bis(trimethylsilyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (**13**, 12 mg, 23.4 μmol, 0.49% yield). Recrystallization from methanol/water and sublimation (90–95 °C (1×10^{-3} torr)) gave yellow-orange crystals: mp 96.5–97.5 °C; *m/e* (relative intensity) 512 (M$^+$, 74.91), 318 (100), 73 (66.17); NMR (CCl$_4$) δ 4.78 (s, 5 H), 0.20 (s, 18 H), 0.17 (s, 18 H); IR (CHCl$_3$) 2141 (C$\equiv$C), 1246 (SiMe$_3$) cm^{-1}.

As the concentration of diethyl ether in the eluent was gradually increased, several reddish brown bands eluted off the column. A prominent dark red band was then collected with 65% diethyl ether/35% pentane eluent to afford (2,4-bis((trimethylsilyl)ethynyl)-3,5-bis(trimethylsilyl)-η^4-cyclopentadienone)(η^5-cyclopentadienyl)cobalt (**14**, 616 mg, 1.14 mmol, 23.7% yield). Recrystallization from hexane gave red needles: mp 167–169 °C (dec); *m/e* (relative intensity) 540 (M$^+$, 21.95), 525 (M − CH$_3$, 100), 467 (M − SiMe$_3$, 81.24); NMR (CCl$_4$) δ 4.86 (s, 5 H), 0.48 (s, 9 H), 0.36 (s, 9 H), 0.24 (s, 9 H), 0.20 (s, 9 H); IR (CHCl$_3$), 2155 (C$\equiv$C), 1587 (C=O), 1248 (SiMe$_3$) cm^{-1}.

A second red band was then eluted off the column with methanol to yield (4(2)-((trimethylsilyl)ethynyl)-2(4)-ethynyl-3,5-bis(trimethylsilyl)-η^4-cyclopentadienone)(η^5-cyclopentadienyl)cobalt (**15**, 603 mg, 1.29 mmol, 26.8% yield). Recrystallization from diethyl ether/hexane gave red crystals: mp 172–174 °C (dec); *m/e* (relative intensity) 468 (M$^+$, 14.45), 73 (100); NMR (CDCl$_3$) δ 4.94 (s, 5 H), 3.22 (s, 1 H), 0.49 (s, 9 H), 0.395 (s, 9 H), 0.20 (s, 9 H); IR (CHCl$_3$) 3306 (C$\equiv$CH), 2156 (C$\equiv$C), 2107 (C$\equiv$C), 1587 (C=O), 1248 (SiMe$_3$) cm^{-1}.

(1,2-Diethynyl-3,4-bis(trimethylsilyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (19). (1,2-Diethynyl-η^4-cyclobutadiene)CpCo complex **13** (302 mg, 0.589 mmol) was dissolved in 30 mL of absolute ethanol containing 1% KOH. The resulting dark yellow solution was magnetically stirred at room temperature under air for 30 min before submitting it to aqueous workup (with added pentane). The resulting yellow solution was dried (MgSO$_4$) and evaporated (<25 °C), and the resulting yellow-orange crystalline residue was chromatographed on alumina with 5% diethyl ether, 95% pentane eluent to provide **19** (204 mg, 0.554 mmol, 94% yield) as the only major yellow band. Recrystallization from methanol/water and sublimation (65 °C (2×10^{-3} torr)) gave yellow-orange crystals: mp 84–85 °C; *m/e* (relative intensity) 368 (M$^+$, 100), 294 (27.93), 246 (62.07), 73 (93.08); NMR (CCl$_4$) δ 4.83 (s, 5 H), 2.98 (s, 2 H), 0.17 (s, 18 H); IR (CHCl$_3$) 3300 (C$\equiv$CH), 2094 (C$\equiv$C), 1247 (SiMe$_3$) cm^{-1}.

(1,3-Diethynyl-2,4-bis(trimethylsilyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (20). (1,3-Diethynyl-η^4-cyclobutadiene)CpCo complex **18** (38 mg, 75 μmol) was protodesilylated as described for the synthesis of **19** to afford solid **20** (27 mg, 73 μmol, 97% yield). Sublimation (35–50 °C (3×10^{-3} torr)) gave yellow-orange crystals: mp 49–51 °C; *m/e* (relative intensity) 368 (M$^+$, 39.02), 246 (31.57), 73 (100); NMR (CCl$_4$) δ 4.86 (s, 5 H), 2.83 (s, 2 H), 0.26 (s, 18 H); IR (CHCl$_3$) 3303 (C$\equiv$CH), 2091 (C$\equiv$C), 1246 (SiMe$_3$) cm^{-1}.

(1,3-Diethynyl-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (21). A. From **20**. A solution of complex **20** (652 mg, 1.77 mmol) in Me$_2$SO (4 mL) was added to a stirred suspension of finely divided tetramethylammonium fluoride (370 mg, 3.97 mmol) in Me$_2$SO (20 mL) containing water (70 μL). The resulting mixture, which consisted of a dark yellow-brown solution and a white solid, was magnetically stirred at room temperature under nitrogen for 1 h before being partitioned between pentane and water. After separation from the pentane phase, the aqueous phase was extracted with three more portions of pentane. The yellow-brown pentane phases were combined, washed with ten portions of water, dried over MgSO$_4$, filtered, and evaporated (<25 °C) to a yellow-brown crystalline residue that was virtually pure **21** (373 mg, 1.664 mmol, 94% yield) according to NMR analysis. The crude **21** was recrystallized from CCl$_4$ (2 mL)/pentane (13 mL) with dry ice coolant and then sublimed (65–70 °C (1×10^{-4} torr)) to yield brownish yellow crystals: mp 95–96 °C (dec); *m/e* (relative intensity) 224 (M$^+$, 59.24), 198 (M − HC$\equiv$CH, 7.38), 174 (M − HC$\equiv$C-C$\equiv$CH, 5.39), 165 (M − Co, 100); NMR (CCl$_4$) δ 4.94 (s, 5 H), 4.45 (s, 2 H), 2.77 (s, 2 H); IR (CHCl$_3$) 3003 (C$\equiv$CH), 2110 (C$\equiv$C) cm^{-1}.

B. From **18**. A solution of **18**, (4.143 g, 8.08 mmol) in absolute diethyl ether (30 mL) was added to a stirred suspension of finely divided tetramethylammonium fluoride trihydrate (7.0 g, 47.56 mmol) in Me$_2$SO (250 mL). The resulting mixture was magnetically stirred at room temperature under air for 45 min and then worked up as above to provide crystalline **21** (1.844 g, 8.23 mmol, 100% yield).

(1,3-Bis((trimethylsilyl)ethynyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (22). *n*-Butyllithium (1.86) in hexane (3.82 mL, 7.11 mmol) was added by syringe in four portions over 10 min to a solution of **21** (765 mg, 3.41 mmol) in dry THF (10 mL) magnetically stirred at −78 °C (dry ice/acetone bath) under

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(59) G. Emanuel, *Int. J. Chem. Kinet.*, 4, 591 (1972).

nitrogen. A yellowish brown solid precipitated. After the reaction mixture had been allowed to warm to room temperature and while it continued to be stirred under nitrogen, chlorotrimethylsilane (0.95 mL, 7.485 mmol) was added by syringe in five portions over 10 min. Within a minute after the chlorotrimethylsilane addition had been completed, the yellowish brown solid dissolved and a white granular solid precipitated. The dark yellow-orange reaction mixture was then stirred magnetically at room temperature under nitrogen for 3.5 h. Aqueous workup as in the preparation of **21** gave a yellow-brown solid residue which was virtually pure **22** (1.217 g, 3.303 mmol, 97%) according to NMR analysis. The crude **22** was recrystallized from hexane and then sublimed (130 °C (1 × 10^{-3} torr)) to give yellow-orange crystals: mp 156–158 °C; *m/e* (relative intensity) 368 (M^+, 100), 246 (10.30); NMR (CCl_4) δ 5.03 (s, 5 H), 4.56 (s, 2 H), 0.16 (s, 18 H); IR ($CHCl_3$) 2134 ($C\equiv C$), 1248 ($SiMe_3$) cm^{-1}.

The Reaction of $CpCo(CO)_2$ with Bis(trimethylsilyl)butadiyne Followed by Basic Workup. A degassed solution of $CpCo(CO)_2$ (4.50 g, 25.0 mmol) and bis(trimethylsilyl)butadiyne (9.82 g, 50.5 mmol) in *n*-decane (75 mL) was added by syringe pump over 11 h to a degassed, magnetically stirred, nitrogen-flushed (15 mL·s^{-1}), refluxing solution of bis(trimethylsilyl)butadiyne (1.23 g, 6.32 mmol) in *n*-decane (1200 mL). After the syringe pump addition had been completed and while magnetic stirring and the nitrogen flush were continued, the dark yellowish brown reaction mixture was refluxed for an additional 20 min before being cooled to room temperature. The solvent was then vacuum distilled off (60–70 °C water bath (0.05 torr)) on a rotary evaporator. The viscous, dark brown oily residue was suspended in 150 mL of absolute ethanol containing 1% KOH, and the resulting mixture was magnetically stirred at room temperature under air for 2 h before being added to diethyl ether (200 mL) and water (400 mL) in a separatory funnel. After the mixture had been shaken vigorously, a copious dark brown greasy emulsion prevented separation of the aqueous and ether phases. Therefore, the entire mixture was suction filtered through a fritted glass filter funnel containing "Celite" filter aid. After the filtered emulsion had been washed with several portions of diethyl ether, the filtrate was poured back into a clean separatory funnel, where the aqueous and ether phases were readily separated. The aqueous phase was then extracted with four more portions of diethyl ether. The ether extracts were combined, washed with saturated aqueous NaCl, dried over $MgSO_4$, filtered, and evaporated to a dark reddish brown oily residue that was subsequently chromatographed on alumina.

The first colorless band was eluted off the column with pentane to provide 1,3,5-triethynyl-2,4,6-tris(trimethylsilyl)benzene[36] (**24**, 766 mg, 2.09 mmol, 11.0% yield). Recrystallization from methanol and then from hexane and sublimation (70 °C (3 × 10^{-3} torr)) gave colorless crystals: mp 166.5–169 °C, (lit.[36] mp 170–172 °C); *m/e* (relative intensity) 366 (M^+, 32.78), 351 ($M - CH_3$, 100); NMR (CCl_4) δ 3.32 (s, 3 H), 0.48 (s, 27 H); IR ($CHCl_3$) 3300 ($C\equiv CH$), 2100 ($C\equiv C$), 1246 ($SiMe_3$) cm^{-1}.

A first yellow band was then eluted off the column with 2% diethyl ether/98% pentane to afford a yellow-orange crystalline solid that was identified on the basis of its NMR and mass spectra as **20** (4.68 g, 12.7 mmol, 51% yield).

A second colorless band was then eluted off the column with 4% diethyl ether/96% pentane to yield 1,2,4-triethynyl-3,5,6-tris(trimethylsilyl)benzene[36] (**25**, 148 mg, 0.404 mmol, 2.13% yield). Recrystallization from methanol/water and sublimation (85 °C (1 × 10^{-3} torr)) gave colorless crystals: mp 102.5–104 °C dec (lit.[36] mp 108 °C dec); *m/e* (relative intensity) 366 (M^+, 24.33), 73 (100); NMR (CCl_4) δ 3.45 (s, 1 H), 3.41 (s, 1 H), 3.31 (s, 1 H), 0.47 (s, 9 H), 0.42 (s, 9 H), 0.40 (s, 9 H); IR ($CHCl_3$) 3303 ($HC\equiv C$), 2101 ($C\equiv C$), 1248 ($SiMe_3$) cm^{-1}.

A second yellow band was then eluted off the column with 7% diethyl ether/93% pentane to provide an orange crystalline solid that was identified on the basis of its NMR and mass spectra as **19** (190 mg, 0.517 mmol, 2.07% yield).

After several minor yellow-orange bands and a reddish brown band had been eluted off the column with diethyl ether, ethyl acetate gave a red band of (2,4-diethynyl-3,5-bis(trimethylsilyl)-η^4-cyclopentadienone)(η^5-cyclopentadienyl)cobalt (**23**, 706 mg, 1.78 mmol, 7.12% yield). Sublimation (150 °C (1 × 10^{-3} torr)) and recrystallization from diethyl ether/hexane yielded dark red crystals: mp 165–167 °C dec; *m/e* (relative intensity) 396 (M^+, 47.17), 395 (24.39), 73 (100); NMR ($CDCl_3$) δ 4.97 (s, 5 H), 3.21 (s, 1 H), 3.09 (s, 1 H), 0.50 (s, 9 H), 0.41 (s, 9 H); IR ($CHCl_3$) 3303 ($C\equiv CH$), 2113 ($C\equiv C$), 1592 ($C=O$), 1247 ($SiMe_3$) cm^{-1}.

Further elution gave a second red band containing (2,4-diethynyl-5-(trimethylsilyl)-η^4-cyclopentadienone)(η^5-cyclopentadienyl)cobalt (**26**) (312 mg, 0.96 mmol, 3.85% yield). Recrystallization from diethyl ether/hexane gave dark red crystals: mp 138.5–140 °C; *m/e* (relative intensity) 324 (M^+, 100), 323 (53.76); NMR ($CDCl_3$) δ 5.66 (s, 1 H), 5.00 (s, 5 H), 3.17 (s, 1 H), 3.07 (s, 1 H), 0.40 (s, 9 H); IR ($CHCl_3$) 3304 ($C\equiv CH$), 2111 ($C\equiv C$), 1590 ($C=O$), 1247 ($SiMe_3$) cm^{-1}.

In a preparation employing $CpCo(CO)_2$ (3.90 g, 21.7 mmol) and bis(trimethylsilyl)butadiyne (19.00 g, 97.7 mmol), a pale brownish orange band was eluted on column chromatography with 3% diethyl ether/97% pentane to provide pale orange crystalline 1,2,4,5-tetrakis((trimethylsilyl)ethynyl)-3,6-bis(trimethylsilyl)benzene (**27**) (3.44 g, 5.66 mmol). This compound was recrystallized from pentane and also from diethyl ether/methanol to yield colorless crystals: mp 275.5–276 °C; *m/e* (relative intensity) 606 (M^+, 100); NMR (CCl_4) δ 0.48 (s, 18 H), 0.25 (s, 36 H); IR ($CHCl_3$) 2141 ($C\equiv C$), 1247 ($SiMe_3$) cm^{-1}.

1,2,4,5-Tetraethynyl-3,6-bis(trimethylsilyl)benzene (28). Tetraethynylbenzene **27** (1.0 g) was protodesilylated as described in the preparation of **19**. The crude **28** was recrystallized from pentane (with dry ice coolant) and then sublimed (60 °C (5 × 10^{-3} torr)) to afford colorless crystals: mp 120.5–121.5 °C dec; *m/e* (relative intensity) 318 (M^+, 100); ^1H NMR (CCl_4) δ 3.40 (s, 4 H), 0.49 (s, 18 H); ^{13}C NMR ($CDCl_3$, $Cr(acac)_3/CDCl_3$) δ (relative peak height) 145.89 (1.00), 131.47 (1.94), 88.12 (3.86), 83.55 (2.09), 2.04 (4.95); IR ($CHCl_3$) 3306 ($C\equiv CH$), 2107 ($C\equiv C$), 1248 ($SiMe_3$) cm^{-1}.

1,4-Bis(trimethylsilyl)-2,3,5,6-tetraethylbenzene (29). Tetraethynylbenzene **28**, (30 mg, 94.2 μmol), benzene (8 mL), absolute ethanol (7 mL), and a magnetic stirring bar were placed inside a Pyrex bomb. The resulting solution was degassed by several freeze–evacuation–thaw cycles before tris(triphenylphosphine)rhodium chloride (87 mg, 94 μmol) was added under a stream of H_2. The bomb was subsequently purged thoroughly with H_2. After the initially brown suspension had been stirred at room temperature under 82 psi of H_2 for 33 h, the resulting brownish green suspension was filtered and the reddish brown filtrate was evaporated under aspirator vacuum on a rotary evaporator. The solid evaporation residue was then extracted with diethyl ether. The ether extracts were evaporated to a pale yellow crystalline residue that contained **29** and no incompletely hydrogenated ethynyl groups according to NMR and TLC analyses. The crude **29** was purified by preparative thin-layer chromatography (silica gel, pentane eluent) and then sublimation (60–70 °C (1 × 10^{-3} torr)) to yield colorless crystals: mp 109–111 °C; *m/e* (relative intensity) 334 (M^+, 19.69), 73 (100.0); NMR (CCl_4) δ 2.77 (q, J = 7.33 Hz, 8 H), 1.08 (t, J = 7.3 Hz, 12 H), 0.41 (s, 18 H); IR ($CHCl_3$) 1248 ($SiMe_3$) cm^{-1}.

Protodesilylation of 1,4-Bis(trimethylsilyl)-2,3,5,6-tetraethylbenzene (29). Trifluoroacetic acid (6.0 μL, 77.9 μmol) was added to a solution of **29** (11 mg, 32.9 μmol) in CCl_4 (0.5 mL) inside an NMR tube to give 1,2,4,5-tetraethylbenzene: NMR (CCl_4) δ 6.75 (s, 2 H), 2.545 (q, J = 7.4 Hz, 8 H), 1.18 (t, J = 7.5 Hz, 12 H). Preparative gas chromatography (20% SE-30 on 60-80 mesh Chromosorb W-AW inside a $^3/_8$ in. × 10 ft glass column at 211 °C; helium flow rate = 50 mL·min^{-1}) of the reaction mixture provided pure 1,2,4,5-tetraethylbenzene (retention time = 13.4 min) as a colorless oil identified (*m/e*, IR, NMR, GC coinjection) by comparison with authentic material.[44]

Bis(trimethylsilyl)hexatriyne. A THF solution of hexatriyne was prepared as follows:[45] 1,6-dichlorohexa-2,4-diyne[55] (2.99 g, 20.3 mmol) was syringed into a degassed suspension of NaOH (31.7 g, thoroughly pulverized and then dried at 110 °C (1 × 10^{-3} torr) for about 10 h) in dry THF (50 mL) magnetically stirred at room temperature under vacuum. After the resulting dark brown reaction mixture had been stirred for 30 s, a clean receiving flask connected to the reaction flask through a bump guard was cooled with liquid nitrogen. The stirred reaction mixture was warmed with a water bath at room temperature while the volatile hexatriyne product and THF solvent vacuum transferred into the liquid-nitrogen-cooled receiving flask. Although the vacuum transfer appeared to be complete after 20 min, the reaction flask was maintained at room temperature, the receiving flask was cooled with liquid nitrogen, and the entire apparatus was kept under static vacuum for an additional 15 min before the vacuum-transferred volatiles were allowed to warm to 0 °C under nitrogen.

The cold pale yellow-brown THF solution of hexatriyne was then immediately syringed under air-free conditions into an ice-cooled THF suspension of ethylmagnesium bromide (50 mmol) stirred under nitrogen. During the addition of hexatriyne, a large amount of white fluffy solid precipitated and a gas, presumably ethane, boiled off the reaction mixture. The reaction mixture was then heated to 35–45 °C for 1 h. After the mixture was cooled to 3 °C, chlorotrimethylsilane (5.99 g, 7.0 mL, 55.2 mmol) was added by syringe over 5 min. The resulting mixture was then stirred at 50 °C under nitrogen for 2 h. During this period, the white fluffy solid completely dissolved to give a clear, light brown solution. A granular white solid, presumably a mixture of magnesium halide salts, precipitated as the reaction mixture was subsequently cooled to room temperature.

The reaction mixture was then partitioned between pentane (50 mL) and a mixture of ice (50 g) and saturated aqueous ammonium chloride (50 mL). After separation from the pentane phase, the aqueous phase was extracted with three more portions of pentane. The light brown pentane phases were combined, dried over $MgSO_4$, filtered, and evaporated to a brown oily residue that solidified on standing. The resulting crude, brown solid product was sublimed (50–55 °C (2×10^{-3} torr)) to provide colorless crystals of bis(trimethylsilyl)hexatriyne[33] (1.666 g, 7.63 mmol, 37.5% yield).

The Reaction of Bis(trimethylsilyl)hexatriyne and $CpCo(CO)_2$ in Refluxing BTMSA. Unambiguous Synthesis of (1,2-Diethynyl-η^4-cyclobutadiene)CpCo Complex 13. A degassed solution of bis(trimethylsilyl)hexatriyne (1.09 g, 5.01 mmol) and $CpCo(CO)_2$ (0.906 g, 5.03 mmol) in BTMSA (3 mL) was added by syringe pump over 53 h to degassed, magnetically stirred, nitrogen-flushed (2 mL·s^{-1}), refluxing BTMSA (100 mL). After the syringe pump addition had been completed and while magnetic stirring and the nitrogen flush were continued, the dark yellowish brown reaction mixture was refluxed for an additional 3.4 h before being cooled to room temperature. Unreacted BTMSA was then vacuum transferred off the reaction mixture (20–45 °C water bath (1×10^{-3} torr)), and the remaining oily brown residue was chromatographed on alumina.

A yellowish pink band was eluted off the column with pentane. Evaporation of the eluent from this band provided a pale yellow crystalline solid that was identified as tetrakis(trimethylsilyl)-butatriene[24d] (30 mg, 88 μmol) on the basis of silica gel TLC, NMR, IR, and mass spectral analyses.

A prominent yellow band was then eluted off the column with pentane. Evaporation of the eluent from this band afforded a yellow-orange crystalline solid identified at **13** (1.648 g, 3.213 mmol, 64.2% yield).

A second yellow band was then eluted off the column with 2% diethyl ether/98% pentane. The eluent from this band was evaporated to an orange oil: *m/e* (relative intensity) 854 (M^+, 65.04), 684 ($M - Me_3SiC{\equiv}CSiMe_3$, 35.56), 660 ($M - Me_3SiC{\equiv}CC{\equiv}CSiMe_3$, 10.25), 560 ($M - CpCo - Me_3SiC{\equiv}CSiMe_3$, 21.96), 294 (100.00); NMR (CCl_4) δ 4.945 (s, 10 H), 0.30 (s, 9 H), 0.25 (b s, 27 H), 0.125 (s, 9 H), 0.075 (3 s, 9 H); IR ($CHCl_3$, selected peaks) 2134 ($C{\equiv}C$), 1246 ($SiMe_3$) cm^{-1}. On the basis of these data, this appears to be a mixture of isomers of bis(cyclobutadiene) complexes derived from **13** by further cocylization with another molecule of triyne (378 mg, 0.442 mmol, 17.6% yield based on triyne).

A third yellow band was then eluted off the column with 20% diethyl ether/80% pentane. Evaporation of the eluent from this band yielded an orange oil identified as (1,2,3-tris(trimethylsilyl)-4-((1-hydroxy-1-methyl)ethyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (50 mg, 0.111 mmol, 1.1% yield based on cobalt). This material was recrystallized from methanol/water and then sublimed (75 °C (1×10^{-3} torr)) to give yellow crystals: mp 220–221.5 °C; *m/e* (relative intensity) 450 (M^+, 7.40), 432 ($M - H_2O$, 22.08), 294 (100.00), 262 ($M - Me_3Si - C{\equiv}C\text{-}SiMe_3 - H_2O$, 37.08); NMR ($CCl_4$) δ 4.87 (s, 5 H), 1.32 (s, 6 H), 1.12 (s, 1 H), 0.20 (s, 27 H); ^{13}C NMR (benzene-d_6, $Cr(acac)_3$/benzene-d_6) δ (relative peak height) 108.79 (1.00), 79.76 (12.47), 71.85 (2.06), 71.35 (1.01), 69.61 (1.89), 32.23 (6.32), 3.434 (8.25), 3.288 (12.76); IR ($CHCl_3$) 3552 (OH), 1244 ($SiMe_3$) cm^{-1}.

A fourth yellow band was then eluted off the column with 20% diethyl ether/80% pentane to provide (1-(trimethylsilyl)-2,3-bis((trimethylsilyl)ethynyl)-4-((1-hydroxy-1-methyl)ethyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (118 mg, 0.237 mmol, 4.7% yield based on cobalt). The compound was sublimed (70–95 °C (1×10^{-3} torr)) to give yellow-orange crystals: mp 83–88 °C; *m/e* (relative intensity) 498 (M^+, 34.78), 480 ($M - H_2O$, 22.12), 286 ($M - Me_3SiC{\equiv}CC{\equiv}CSiMe_3 - H_2O$, 9.12), 262 ($M - Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CSiMe_3 - H_2O$, 59.02), 73 (100.00); NMR (CCl_4) δ 4.84 (s, 5 H), 1.40 (b s, 3 H), 1.30 (b s, 3 H), 1.17 (b s, 1 H), 0.22 (s, 27 H); IR ($CHCl_3$) 3559 (OH, m), 2139 ($C{\equiv}C$), 1248 ($SiMe_3$) cm^{-1}.

The orange oil obtained from the second yellow band and tentatively identified as a mixture of bis(cyclobutadiene) isomers (378 mg, 0.442 mmol) was protodesilylated as described in the preparation of **19**.

Four yellow bands were eluted off alumina with 2–6% diethyl ether/98–94% pentane. The eluent from each of these bands was collected and the solvent evaporated. On the basis of NMR analyses, the resulting reddish orange oils appeared to be mixtures of isomers of protodesilylated bis(cyclobutadiene) complexes.

The fifth and most prominent yellow band was then eluted off the column with 10% diethyl ether/90% pentane. Evaporation of the eluent from this band gave an orange oil tentatively identified as a single diastereomer of (2-butadiynyl-2′-ethynyl-3,3′,4,4′-tetrakis(trimethylsilyl)-1:1′-bi(η^4-cyclobutadienyl))bis-((η^5-cyclopentadienyl)cobalt) (128 mg, 0.18 mmol, 7.16% yield based on $CpCo(CO)_2$). The compound was crystallized from methanol/water to yield yellow-orange crystals: mp 126–128 °C dec; *m/e* (relative intensity) 710 (M^+, 100.00), 588 ($M - Me_3SiC{\equiv}CC{\equiv}CH$, 1.83), 540 ($M - Me_3SiC{\equiv}CSiMe_3$, 24.85), 516 ($M - Me_3SiC{\equiv}CC{\equiv}C\text{-}SiMe_3$, 6.01); NMR ($CCl_4$) δ 4.96 (s, 5 H), 4.89 (s, 5 H), 3.18 (s, 1 H), 1.99 (s, 1 H), 0.21 (s, 9 H), 0.195 (s, 9 H), 0.11 (s, 9 H), 0.035 (s, 9 H); ^{13}C NMR (benzene-d_6, $Cr(acac)_3$/benzene-d_6 δ (relative peak height) 105.94 (1.00), 97.33 (1.32), 85.88 (1.14), 83.20 (14.73), 82.62 (1.12), 81.80 (17.13), 81.42 (3.49), 81.12 (3.26), 80.83 (2.14), 72.04 (1.19), 71.26 (1.16), 70.34 (1.14), 65.38 (1.41), 62.63 (1.08), 61.74 (1.13), 1.054 (8.70), 0.914 (7.78), 0.328 (7.96), 0.148 (6.48); IR ($CHCl_3$) 3293 ($C{\equiv}CH$), 2128 ($C{\equiv}C$), 2096 ($C{\equiv}C$), 1247 ($SiMe_3$) cm^{-1}.

The Reaction of (1,2-Diethynyl-η^4-cyclobutadiene)CpCo Complex 19 and $CpCo(CO)_2$ in Refluxing BTMSA. A degassed solution of **19** (109 mg, 0.296 mmol) and $CpCo(CO)_2$ (53.3 mg, 37 μL, 0.296 mmol) in BTMSA (5 mL) was reacted as in the synthesis of **13** (using BTMSA). The resulting yellowish brown oily residue was chromatographed on alumina.

A faint yellow band was eluted off the column with pentane. Evaporation of the eluent from this band provided a yellow oil identified as (1,2,3-tris(trimethylsilyl)-4-((trimethylsilyl)-ethynyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt[24d] (0.69 mg, 1.41 μmol, 0.48% yield based on cobalt) on the basis of its mass spectrum.

A second yellow band was then eluted off the column with 1% diethyl ether/99% pentane to afford the minor diastereomer of (3-ethynyl-2,3,2′,3′-tetrakis(trimethylsilyl)-1:1′-bi(η^4-cyclobutadienyl))bis((η^5-cyclopentadienyl)cobalt) (**53**) [9 mg, 14 μmol, 4.6% yield based on $CpCo(CO)_2$]. This compound was sublimed (120 °C (1×10^{-3} torr)) to give yellow-orange crystals: mp 110–116 °C; *m/e* (relative intensity) 662 (M^+, 46.34), 564 ($M - Me_3SiC{\equiv}CH$, 3.91), 540 ($M - Me_3SiC{\equiv}C\text{-}C{\equiv}CH$, 2.27), 492 ($M - Me_3SiC{\equiv}CSiMe_3$, 17.42), 294 (100.00); NMR (benzene-d_6/benzene-d_5 δ 4.884 (s, 5 H), 4.703 (s, 5 H), 4.536 (s, 1 H), 2.78 (s, 1 H), 0.433 (s, 9 H), 0.248 (s, 9 H), 0.212 (s, 9 H), 0.115 (s, 9 H); ^1H NMR (CCl_4) δ 4.73 (s, 10 H), 4.23 (s, 1 H), 3.03 (s, 1 H), 0.31 (s, 9 H), 0.23 (s, 18 H), 0.107 (s, 9 H); IR ($CHCl_3$) 3300 ($C{\equiv}CH$), 2088 ($C{\equiv}C$), 1243 ($SiMe_3$) cm^{-1}.

A third yellow band was then eluted off the column with 1% diethyl ether/99% pentane. Evaporation of the eluent from this band yielded a yellow oil identified as the major meso diastereomer of (2,3,3′,4′,2″,3″-hexakis(trimethylsilyl)-1:1,2′:1″-ter(η^4-cyclobutadienyl))tris((η^5-cyclopentadienyl)cobalt) (**54**) (7 mg, 7.3 μmol, 4.94% yield based on $CpCo(CO)_2$): *m/e* (relative intensity) 956 (M^+, 9.30), 786 ($M - Me_3SiC{\equiv}CSiMe_3$, 9.56), 616 ($M - 2\,Me_3SiC{\equiv}CSiMe_3$, 7.93), 540 ($M - CpCo - Me_3SiC{\equiv}CC{\equiv}CH - Me_3SiC{\equiv}CSiMe_3$, 100.00); NMR ($CCl_4$) δ 4.74 (s, 15 H), 4.33 (b s, 2 H), 0.26 (s, 18 H), 0.20 (s, 18 H), 0.17 (s, 18 H); NMR (benzene-d_6/benzene-d_5) δ 4.89 (s, 15 H), 4.43 (b s, 2 H), 0.304 (s, 18 H), 0.255 (s, 18 H), 0.21 (s, 18 H); IR ($CHCl_3$) 1246 ($SiMe_3$) cm^{-1}.

The fourth and most prominent yellow band was then eluted off the column with 2% diethyl ether/98% pentane to provide the major diastereomer of **53** (111 mg, 0.167 mmol, 56.6% yield). This compound was sublimed (120 °C (1 × 10^{-3} torr)) to afford yellow-orange crystals: mp 138–141 °C; *m/e* (relative intensity) 662 (M^+, 70.61), 564 (M − $Me_3SiC{\equiv}CH$, 2.99), 492 (M − $Me_3SiC{\equiv}CSiMe_3$, 19.09), 294 (100.00); NMR (CCl_4) δ 4.965 (s, 5 H), 4.847 (s, 5 H), 4.053 (s, 1 H), 3.08 (s, 1 H), 0.171 (s, 9 H), 0.077 (s, 9 H), 0.040 (s, 9 H), 0.024 (s, 9 H); IR ($CHCl_3$) 3300 ($C{\equiv}CH$), 2088 ($C{\equiv}C$), 1244 ($SiMe_3$) cm^{-1}.

A faint fifth yellow band was then eluted off the column with 4% diethyl ether/96% pentane. Evaporation of the solvent yielded a yellow oil identified as the minor meso diastereomer of **54** (0.80 mg, 0.84 μmol, 0.56% yield based on $CpCo(CO)_2$): *m/e* (relative intensity) 956 (M^+, 19.19), 786 (M − $Me_3SiC{\equiv}CSiMe_3$, 20.29); NMR (benzene-d_6/benzene-d_5) δ 4.927 (s, 5 H), 4.907 (s, 10 H), 4.39 (s, 2 H), 0.358 (s, 18 H), 0.228 (s, 18 H), 0.176 (s, 18 H).

A faint sixth yellow band was then eluted off the column with 4% diethyl ether/96% pentane to afford a yellow oil identified as the *d,l*-diastereomer of **54** (1.25 mg, 1.31 μmol, 0.88% yield based on $CpCo(CO)_2$): *m/e* (relative intensity) 956 (M^+, 69.31), 786 (M − $M_3SiC{\equiv}CSiMe_3$, 31.29), 616 (M − $2Me_3SiC{\equiv}CSiMe_3$, 2.60), 540 (100.00): NMR (benzene-d_6/benzene-d_5) δ 4.950 (s, 5 H), 4.933 (s, 10 H), 4.662 (s, 1 H), 4.559 (s, 1 H), 0.403 (s, 9 H), 0.257 (s, 9 H), 0.233 (s, 9 H), 0.182 (s, 9 H), 0.136 (s, 9 H), 0.053 (s, 9 H).

Five faint yellow bands were then eluted off the column with 50% pentane/50% diethyl ether. NMR and mass spectra of the resulting yellow-orange oils provided no evidence for the presence of any other materials derived from the cocyclization of **19** with BTMSA.

The Diethynylcyclobutadiene Rearrangement of 19 to (1,2-Bis((trimethylsilyl)ethynyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (30). With use of the general FVP procedure, freshly chromatographed **19** (38 mg, 103 μmol) was sublimed at 40–50 °C over 10.5 h through a hot (525 °C) quartz tube. The yellow-orange crystalline pyrolysate which collected inside the cold trap was then isolated as a CCl_4 (1% $SiMe_4$) solution inside an NMR tube sealed under vacuum. The NMR spectrum of this solution showed a single compound subsequently identified as **30**. After solvent had been evaporated, the resulting yellow-orange residue was chromatographed on alumina with 0.6% diethyl ether/99.4% pentane eluent to give a yellow-orange solid **30** [24 mg, 65.1 μmol, 63.1% yield based on total (sublimed and unsublimed) **19**]. Sublimation (50 °C (1 × 10^{-3} torr)) gave yellow-orange crystals: mp 62–63 °C; *m/e* (relative intensity) 368 (M^+, 61.59), 342 (M − $HC{\equiv}CH$, 1.15), 270 (M − $Me_3SiC{\equiv}CH$, 4.87), 246 (M − $Me_3SiC{\equiv}CC{\equiv}CH$, 7.30), 73 (100.00); NMR (CCl_4) (180 MHz) δ 4.89 [s, 5 H; ^{13}C satellites, $J(^{13}C{-}H)$ = 176.6 Hz, m], 3.97 [s, 2 H; ^{13}C satellites, $J(^{13}C{-}H)$ = 190.7 Hz, s; $J(^{13}C{-}H)$ = 13.75 Hz, s; $J_{HH} \approx$ half-width of ^{13}C satellite peaks = 0.35 Hz], 0.20 (s, 18 H); ^{13}C NMR (benzene-d_6; $Cr(acac)_3$/benzene-d_6 (chemical shifts and relative peak heights taken from proton-decoupled spectrum; splitting patterns and coupling constants taken from proton-coupled spectrum)) δ 102.43 (s; 1.4), 97.69 (s; 1.3), 81.98 [d, $J(^{13}C{-}H)$ = 176 Hz; 4.3], 62.50 [d, $J(^{13}C{-}H)$ = 190 Hz; 2.0], 59.32 (s, 1.0)e, 0.336 [q, $J(^{13}C{-}H)$ = 123 Hz; 3.9]; IR ($CHCl_3$) 2137 ($C{\equiv}C$), 1248 ($SiMe_3$) cm^{-1}.

A similar FVP at 451 °C gave **30** (70.0%), unconverted **19** (30.0%), and no other compounds.

The quartz FVP tube remained clean during both pyrolyses. However, unsublimed brown oily starting material residues (30–40%) remained. ^1H NMR analysis found them to contain no **30**, very little **19**, and mostly decomposition products that were not identified.

(1,2-Diethynyl-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (9). Complex **30** (20 mg, 54.3 μmol) was protodesilylated as described in the synthesis of **19** to give a heat sensitive brownish yellow solid identified as **9**: *m/e* (relative intensity) 224 (M^+, 55.97), 198 (M − $HC{\equiv}CH$, 5.55), 174 (M − $HC{\equiv}CC{\equiv}H$, 5.0), 165 (100.0); NMR (CCl_4) δ 4.94 (s, 5 H), 3.98 (s, 2 H), 2.95 (s, 2 H); IR (neat) 3289 ($C{\equiv}CH$), 2099 ($C{\equiv}C$) cm^{-1}.

(1,2-Bis(deuterioethynyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (49). Complex **30** (40 mg, 108.5 μmol) was dissolved under nitrogen in 7 mL of a degassed 0.174 M solution of CH_3OK in CH_3OD. The resulting yellow solution was then stirred magnetically at room temperature under nitrogen for 70 min before being partitioned between D_2O (15 mL) and dry pentane (15 mL). After separation from the pentane phase, the D_2O phase was extracted with three more portions of *dry* pentane. The yellow pentane phases were combined, dried over $MgSO_4$, filtered, and evaporated (≤25 °C). The resulting **49** was found to contain the analogous d_1 compound as its only impurity: *m/e* (relative intensity) 226 (M^+, 65.36), 225 (M^+ for d_1 impurity, 5.33), 200 (M − $HC{\equiv}CH$, 4.07), 199 (M − $DC{\equiv}CH$, 3.81), 175 (M − $DC{\equiv}CC{\equiv}CH$, 4.96), 124 (100.00); NMR (CCl_4) δ 4.94 (s, 5 H), 3.99 (s, 2 H); IR ($CHCl_3$) 2581 ($C{\equiv}CD$), 1974 ($C{\equiv}C$) cm^{-1}.

FVP of (1,2-Bis(deuterioethynyl)-η^4-cyclobutadiene)CpCo (49). Complex **49** (24 mg, 106 μmol) freshly prepared from the previously described experiment was pyrolyzed at 520 °C as described in the synthesis of **30**. The brownish yellow oily solid was found to consist of an equimolar mixture of **49** and **50**: *m/e* (relative intensity) 226 (M^+, 67.69), 225 (M^+ for d_1 impurity, 11.30),200 (M − $HC{\equiv}CH$, 6.09), 199 (M − $DC{\equiv}CH$, 4.81), 175 (M − $DC{\equiv}CC{\equiv}CH$, 6.95), 59 (100.00); NMR (CCl_4) δ 4.94 (s, 5 H), 3.97 (s, 1.00 H), 2.94 (s, 1.00 H); IR ($CHCl_3$) 3300 ($C{\equiv}CH$), 2584 ($C{\equiv}CD$), 2101 ($C{\equiv}CH$), 1974 ($C{\equiv}CD$) cm^{-1}.

The pyrolysate of **49** was dissolved under nitrogen in a degassed, 0.211 M solution of KOH in absolute methanol (7 mL). The resulting yellow solution was magnetically stirred at room temperature under nitrogen for 20 min before being exposed to aqueous workup. An equimolar mixture of **50** and **9** was obtained: *m/e* (relative intensity) 226 (M^+ for **50**, 28.99), 225 (d_1 impurity in **50** and M + 1 peak of **9**, 6.94), 224 (M^+ for **9**, 30.21), 200 (**50** − $HC{\equiv}CH$, 1.91), 199 (**50** − $DC{\equiv}CH$, 1.91), 198 (**50** − $DC{\equiv}CD$, **9** − $HC{\equiv}CH$, 3.95), 175 (**50** − $DC{\equiv}CC{\equiv}CH$, 3.23), 174 (**9** − $HC{\equiv}CC{\equiv}CH$, 3.29), 124 (100.00); NMR (benzene-d_6/benzene-d_5) δ 4.70 (s, 5 H), 3.68 (s, 1.00 H), 2.80 (s, 2.00 H); IR ($CHCl_3$) 3300 ($C{\equiv}CH$, s), 2101 ($C{\equiv}C$) cm^{-1}.

Exact mass calcd for **50** ($C_{13}H_7D_2Co$): 226.0162. Found: 226.0159.

Exact mass calcd for **9** ($C_{13}H_9Co$): 224.0036. Found: 224.0032.

Exact mass calcd for $C_{13}H_8DCo$: 225.0099. Exact mass calcd for $^{12}C_{12}{}^{13}CH_9Co$: 225.0069. Found: 225.0086.

Diethynylcyclobutadiene Rearrangement of 19 to 30 in Refluxing Pristane. A degassed solution of freshly chromatographed **19** (94 mg, 225 μmol) in 2,6,10,14-tetramethylpentadecane (pristane, 5 mL) was added by syringe over 60 s to degassed, mechanically stirred, nitrogen-flushed (2 $mL{\cdot}s^{-1}$), refluxing pristane (60 mL, bp 300 °C). During the addition of **19**, the reaction mixture initially turned yellow but then very suddenly turned dark yellowish brown. After the addition of **19** had been completed and while mechanical stirring and the nitrogen flush were continued, the reaction mixture was refluxed for an additional 60 s. The reaction flask was then allowed to cool in air for 75 s before the mechanically stirred reaction mixture was cooled to room temperature under nitrogen with a water bath.

The crude, unconcentrated mixture was then chromatographed on alumina. After the pristane reaction solvent had been eluted off the column with pentane, a faint yellow band was collected as elution with pentane continued. Evaporation of solvent gave a pale yellow oil (2 mg) whose NMR spectrum showed four cyclopentadienyl proton resonances (δ 4.9–4.5), aliphatic proton resonances (δ 1.7–0.8) similar to those of pristane, and a trimethylsilyl proton region (δ 0.5–0.1) consisting of four major peaks and many minor peaks. According to this spectrum, the pale yellow oil contained none of the known (η^4-1,2-bis(trimethylsilyl)benzocyclobutadiene)(η^5-cyclopentadienylcobalt).[24c] However, a mass spectrum of the crude product showed a parent ion at *m/e* 636 (13.54% relative intensity), which corresponds to an adduct between **19** and pristane. This might be indicative of some radical intermediates but is inconclusive.

A second yellow band was then eluted off the column with 1% diethyl ether/99% pentane. Evaporation of the eluent from this band yielded a yellow-orange crystalline residue identified as **30** (11 mg, 29.8 μmol, 11.7% yield) on the basis of its NMR and IR spectra.

A third yellow band was eluted off the column with 3% diethyl ether/97% pentane to afford an orange oily solid identified as (1-((trimethylsilyl)ethynyl)-2-ethynyl-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (8 mg, 27 μmol, 10.6% yield): *m/e* (relative intensity) 296 (M^+, 47.76), 85 (100.00); NMR (CCl_4) δ 4.88 (s, 5 H), 3.96 (s, 2 H), 2.95 (s, 1 H), 0.19 (s, 9 H).

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Photoreaction of $(\eta^5\text{-}C_5H_5)M(CO)_2R$ (M = Fe, Ru; R = CH_3, C_2H_5, $n\text{-}C_5H_{11}$) and $(\eta^5\text{-}C_5Me_5)Fe(CO)_2C_2H_5$ involves dissociative loss of CO as the primary photoprocess following near-UV excitation. The quantum yield for photosubstitution of $(\eta^5\text{-}C_5H_5)M(CO)_2CH_3$ is independent of the incoming ligand or its concentration (above 10^{-3} M); the quantum yield is 0.4 ± 0.05 for M = Ru and 0.7 ± 0.03 for M = Fe. All of the complexes for R having β-hydrogens yield the analogous $(\eta^5\text{-}C_5R'_5)M(CO)_2H$ (R′ = H, Me) complexes upon near-UV irradiation at 298 K in fluid, alkane solution. For the $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ complex the photochemical formation of the hydride occurs even at 77 K in alkane matrices, and there are no infrared detectable intermediates at an extent conversion of <5%. Irradiation of $(\eta^5\text{-}C_5H_5)Ru(CO)_2C_2H_5$ yields photoreaction at 77 K, initially giving infrared spectral changes consistent with the formation of $(\eta^5\text{-}C_5H_5)Ru(CO)(C_2H_4)(H)$ followed by spectral changes consistent with the formation of the $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$. Likewise in rigid (paraffin) media at 298 K, initial spectral changes accompanying near-UV irradiation of $(\eta^5\text{-}C_5H_5)Ru(CO)_2C_2H_5$ are consistent with the formation of the ethylene–hydride complex. At 298 K, high concentrations of PPh_3 suppress the formation of iron–hydride products from irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ in a manner consistent with the intermediacy of $(\eta^5\text{-}C_5H_5)Fe(CO)C_2H_5$ from the dissociative loss of CO from the starting dicarbonyl. For the $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$, irradiation at 77 K in an alkane matrix yields infrared spectral changes consistent with the formation of $(\eta^5\text{-}C_5H_5)Ru(CO)CH_3$, providing direct evidence for the photogeneration of a 16-valence-electron intermediate. The rate of β-hydrogen transfer for the Fe species created by light is estimated to be $>3 \times 10^2\ s^{-1}$ at 298 K, and 77 K data suggest that the activation energy for β-hydrogen transfer from photogenerated intermediates is less than ~6 kcal/mol for both the Fe and Ru complexes.

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may allow the generation and characterization of species that would be thermally unstable at temperatures where it would ordinarily be thermally accessible. For example, thermal routes to $(\eta^5\text{-}C_5H_5)W(CO)_2(n\text{-pentyl})$ would likely involve more activation energy than does the β-hydrogen-transfer process represented by eq 1. Generally, using light to change the rate-limiting step in a reaction sequence may have consequence with respect to possible reaction products and can provide insight into reaction mechanisms.

Our follow-up studies of the $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$ and related complexes have confirmed that the alkene hydride product is the trans isomer,[3,4] and this may ac-

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count for the fact that the process represented by eq 2 is

$$(\eta^5\text{-}C_5H_5)W(CO)_2(\text{1-pentene})(H) \rightarrow (\eta^5\text{-}C_5H_5)W(CO)_2(n\text{-pentyl}) \quad (2)$$

slow.[3] The thermal activation energy for the chemistry represented by eq 1 is ~10 kcal/mol, consistent with a fast, reversible transformation of $(\eta^5\text{-}C_5H_5)W(CO)_2(n\text{-pentyl})$ to the *cis*-$(\eta^5\text{-}C_5H_5)W(CO)_2(\text{1-pentene})(H)$ with a subsequent cis → trans isomerization actually being the rate-limiting step.

With the hope of clarifying aspects of the mechanism of the reaction of 16-valence-electron alkyls, we undertook an investigation of the photochemistry of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$ and related complexes. An $(\eta^5\text{-}C_5H_5)Fe(CO)(\text{1-pentene})(H)$ must have a cis disposition of the hydride and alkene. In this case, it has already been proposed that photoexcitation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ (R = CH_3, C_2H_5) yields dissociative loss of CO,[5] as proposed for other $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ systems.[1,5-8] For R = C_2H_5, photoexcitation of the complex yields $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ even at 10 K in an Ar matrix![9] Study of the thermal chemistry of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C_2H_5)$ showed the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(H)$ and ethylene at ~60 °C.[10] The thermal mechanism was proposed to involve PPh_3 dissociation as the initiating step to give $(\eta^5\text{-}C_5H_5)Fe(CO)(C_2H_5)$ as proposed in the photochemistry of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_2H_5)$.[5] At least for $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$, the loss of CO has a large activation energy. Our data actually show that the β-hydrogen transfer and its reverse occur with great facility at low temperature, consistent with loss of a two-electron donor from an 18-valence-electron alkyl as the rate-limiting step in thermally induced reactions of the starting alkyl complex. Thus, photoexcitation brings about a change in the nature of the rate-limiting step of $(\eta^5\text{-}C_5H_5)Fe(CO)(L)(H)$ formation from $(\eta^5\text{-}C_5H_5)Fe(CO)(L)(C_2H_5)$. From the studies thus far of the Fe complexes there are no data establishing the rate of the β-hydrogen transfer of the presumed 16-electron intermediate. Further, there are no data concerning a mechanism involving an $\eta^5\text{-}C_5H_5 \rightarrow \eta^3\text{-}C_5H_5$ "ring slippage" to open the coordination site that would appear to be necessary to effect the β-hydrogen transfer. The Ru analogues of the Fe complexes have not been previously studied. We find that these Ru complexes yield intermediates than cannot be observed for the Fe species and provide more direct evidence for the mechanism of β-hydrogen transfer.

Experimental Section

Instruments. UV-visible spectra were recorded by using a Cary 17 spectrophotometer; infrared spectra were recorded by using a Perkin-Elmer 180 or Nicolet 7199 Fourier transform spectrometer; NMR spectra were recorded by using a Varian T-60, a JEOL FX90Q Fourier transform, or a Brucker 250 MHz Fourier transform spectrometer. Gas-liquid chromatographic separations were accomplished by using a Varian 2440 or 1440 gas chromatograph with flame ionization detectors and interfaced with a Hewlett-Packard Model 3380S electronic integrator. *n*-Pentane and the linear pentenes were separated by using a 0.3 cm × 9.2 m column of 20% propylene carbonate on Chromasorb P at 25 °C. *n*-Decane analysis was done by using a 0.3 cm × 7.7 m column of Poropak Q at 190 °C with *n*-heptane as an internal standard. All manipulations of the organometallic complexes were done under N_2 by using a Vacuum Atmospheres drybox or under Ar by using conventional Schlenk line techniques unless otherwise noted.

Chemicals. Hexane and toluene were reagent grade and were freshly distilled from CaH_2 under N_2. Tetrahydrofuran (THF) was freshly distilled from benzophenone dianion under N_2. Spectroquality isooctane was further purified by stirring over concentrated H_2SO_4/HNO_3 overnight, washing with H_2O and dilute $NaHCO_3$ and then repeating the acid wash 2 more times. Isooctane was then stirred over 2% $KMnO_4$ in 10% H_2SO_4 overnight, washed, dried over $MgSO_4$, and distilled under N_2 from CaH_2. Finally, the distilled isooctane was passed down grade No. 1 alumina (neutral, Woelm) before use. Methylcyclohexane was washed twice with concentrated H_2SO_4 for several hours and then with fuming H_2SO_4, washed with H_2O, dilute $NaHCO_3$, and saturated NaCl, predried over $CaCl_2$, and then passed down grade No. 1 Al_2O_3. PPh_3 (Aldrich) was recrystallized three times from absolute C_2H_5OH. $P(O\text{-}o\text{-tolyl})_3$ (Strem), 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (Strem), 90% ^{13}CO (Merck), and paraffin (Fischer) were used as received. Tricyclohexylphosphine (Strem) was recrystallized from hexanes under N_2 prior to use. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (Strem) was recrystallized from CH_2Cl_2/hexanes. $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ was available from previous work.[11] $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)C(O)CH_3$ was a gift from A. Davison's research group. Literature procedures were used to prepare $(\eta^5\text{-}C_5H_5)M(CO)_2CH_3$,[12] $(\eta^5\text{-}C_5H_5)M(CO)_2CH_2CH_3$,[13] $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2CH_3$,[14] and $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$.[15] $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\text{2-pentyl})$, and $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_3$ were prepared by procedures analogous to those for $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$ by reducing the appropriate dimer with 1% sodium amalgam in THF followed by addition of 1-iodopentane, 2-bromopentane, or ethyl bromide. The compounds were purified by column chromatography on neutral alumina, eluting with hexanes. $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$: ^1H NMR (60 MHz, C_6D_6) δ 4.88 (s), 1.7–0.6 (m), integration 5:11. Mass spectrum (70 eV) shows a parent ion at *m/z* 248 (calcd 248). The 2-pentyl complex is similar in the ^1H NMR, but the 2-pentyl complex and the *n*-pentyl complex were determined to be different by using ^{13}C NMR (62.8 MHz, C_6D_6). For the *n*-pentyl complex we find peaks (in δ, Me_4Si δ 0) at 218.2 for the CO's, at 85.3 for the C_5H_5, and at 38.3, 37.5, 22.7, 14.4, and 3.8 for the *n*-pentyl group. For the 2-pentyl complex we find peaks at 218.6 for the CO's, at 85.8 for the C_5H_5, and at 49.4, 29.3, 23.7, 20.6, and 14.3 for the 2-pentyl group. The five different resonances for *n*-pentyl are different from those for 2-pentyl, confirming the structural assignments. Infrared and UV-visible absorption properties of compounds relevant to this study are given in Table I.

Irradiations. Two GE blacklight bulbs (355 ± 20 nm, ~2 × 10^{-6} einstein/min) were used for irradiation unless otherwise noted. Quantum yields at 366 or 313 nm were carried out by using ~10^{-3} M $(\eta^5\text{-}C_5H_5)M(CO)_2R$ with the appropriate ligand concentration. Samples (3.0 mL) in 13 × 100 mm test tubes were freeze-pump-thaw degassed and hermetically sealed prior to irradiation. The light source was a 550-W medium-pressure Hg lamp equipped with Corning glass filters and filter solutions to isolate the 366- or 313 nm Hg emissions. Ferrioxalate actinometry[16] was used to determine light intensity which was typically ~10^{-7} einstein/min. Quantum yields are corrected to account for incomplete light

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Table I. Spectroscopic Data for Relevant Compounds[a]

compd	ν_{CO}, cm^{-1} (ϵ, M^{-1} cm^{-1} or rel abs)	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$	2015 (5540), 1960 (6360)	345 (770), 275 (sh)
$(\eta^5\text{-}C_5H_5)Fe(^{13}CO)_2CH_3$	1969 (1.00), 1918 (1.2)	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$	2011 (4700), 1957 (5420)	352 (744), 275 (sh)
$(\eta^5\text{-}C_5H_5)Fe(CO)_2$(*n*-pentyl)	2009 (5100), 1955 (5770)	351 (749), 275 (sh)
$(\eta^5\text{-}C_5H_5)Fe(CO)_2$(2-pentyl)	2007 (1.00), 1953 (1.2)	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2H$	2024 (1.0), 1967 (~1.0)	
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$	2006 (3000), 1962 (6400), 1794 (6200)	535 (650), 410 (1700), 348 (7700)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$	1916 (3200) or 1906 (2300)[b]	400 (sh), 280 (sh, ~6200)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_3$	1921	
$(\eta^5\text{-}C_5H_5)Fe(CO)(P(OPh)_3)CH_3$	~1943	
$(\eta^5\text{-}C_5H_5)Fe(CO)(P(OCH_2)_3CCH_2CH_3)CH_3$	~1952	
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)H$[c]	1923	
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)C(O)CH_3$	1923 (1.0), 1620 (0.14)	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2C(O)CH_2CH_3$	2020 (1.0), 1963 (2.0), 1666 (0.4)	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$[d]	2056 (3700), 2004 (3400)	480 (sh), 396 (690), 338 (1020), 285 (1830)
$(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_3$	1990 (5600), 1935 (6600)	358 (880), 285 (sh, 4200)
$(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$	2004 (1.0), 1946 (0.8)	
$[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$	1933 (1.0), 1765 (0.6)	
$(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_2CH_3$	2021 (1.0), 1961 (1.1)	
$(\eta^5\text{-}C_5H_5)Ru(CO)_2H$	2035 (1.0), 1975 (1.0)	
$(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$	2025 (5400), 1967 (6700)	280 (2500), 235 (sh)
$(\eta^5\text{-}C_5H_5)Ru(CO)(P(c\text{-}Hx)_3)CH_3$	1917	
$(\eta^5\text{-}C_5H_5)Ru(CO)(P(OCH_2)_3CCH_2CH_3)CH_3$	1963	

[a] All measurements were made in isooctane solution at 25 °C unless otherwise noted. [b] Toluene solution. [c] Benzene solution from: Su, S. R.; Wojcicki, A. *J. Organomet. Chem.* 1971, *27*, 231. [d] Isooctane/CH_2Cl_2 solution.

Table II. Quantum Yields for Disappearance of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ at 366 nm in the Presence of L[a]

L, M	$\Phi \pm 0.03$
PPh_3, 5.2×10^{-3}	0.71
PPh_3, 4.9×10^{-2}	0.68
P(O-*o*-tolyl)$_3$, 4.7×10^{-3}	0.72
P(O-*o*-tolyl)$_3$, 5.1×10^{-2}	0.71
$P(OCH_2)_3CCH_2CH_3$, 4.7×10^{-3}	0.72
$P(OCH_2)_3CCH_2CH_3$, 5.1×10^{-2}	0.71
^{13}CO, 1.0×10^{-2}	0.67

[a] All experiments carried out in deoxygenated isooctane solutions of L and 10^{-3} M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$. All samples are 3.00 mL in Pyrex ampules and were analyzed by infrared spectroscopy after <15% conversion to product. Irradiation carried out at 25 °C in a 366-nm merry-go-round at a light intensity of ~10^{-7} einstein/min. The only detectable product is $(\eta^5\text{-}C_5H_5)Fe(CO)(L)CH_3$.

absorption, typically only 90%.

Low-Temperature Spectra. Low-temperature IR spectra were obtained by using either a Precision Cell, Inc., Model P/N 21.000 variable-temperature cell with NaCl outer windows using liquid nitrogen as coolant or a low-temperature cell built in-house based on a published design[17] using CaF_2 windows mounted in a Cryogenics Technology, Inc., Spectrim II cryocooler with NaCl windows. Temperature was measured by using a thermocouple (chromel vs. Au –0.7 at % Fe) with the reference junction at room temperature. The thermocouple was attached to the copper body of the IR cell with Ag epoxy. Thermocouple output was measured with a Hewlett-Packard 3465A digital multimeter and converted to temperature by using published calibration curves[18] which were checked with liquid nitrogen, dry ice/acetone, and ice/water. Temperatures are considered accurate to ±2 °C at fixed temperatures and ±10 °C while being warmed or cooled. The data for Figures 3 and 4 were obtained by using ~1 mM $(\eta^5\text{-}C_5H_5)M(CO)_2CH_2CH_3$ dissolved in liquid paraffin (mp ~52 °C) and coated (~1 mm) onto a KBr pellet.

Results and Discussion

a. Photosubstitution of $(\eta^5\text{-}C_5H_5)M(CO)_2CH_3$ (M = Fe, Ru). Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$, as is known from previous work,[1,5,7] results in the substitution of CO by P-donor groups. We have examined the 366-nm quantum yield for the ligand substitution represented by eq 3 in isooctane solutions of different ligands L and at

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3 \xrightarrow[L]{h\nu} (\eta^5\text{-}C_5H_5)Fe(CO)(L)(CH_3) + CO \quad (3)$$

variable concentrations of L. Representative quantum yield data are given in Table II. In the presence of the P-donor ligands or ^{13}CO we find no other primary products other than the substitution product. Thus, disappearance yields can be equated with formation quantum yields of product. The quantum yields establish ligand substitution to account for most of the excited-state decay, and there is no effect on quantum yield, within experimental error, upon variation in the concentration of L or upon variation in the electronic character or structural demands of the entering P-donor ligand.[19]

The lack of variation in quantum yield upon variation in L or its concentration requires the intermediacy of a relatively long-lived and indiscriminate coordinatively unsaturated species. An $(\eta^3\text{-}C_5H_5)Fe(CO)_2CH_3$ intermediate, a ring slippage product, would seemingly be short-lived and structurally demanding compared to the 16-electron $(\eta^5\text{-}C_5H_5)Fe(CO)CH_3$ formed by dissociative loss of CO from the photoexcited complex (eq 4 and 5).

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3 \xrightarrow[366\ nm]{h\nu} [(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3]^* \quad (4)$$

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(17) Edgell, W. F.; Hegde, S.; Barbetta, A. *J. Am. Chem. Soc.* **1978**, *100*, 1406.

(18) Sparks, L. L.; Powell, R. L. *J. Res. Natl. Bur. Stand., Sect. A* **1972**, *76*, 263.

(19) Tolman, C. A. *Chem. Rev.* 1977, *77*, 313.

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3]^* \xrightarrow{k_5} (\eta^5\text{-}C_5H_5)Fe(CO)CH_3 + CO \quad (5)$$

Consistent with photochemical generation of $(\eta^5\text{-}C_5H_5)Fe(CO)CH_3$ we find that $(\eta^5\text{-}C_5H_5)Fe(^{13}CO)(CO)CH_3$ is rapidly formed when $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ is irradiated in isooctane solution exposed to 1 atm of 90% ^{13}CO (15-fold excess of ^{13}CO compared to amount required to completely exchange the ^{12}CO in the starting complex). Inasmuch as ^{13}CO cannot be regarded as a nucleophile, it represents a very different entering group compared to the P-donor ligands. The rapid, efficient ^{13}CO exchange during irradiation is most consistent with dissociative loss of CO as the mechanism of ligand substitution. The fact that the ^{13}CO substitution quantum yield is the same as for P-donor entering groups is especially convincing. If the intermediate in the substitution were the ring slippage product, the quantum yield for substitution by the ^{13}CO would be lower than for the P donors provided the CO's equilibrate at the $(\eta^3\text{-}C_5H_5)Fe(CO)_2(^{13}CO)CH_3$ stage.

The chemical efficiency for the formation of simple substitution products in the presence of L rules out two other conceivable primary photoreactions: homolytic Fe–CH_3 cleavage and –CH_3 migration. We do not observe the $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_n(L)_{4-n}$ products that would be expected[20] if $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ was formed as a primary product from $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$. Nor do we observe $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C(O)CH_3)$ that would be formed if $(\eta^5\text{-}C_5H_5)Fe(CO)(C(O)CH_3)$ was a result of excited-state decay.

Our studies of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ thus lead to the straightforward and expected conclusion that photoexcitation in solution leads to dissociative loss of CO. The photochemistry of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+$ may proceed by ring slippage as a result of photoexcitation,[21] but we find that the data are most consistent with CO loss as the principal result of excited-state decay in solution for the $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ species. The quantum yield of 0.7 is the lower limit for the quantum efficiency for the loss of CO; the actual quantum yield for CO loss could be higher with the net quantum yield for substitution being attenuated by inefficient cage escape of the photoejected CO. In toluene solvent that can be weakly coordinated to 16-electron metal carbonyls, we find that the quantum yield for $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_3$ formation is 1.0 ± 15% at 366 nm. This means that the previous finding[5] of CH_4 formation from the $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ does not proceed via loss of CH_3 as a primary photoproduct. Completely efficient loss of CO from the excited species, (eq 5) means that k_5 dominates all other rate constants for excited-state decay. The lowest excited state of $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ is likely ligand field in character and involves the population of an orbital that is strongly σ antibonding.[22] Apparently, the degree of labilization of the CO is sufficiently great that virtually every excited species loses CO within its lifetime. Such is not uncommon for mononuclear metal carbonyls having ligand field lowest excited states.[1]

The disappointing finding concerning the photochemistry is that we have not been able to observe the 16-electron $(\eta^5\text{-}C_5H_5)Fe(CO)CH_3$ by irradiating $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ in inert (paraffin) matrices at low temperature (40–77 K). Duplicating experimental conditions that have proven successful with $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ to observe $(\eta^5\text{-}C_5H_5)W(CO)_2CH_3$ have failed to yield spectroscopically detectable $(\eta^5\text{-}C_5H_5)Fe(CO)CH_3$. The reason for this failure is not clear, particularly inasmuch as we do see the analogous Ru species (vide infra). It may be that k_5 is strongly temperature dependent, giving a quantum yield that is too low to observe product on the timescale of our photolyses. Another possibility is that CO loss is indeed quite efficient but that the back-reaction is fast and cage escape of CO at low temperature in the rigid medium is too slow to compete with regeneration of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$. Experiments with $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ (vide infra) suggest that it is the latter explanation that accounts for our inability to photogenerate spectroscopically detectable quantities of $(\eta^5\text{-}C_5H_5)Fe(CO)CH_3$ in low-temperature paraffin matrices. Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ in an Ar matrix at 10 K also does not yield a monocarbonyl product, even though $^{12}CO/^{13}CO$ exchange can be induced photochemically when ^{13}CO is present in the 10 K matrix.[9] Consistent with this finding, irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ in neat 1-pentene at 77 K leads to loss of the two CO absorptions due to the dicarbonyl (2005, 1948 cm^{-1}), the growth of absorption due to free CO (2135 cm^{-1}), and the growth of a single absorption at ~1948 cm^{-1} under the lower energy absorption of the dicarbonyl. We attribute the single product peak at ~1948 cm^{-1} to $(\eta^5\text{-}C_5H_5)Fe(CO)(1\text{-pentene})CH_3$. Irradiations at low temperature in fluid solutions confirm this assignment, as described in the following paragraph.

Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ in 1-pentene-containing solution at low temperature also shows that CO loss can occur at temperatures as low as −90 °C. Figure 1a shows infrared spectral changes resulting from irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ in the presence of 1 M 1-pentene. The decline of the two CO absorptions due to the starting complex is not the same, and the growth of absorbance on the low-energy side of the 1959 cm^{-1} starting material absorption indicates that there is a single CO infrared absorption for a product at ~1957 cm^{-1}. We attribute the ~1957-cm^{-1} absorption to $(\eta^5\text{-}C_5H_5)Fe(CO)(1\text{-pentene})CH_3$. Warming the solution to −20 °C results in nearly complete regeneration of the absorptions attributable to $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ concomitant with decline of the ~1957-cm^{-1} absorption. These data suggest that the $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ is not only photolabile at −90 °C but that the $(\eta^5\text{-}C_5H_5)Fe(CO)(alkene)CH_3$ complexes are very thermally labile. Note that in the experiment summarized in Figure 1a the photoreleased CO is no more than 5×10^{-3} M while the 1-pentene concentration is 1 M and still nearly complete regeneration of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ occurs at −20 °C. To confirm that the ~1957 cm^{-1} is a substitution labile product, we generated it in a second experiment by irradiating at −78 °C and then introduced PPh_3 and warmed the sample to 25 °C. Infrared analysis (Figure 1b) shows the net formation of the inert $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_3$.

The photosubstitution behavior of $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$ at 25 °C parallels that detailed above for the Fe analogue. The quantum yields for substitution (Table III) are again independent of the nature of the ligand or its concentration. This result is in full accord with a mechanism that involves the dissociative loss of CO. The quantum efficiency, 0.40 ± 0.05, is somewhat lower than for the Fe complex, but this value still gives what would be regarded as an efficient photoreaction. The quantum yields for the Ru complex are reported for 313 nm, since the principal absorption for the Ru complexes is higher

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[20] The substitution lability and coupling reactions of 17-electron metal-centered radicals are well established. See ref 11 and references therein.

[21] Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1980**, *19*, 3007.

[22] (a) Lichtenberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 50. (b) Alway, D. G.; Barnett, K. W. *Adv. Chem. Ser.* **1978**, *No. 168*, 115.

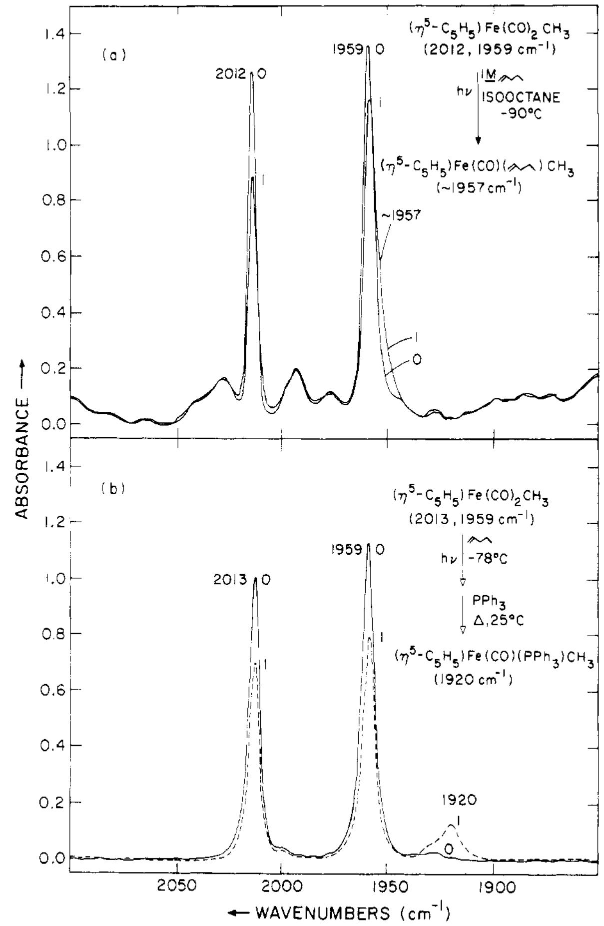

Figure 1. Infrared spectral changes accompanying irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$. (a) Trace 0 shows $\sim 10^{-3}$ M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ in degassed 1 M 1-pentene in isooctane at −90 °C. Trace 1 is after 6-min irradiation. (b) Trace 0 shows $\sim 5 \times 10^{-3}$ M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ in 1-pentene. Trace 1 is after cooling to −78 °C, irradiation for 5 min, and then addition of PPh_3 followed by warming to 25 °C. Unidentified peaks in (a) are due to solvent in this single-beam measurement.

Table III. Quantum Yields for Photosubstitution of $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$[a]

L, M	Φ ± 0.05
$P(c\text{-}Hx)_3$, 5.7×10^{-3}	0.40
$P(c\text{-}Hx)_3$, 5.2×10^{-2}	0.47
$P(OCH_2)_3CCH_2CH_3$, 4.9×10^{-3}	0.43
$P(OCH_2)_3CCH_2CH_3$, 5.5×10^{-2}	0.38

[a] All experiments carried out in deoxygenated isooctane solutions of L and $\sim 10^{-3}$ M $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$. All samples are 3.00 mL in Pyrex ampules and were analyzed by infrared spectroscopy after <15% conversion to $(\eta^5\text{-}C_5H_5)Ru(CO)(L)(CH_3)$. Irradiation was carried out at 25 °C in a 313-nm merry-go-round at a light intensity of $\sim 10^{-7}$ einstein/min.

in energy than for the Fe species.

Fortunately, and in contrast to the $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$, we find that UV irradiation of $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$ at 77 K in a methylcyclohexane matrix gives infrared spectral changes that are consistent with the formation of $(\eta^5\text{-}C_5H_5)Ru(CO)CH_3$, the proposed intermediate in light-induced substitution. Bands for the dicarbonyl (2018, 1958 cm^{-1}) smoothly decline while a single absorption grows at ~ 1937 cm^{-1} (77 K in methylcyclohexane) that we would associate with the 16-valence-electron species. In accord with this assertion we also observe the growth of a feature at ~ 2135 cm^{-1} that is the absorption of free CO. In a methylcyclohexane solution containing 0.1 M $P(c\text{-}Hx)_3$ (c-Hx = cyclohexyl) we find that irradiation of $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$ at 77 K yields two infrared features, one that we attribute to the 16-valence-electron species and one that we attribute to $(\eta^5\text{-}C_5H_5)Ru(CO)(P(c\text{-}Hx)_3)CH_3$. Warm-up to 298 K yields a diminution in the feature attributable to the 16-valence-electron species, leaving the one absorption feature at 1916 cm^{-1} (alkane, 298 K) for the monosubstitution product. Consistent with the lability of CO in methylcyclohexane, we find that irradiation of $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$ in neat 1-pentene at 77 K yields disappearance of the dicarbonyl at 2015 and 1952 cm^{-1}, growth of the free CO absorption at ~ 2135 cm^{-1}, and the growth of a single absorption at 1943 cm^{-1} (1-pentene, 77 K) attributable to $(\eta^5\text{-}C_5H_5)Ru(CO)(1\text{-pentene})CH_3$. The 77 K experiments with $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$ directly establish the mechanism for photosubstitution to begin with the dissociative loss of CO, as we found for $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ by similar means.[3]

b. Photochemistry of Alkyl Complexes Where the Alkyl Group Has β-Hydrogens. Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ in isooctane solution proceeds according to eq 6. Figure 2 compares the infrared spectral

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5 \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)Fe(CO)_2H + C_2H_4 \qquad (6)$$

changes accompanying photoreaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ in toluene/0.5 M PPh_3 and photoreaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ in isooctane containing no deliberately added entering groups. Like the $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ included in Figure 2 for comparison, irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ in the presence of 0.5 M PPh_3 results in efficient CO substitution. The product is $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C_2H_5)$ and specifically not $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(H)$ or $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C(O)C_2H_5)$, since the infrared spectrum for the product does not correspond to these species. In the absence of entering group in isooctane, photolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ yields the $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$. Likewise, $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$ yields the same metal carbonyl species, as deduced from the infrared spectrum. The $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ exhibits infrared absorptions at 2024 and 1967 cm^{-1} (Table I) that are the same as those for an authentic sample prepared from reaction of acetic acid with $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$.[23] Further, as shown in Figure 2 the $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ reacts with CCl_4 to form $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, as expected. A hydride signal is detectable in the ^1H NMR of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ at δ −11.88 (s) in C_6D_6, and this signal is found upon irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$ in C_6D_6.

Although $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ is observed in dilute ($\sim 10^{-2}$ M) solutions, decomposition of the hydride to form $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ does occur. Indeed, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ is found as a secondary photoproduct. After prolonged photolysis the $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ is the only detectable metal carbonyl, and it accounts for all of the starting $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ or $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$, within experimental error. After extensive irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$ we find *n*-pentane and the linear pentenes, mainly 1-pentene, as the products from the *n*-pentyl group. The ratio of *n*-pentane to linear pentenes is $\sim 1/1$. No *n*-decane was detected (<0.1% of *n*-pentyl) by gas chromatography from irradiation of the

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(23) Sodium borohydride reduction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ has been used to prepare $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ on a synthetic scale. However, anion acidification such as that used to prepare $(\eta^5\text{-}C_5H_5)M(CO)_3H$ (M = Cr, Mo, W) (ref. 12) is more convenient when separation of acetic acid and the volatile hydride is not required.

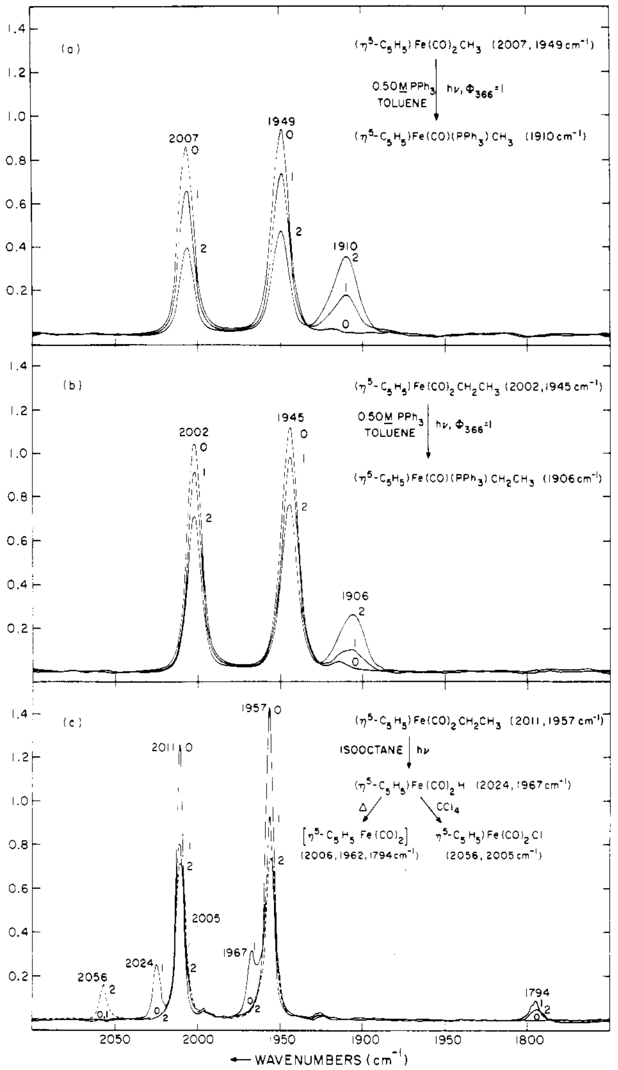

Figure 2. Infrared spectral changes accompanying irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$. (a) Trace 0 shows ~3 × 10^{-2} M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ in degassed toluene containing 0.50 M PPh_3. Traces 1 and 2 are after 30- and 90-s irradiation, respectively. The observed product is $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_3$. (b) Trace 0 shows ~8 × 10^{-3} M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$ in degassed toluene containing 0.50 M PPh_3. Traces 1 and 2 are after 15- and 60-s irradiation, respectively. The observed product is $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2CH_3$. The ordinate has been expanded 2.0 times for these spectra. (c) Trace 0 shows ~1 × 10^{-2} M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$ in degassed isooctane. Trace 1 is after one flash from a Xenon flash lamp. Trace 2 is after addition of 10 μL degassed CCl_4 to the IR cell.

n-pentyl complex in toluene solution.

Table IV. Disappearance Quantum Yields for $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\text{alkyl})$[a]

complex	solvent	entering group, M	Φ ± 15%
$(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$	isooctane	none	0.36
$(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$	isooctane	none	1.00
$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$	isooctane	none	0.07
$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$	isooctane	PPh_3, 0.049	0.68[b]
$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$	toluene	PPh_3, 0.5	1.00
$(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$	toluene	PPh_3, 0.5	1.00

[a] All samples irradiated in deoxygenated, 3.00 mL, 25 °C, solutions at ~10^{-2} M of complex. Irradiation was at 366 nm, ~10^{-7} einstein/min, and quantum yields are for <15% conversion. Irradiations in the presence of PPh_3 yield only $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R$. In isooctane alone the ethyl and *n*-pentyl complexes yield $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$; the methyl complex yields some decomposition to unidentified products and some $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$. [b] This value has a smaller error, ±0.03; cf. Table II.

While they have not been investigated in detail, $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_3$ and $(\eta^5\text{-}C_5H_5)Ru(CO)_2C_2H_5$ both yield clean photoreaction in isooctane at 25 °C to give $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$ and $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$, respectively. Thus, like $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$ the initially observable product from photolysis in isooctane is not an alkene–hydride complex as found in the irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$.[3] The 366-nm quantum yields for disappearance of the ethyl and *n*-pentyl Fe complexes in isooctane solution are significantly higher than for the methyl complex (Table IV). For the methyl complex the irradiation does not cleanly yield tractable product; a small amount (~15%) of $(\eta^5\text{-}C_5H_5)_2Fe(CO)_4$ is formed and ~20% CH_4 is detected, but there is no C_2H_6 or C_2H_4 detected. The mechanism of the formation of these products is under study. The low quantum yield for dissapearance of the methyl complex is consistent with the primary process represented by eq 5 and the finding that photolysis under ^{13}CO leads to facile exchange. Larger disappearance quantum yields for the ethyl and *n*-pentyl complexes in isooctane are consistent with the possibility of the β-hydrogen transfer allowed by loss of alkene (eq 7–9). The $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ then

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2(\text{alkyl}) \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)Fe(CO)(\text{alkyl}) + CO \quad (7)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)(\text{alkyl}) \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} (\eta^5\text{-}C_5H_5)Fe(CO)(\text{alkene})(H) \quad (8)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)(\text{alkene})(H) \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} (\eta^5\text{-}C_5H_5)Fe(CO)(H) + \text{alkene} \quad (9)$$

forms by capture of CO (eq 10). Apparently, the sequence

$$(\eta^5\text{-}C_5H_5)Fe(CO)(H) + CO \xrightarrow{k_{10}} (\eta^5\text{-}C_5H_5)Fe(CO)_2H \quad (10)$$

of (8) and (9) to yield loss of alkene is faster than the back-reaction of the 16-electron alkyl complex with photoreleased CO, (eq 11), since the quantum yields are very

$$(\eta^5\text{-}C_5H_5)Fe(CO)(\text{alkyl}) + CO \xrightarrow{k_{11}} (\eta^5\text{-}C_5H_5)Fe(CO)_2(\text{alkyl}) \quad (11)$$

high. It is perhaps not surprising that we do not observe the $(\eta^5\text{-}C_5H_5)Fe(CO)(\text{alkene})(H)$ at 25 °C, since our data for $(\eta^5\text{-}C_5H_5)Fe(CO)(\text{alkene})CH_3$ show the alkene to be only weakly bound and that it will react at −20 °C (or lower) with the photoreleased CO from its formation, even with 1 M 1-pentene present (vide supra and Figure 1). Nor is it surprising that the photoreleased CO cannot efficiently recapture the 16-electron alkyl complex at 25 °C; the β-hydrogen transfer is a unimolecular process that can occur at a fast rate.[3,4]

Consistent with the mechanistic proposal represented by eq 7–10, we find that photolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ or $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$ in isooctane that contains added PPh_3 yields two additional products (in a ratio and amount that depends on added PPh_3 concentration) from reaction of the proposed 16-electron species with PPh_3 (eq 12 and 13). Indeed, at sufficiently high

$$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(alkyl)} + \text{PPh}_3 \xrightarrow{k_{12}} (\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(PPh}_3\text{)(alkyl)} \tag{12}$$

$$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(H)} + \text{PPh}_3 \xrightarrow{k_{13}} (\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(PPh}_3\text{)(H)} \tag{13}$$

PPh_3 concentration the product is mainly the substitution product $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(PPh}_3\text{)(alkyl)}$ (alkyl = C_2H_5 or *n*-pentyl) (Figure 2). Thus, sufficient concentrations of nucleophile can apparently intercept the primary 16-electron photoproduct to suppress the product from β-hydrogen transfer (Table V). Likewise, P-donor ligands in solution can effectively suppress β-hydrogen transfer products for the ruthenium ethyl species, though a higher concentration of the P-donor group is needed.

We propose that the transfer of the β-hydrogen is reversible (eq 8), since we find some of the 2-pentenes from photolysis of the *n*-pentyl complex. Study of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(PPh}_3\text{)(alkyl)}$ also led to this conclusion.[10] However, we do not find extensive isomerization of 1-pentene to the 2-pentenes by irradiation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2(n\text{-pentyl})$ in the presence of added 1-pentene, but there is enough in the way of catalysis (greater than five turnovers based on molecules of 2-pentene formed per molecule of Fe complex) to invoke the same mechanism involved in the thermolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(PPh}_3\text{)(alkyl)}$, where loss of PPh_3 yields the same 16-electron species that we invoke here. The photoassisted isomerization of 1-pentene is proposed to proceed as in eq 14–20. In principle, the

$$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2(n\text{-pentyl}) \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} (\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}(n\text{-pentyl}) + \text{CO} \underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}} (\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(1-pentene)(H)} + \text{CO} \tag{14}$$

$$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(1-pentene)(H)} \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} (\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(2-pentyl)} \tag{15}$$

$$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(2-pentyl)} \underset{k_{-16}}{\overset{k_{16}}{\rightleftharpoons}} (\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}(\textit{cis}\text{-2-pentene})\text{(H)} \tag{16}$$

$$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(2-pentyl)} \underset{k_{-17}}{\overset{k_{17}}{\rightleftharpoons}} (\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}(\textit{trans}\text{-2-pentene})\text{(H)} \tag{17}$$

$$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}(\textit{cis}\text{-2-pentene})\text{(H)} \underset{k_{-18}}{\overset{k_{18}}{\rightleftharpoons}} (\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(H)} + \textit{cis}\text{-2-pentene} \tag{18}$$

$$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}(\textit{trans}\text{-2-pentene})\text{(H)} \underset{k_{-19}}{\overset{k_{19}}{\rightleftharpoons}} (\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(H)} + \textit{trans}\text{-2-pentene} \tag{19}$$

$$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(1-pentene)(H)} \underset{k_{-20}}{\overset{k_{20}}{\rightleftharpoons}} (\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(H)} + \text{1-pentene} \tag{20}$$

quantum efficiency for the isomerization could be greater than unity, but, in fact, there is a very low quantum yield for isomerization ($<10^{-2}$). The low extent conversion for the isomerization and the low quantum yields do not mean that the thermal steps in the catalytic cycle are slow. Rather, the low quantum efficiency is likely due to the fact that the hydride effects reduction of pentene to *n*-pentane while $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{(CO)}_4$ is formed. The Fe dimer is not an active isomerization catalyst at 25 °C either in the dark or under irradiation.[24]

Further confirmation of the reversibility of the alkene–hydride formation is provided by results from the irradiation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{(2-pentyl)}$ in toluene. We find the formation of *n*-pentane, 1-pentene, *cis*-2-pentene, and *trans*-2-pentene in a distribution at ~50% conversion very similar to that from irradiating the *n*-pentyl complex under the same conditions. Presumably, rapid isomerization catalysis of an added alkene would result if the consumption of hydride could be prevented. Studies aimed at preventing the dimer formation are now underway employing surface-confined $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{R}$ catalyst precursors.

c. Low-Temperature Irradiation of $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_2\text{C}_2\text{H}_5$. W find that the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{C}_2\text{H}_5$ is photoreactive in inert matrices at low temperature. Irradiation of the ethyl complex at 77 K in a paraffin matrix results in the formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{H}$ (Figure 3). Even at the very low conversions illustrated in Figure 3, we observe no infrared absorptions attributable to an intermediate $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(C}_2\text{H}_4\text{)(H)}$. The photochemical reaction of the ethyl complex at 77 K is consistent with the fact that others have observed the same reaction to occur even at 10 K in an Ar matrix.[9] Since the logical intermediate in the reaction is the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(C}_2\text{H}_4\text{)(H)}$, having only one CO stretch in the infrared that may be close to the low-energy CO absorption in $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{C}_2\text{H}_5$, we have carefully compared the relative diminution in the two bands due to the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{C}_2\text{H}_5$ (Figure 3b). We find no evidence for any hidden absorption; both bands of the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{C}_2\text{H}_5$ decline at the same rate. The only primary product that is detectable is $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{H}$.

Irradiation of $(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2\text{C}_2\text{H}_5$ at 77 K in an alkane matrix also results in reaction (Figure 4). In this case the initial spectral changes show that $(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2\text{H}$ is *not* the primary photoproduct. Indeed, spectra at low conversion show a significant difference compared to what would be expected for the $(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2\text{H}$. The noteworthy feature of the spectra at low conversion is the single CO stretching frequency at 1966 cm^{-1}, consistent with a monocarbonyl photoproduct. The constancy of the ratio of the two negative peaks (2017, 2055 cm^{-1}) for the disappearing $(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2\text{C}_2\text{H}_5$ reveals that there are no peaks associated with product under those for the starting material. The position of the single product peak, higher in energy than the low-energy peak of the dicarbonyl, is inconsistent with it being the coordinatively unsaturated $(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)C}_2\text{H}_5$, inasmuch as $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)CH}_3$ has its single CO absorption below that for the dicarbonyl. Further, $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)(alkene)CH}_3$ has its absorption below that for $(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2\text{CH}_3$. We therefore assign the 1966 cm^{-1} absorption to the $(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)(C}_2\text{H}_4\text{)(H)}$. Continued irradiation at 77 K results in the formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2\text{H}$ (2032, 1971 cm^{-1}). The observation of the 1966-cm^{-1} photoproduct peak that we associate with $(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)(C}_2\text{H}_4\text{)(H)}$ provides direct proof that one-step formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2\text{H}$ does not occur; the results are consistent with a mechanism involving the dissociative loss of CO as the primary photoprocess. Unfortunately, the $(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)(C}_2\text{H}_4\text{)(H)}$ is photochemically and thermally labile and has not been fully characterized. It is noteworthy that relatively inert complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Ru(PPh}_3\text{)(alkene)(H)}$ can be formed from an 80 °C thermolysis of the $(\eta^5\text{-C}_5\text{H}_5)\text{Ru(PPh}_3\text{)}_2\text{(alkyl)}$ precursor.[25]

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[24] Reichel, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 6769.

[25] Lehmkuhl, H.; Grundke, J.; Benn, R.; Schroth, G.; Mynott, R. *J. Organomet. Chem.* **1981**, *217*, C5.

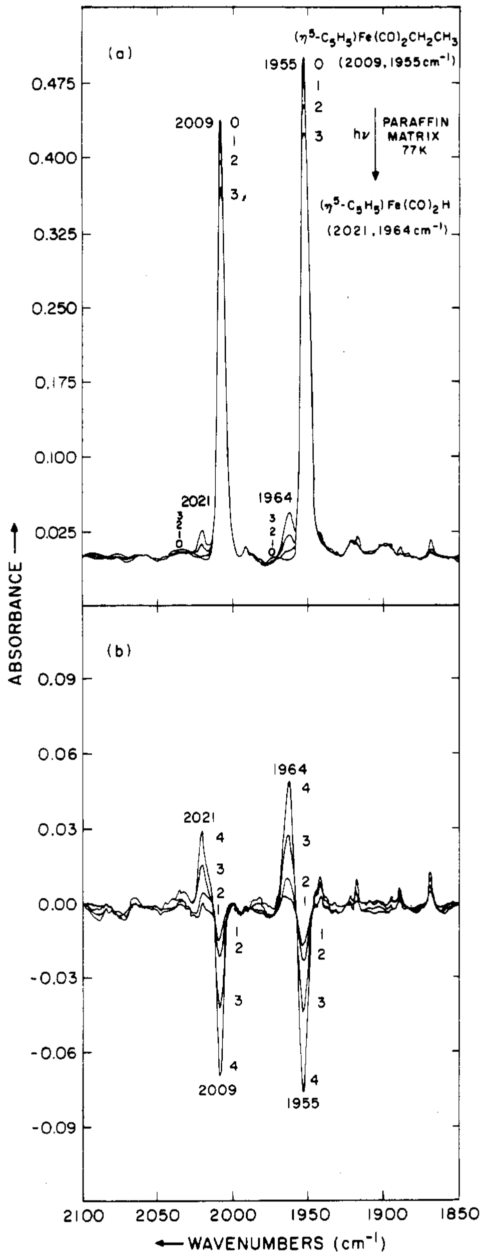

Figure 3. Infrared spectral changes accompanying irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$. (a) Trace 0 shows $\sim 10^{-3}$ M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$ in a paraffin matrix at 77 K. Traces 1, 2, and 3 are after 15-, 40-, and 80-min irradiation, respectively. (b) Traces 1, 2, 3, and 4 show subtraction spectra obtained by subtracting the initial spectrum from spectra obtained after 5-, 15-, 40-, and 80-min irradiation, respectively.

Apparently, the PPh_3 stabilizes the alkene–hydride complex. It is also noteworthy that the monocarbonyl photoproduct that we assign as $(\eta^5\text{-}C_5H_5)Ru(CO)(C_2H_4)(H)$ can also be observed in a paraffin matrix at 25 °C at low conversion. However, irradiation in isooctane at 25 °C yields $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ as the only detectable product at <5% conversion. These findings are consistent with a cage effect on the loss of C_2H_4 from the Ru.

To confirm the existence of the $(\eta^5\text{-}C_5H_5)Ru(CO)$(alkene)(H), we prepared $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ and irradiated it in neat 1-pentene at 77 K. In neat 1-pentene the two bands for $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ are at 2015 and 1952 cm^{-1}. The infrared spectral changes are in accord with CO substitution: the free CO absorption grows, the dicarbonyl features decline, and a single absorption at ~ 1954 cm^{-1} (1-pentene, 77 K) grows in that we attribute to $(\eta^5\text{-}C_5H_5)Ru(CO)$(1-pentene)(H). The ~ 1954-cm^{-1} position is ~ 12 cm^{-1} lower in energy than for the ethylene–hydride but this is expected on the basis of the fact that the 1-pentene complex will likely absorb at a lower frequency and the 1-pentene vs. methylcyclohexane matrix gives a 3–6-cm^{-1} shift to lower frequencies for these complexes. Thus, irradiation of the $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ provides an independent entry to alkene hydride products as we found for $(\eta^5\text{-}C_5H_5)W(CO)_3H$.[3]

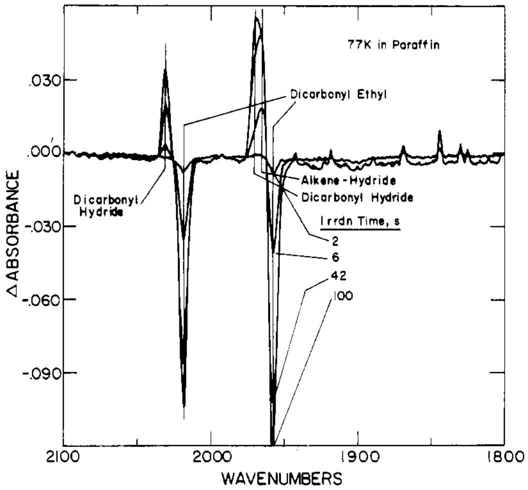

Figure 4. Infrared spectral changes accompanying the irradiation of $(\eta^5\text{-}C_5H_5)Ru(CO)_2C_2H_5$ at 77 K in a paraffin matrix. Note that the starting material peaks at ~ 2020 and 1960 cm^{-1} represent consumption and the peak ratios are independent of irradiation time. The primary product peak is at ~ 1970 cm^{-1} that we associate with $(\eta^5\text{-}C_5H_5)Ru(CO)(C_2H_4)(H)$ and longer irradiation yields peaks at ~ 2040 and ~ 1980 cm^{-1} characteristic of $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$.

Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$(*n*-pentyl) in neat 1-pentene solution at −140 °C leads to a diminution in the two bands due to the *n*-pentyl complex and the growth of a new absorption at ~ 1947 cm^{-1} (Figure 5). Warming the solution to −40 °C yields $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ at the expense of the product associated with the ~ 1947-cm^{-1} absorption. Specifically, we do not observe the regeneration of $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ (R = alkyl) as was observed for R = CH_3 (vide supra). Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ at −78 °C in neat 1-pentene followed by addition of PPh_3 at −78 °C followed by warm-up to 25 °C yields $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R$ (R = alkyl), not $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(H)$. ^1H NMR of the product shows it to be $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$(*n*-pentyl), not the ethyl complex. These results suggest that the ~ 1947-cm^{-1} absorption is due to $(\eta^5\text{-}C_5H_5)Fe(CO)$(1-pentene)(*n*-pentyl) that is very substitution labile, as is $(\eta^5\text{-}C_5H_5)Fe(CO)$(1-pentene)$(CH_3)$ (vide supra).

Irradiation of $(\eta^5\text{-}C_5H_5)M(CO)_2C_2H_5$ (M = Fe, Ru) at 77 K in neat 1-pentene leads to rapid photoreaction. For M = Fe the principal product appears to be $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ with an alkene monocarbonyl as a possible minor product. By way of contrast we find that the Ru complex appears to give mainly $(\eta^5\text{-}C_5H_5)Ru(CO)$(alkene)(H). Interestingly, it does not appear that the neat 1-pentene matrix suppresses β-hydrogen transfer. While the matrix is a pure two-electron donor that could capture a photogenerated, 16-valence-electron intermediate prior to β-hydrogen transfer as with PPh_3 in fluid solution, apparently the rigidity of the matrix prevents suppression of the β-hydrogen transfer.

At the present time we are still not in a position to unambiguously rule out $\eta^5\text{-}C_5H_5 \rightarrow \eta^3\text{-}C_5H_5$ ring slippage as the pathway for β-hydrogen transfer, but results for the Ru methyl complex compel us to adopt the mechanism

Table V. Effect of PPh_3 Concentration on Photoproduct Distribution from $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$

	photoproducts,[a] %		
$[PPh_3]$, M	$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C_2H_5)$	$(\eta^5\text{-}C_5H_5)Fe(CO)(L)(H)$ (L = CO or PPh_3)	(substitution/hydride)[b]
0	0	100	0
0.002	3.8	96.2	0.04
0.012	14.5	85.5	0.17
0.020	24.8	75.2	0.33
0.029	29.6	70.4	0.42
0.035	30.6	69.4	0.44
0.055	40.1	59.9	0.67

[a] Photoproducts determined, quantitatively by IR, cf. Table I. All irradiations were carried out in deoxygenated isooctane solutions containing ~0.01 M $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ and PPh_3. The irradiation was a single flash from a pair of Xenon flash lamps (~10-μs flash) to avoid secondary photolysis. The hydride products are a mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)H$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$; cf. text eq 10 and 13. [b] Ratio of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C_2H_5)$ to the sum of the two hydride products. Assuming k_{-8} to be small, the ratio should equal $k_{12}[PPh_3]/k_8$; a plot of the ratio vs. $[PPh_3]$ is a straight line with an intercept of zero.

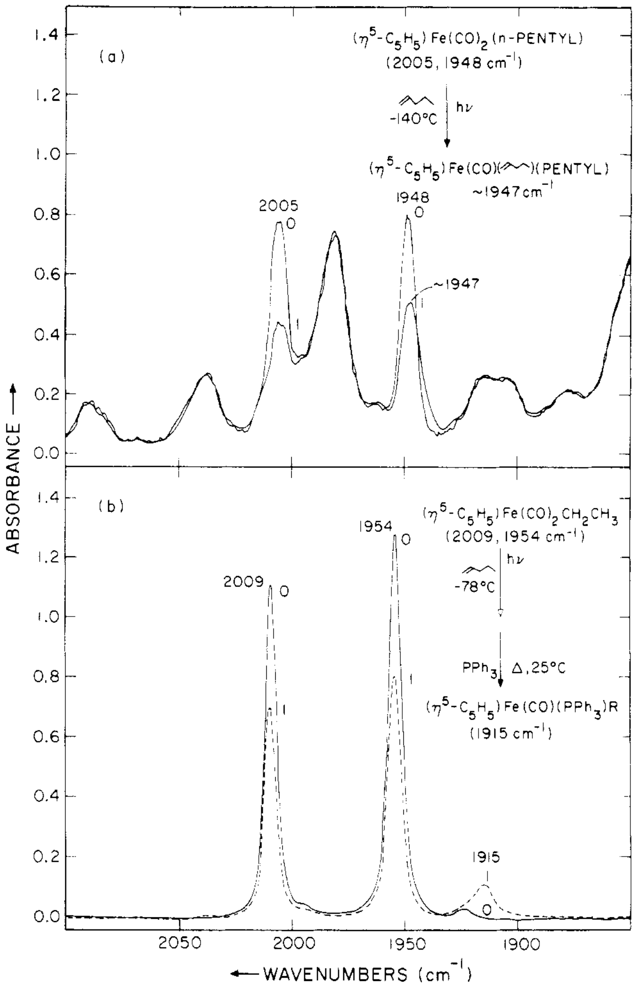

Figure 5. Infrared spectral changes accompanying irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$. (a) Trace 0 shows ~$10^{-3}$ M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$ in degassed 1-pentene at −140 °C. Trace 1 is after 22-min irradiation. (b) Trace 0 shows ~5 × 10^{-3} M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$ in 1-pentene. Trace 1 is after cooling to −78 °C, irradiation for 5 min, and then addition of PPh_3 followed by warming to 25 °C. The unidentified peaks in (a) are due to solvent in the single-beam measurement.

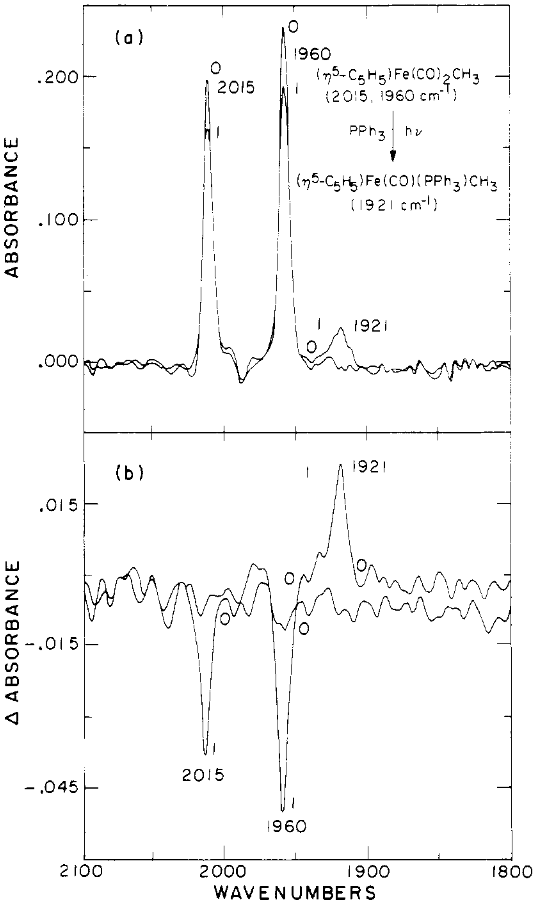

Figure 6. Spectra of ~1 mM $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$/1 mM PPh_3/isooctane before (0) and <200 ms after (1) a flash photolysis to generate $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_3$. In (a) the spectra are shown and in (b) difference spectra are shown. No $(\eta^5\text{-}C_5H_5)Fe(CO)CH_3$ intermediate, expected to absorb between 1960 and 1921 cm^{-1} is observed, indicating that capture of the 16-electron species occurs in <200 ms. A spectrum recorded 25 s after the flash is the same as scan 1, indicating that reaction is complete in <200 ms.

involving dissociative CO loss as the preferred path. For Fe complexes, the low-temperature experimentation does indicate that photoejected CO does not efficiently escape into the matrix. The 25 °C studies of the methyl complexes show no entering group structural effects in substitution (Tables II and III), and there is no reason to suspect that results for the ethyl and *n*-pentyl complexes would be different. The lack of entering group effects in substitution is most consistent with the dissociative loss of CO.

Having concluded that the immediate precursor to β-hydrogen transfer is the 16-electron $(\eta^5\text{-}C_5R'_5)M(CO)R$, we now consider the rate of β-hydrogen transfer. The inability to observe $(\eta^5\text{-}C_5H_5)Ru(CO)C_2H_5$ under conditions where $(\eta^5\text{-}C_5H_5)Ru(CO)CH_3$ is observable indicates that β-hydrogen transfer is very fast and much faster than for Mo and W complexes.[3,4] At 77 K, we find that $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ or $(\eta^5\text{-}C_5H_5)Ru(CO)(C_2H_4)(H)$ can be formed photochemically in a time that depends on the intensity of the light source. Conservatively, we can say that the half-time for photoreaction at 77 K can be <60 s. We can thus put a limit on the rate constant associated with the thermal conversion of the photogenerated 16-valence-electron intermediate I to the metal hydride (eq 21). We

$$\mathrm{I} \xrightarrow{k_{21}} \text{metal hydride} \tag{21}$$

conclude that k_{21} must be $\sim 10^{-2}\ s^{-1}$ at 77 K. Assuming the highest frequency factor possible for a unimolecular reaction, $A = 10^{14}\ s^{-1}$, this leads to the conclusion that the activation energy for the metal hydride formation from I is <6 kcal/mol. This is in accord with the data for the β-hydrogen transfer in the Mo and W complexes $(\eta^5\text{-}C_5H_5)M(CO)_2R$,[3,4] where the activation energy is ~ 10 kcal/mol; these complexes do not give significant rates for β-hydrogen transfer at 77 K.

Assuming that $(\eta^5\text{-}C_5H_5)Fe(CO)C_2H_5$ can be directly intercepted by PPh_3 to give substitution prior to any β-hydrogen transfer and assuming the substitution of the methyl complex proceeds by the same kind of intermediate with the same rate, allow us to place a limit on the 25 °C rate of β-hydrogen transfer. Using the rapid scan (7 scans/s) Fourier transform infrared technique, we have shown that the substitution of CO in the iron–methyl complex by 1×10^{-3} M PPh_3 is at least 75% complete within 200 ms after a flash excitation to produce $\sim 10^{-4}$ M I (Figure 6). This gives us a lower limit on the rate constant for capturing the 16-electron species by PPh_3, k_{22}, eq 22, of $\sim 3 \times 10^3\ M^{-1}\ s^{-1}$. Under the same conditions,

$$(\eta^5\text{-}C_5H_5)Fe(CO)R + PPh_3 \xrightarrow[\text{isooctane}]{k_{22}} (\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R \tag{22}$$

$$R = CH_3$$

~ 0.1 M PPh_3 is required to observe $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C_2H_5)$ at 50% of the product mixture from irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ in isooctane solution (Table V). These results suggest that k_{21} at 25 °C is $>3 \times 10^2\ s^{-1}$ consistent with the extrapolation of our 77 K lower limit for k_{21} and the activation energy. The value of k_{22} is probably much higher that $3 \times 10^3\ M^{-1}\ s^{-1}$, on the basis of flash photolysis studies;[26] this means that k_{21} would be much larger than $3 \times 10^2\ s^{-1}$.

These considerations of the 16-valence-electron species indicate that transfer of a β-hydrogen from the alkyl group onto the metal occurs with facility even at very low temperatures. Direct monitoring of the progress of the transfer of the β-hydrogen atom has not proven to be possible with the techniques that we used for the $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$. Flash photolysis with a time resolution of at least nanoseconds and perhaps picoseconds is required to directly monitor reaction to give a hydride product at 298 K. Conventional, greater than microsecond timescale, flash photolysis could prove useful in obtaining good rate constants for conversion of 16-valence-electron alkyls to hydride product by using the interception by PPh_3 as an internal clock. Development of the instrumentation for monitoring the products from flash photolysis by Raman spectroscopy and infrared spectroscopy is now in progress.

Acknowledgment. We thank the National Science Foundation for support of this research by grant support to M.S.W. and a predoctoral fellowship to R.J.K. (1978–1981).

Note Added in Proof. We wish to call attention to the recently reported claim of ring-slippage upon radiation of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_3$ at 12 K in a CO matrix: *J. Chem. Soc., Dalton Trans.* **1981**, 2311.

Registry No. $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$, 12080-06-7; $(\eta^5\text{-}C_5H_5)Fe(^{13}CO)_2CH_3$, 80409-88-7; $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$, 32611-65-7; $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$, 69005-48-7; $(\eta^5\text{-}C_5H_5)Fe(CO)_2(2\text{-pentyl})$, 69661-75-2; $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$, 35913-82-7; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 12154-95-9; $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2CH_3$, 32824-72-9; $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_3$, 12100-51-5; $(\eta^5\text{-}C_5H_5)Fe(CO)(P(OPh)_3)CH_3$, 12290-98-1; $(\eta^5\text{-}C_5H_5)Fe(CO)(P(OCH_2)_3CCH_2CH_3)CH_3$, 80409-89-8; $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)H$, 32660-22-3; $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)C(O)CH_3$, 12101-02-9; $(\eta^5\text{-}C_5H_5)Fe(CO)_2C(O)CH_2CH_3$, 53403-10-4; $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, 12107-04-9; $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_3$, 80409-90-1; $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$, 80409-91-2; $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$, 35344-11-7; $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_2CH_3$, 72042-46-7; $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$, 57349-59-4; $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$, 53449-90-4; $(\eta^5\text{-}C_5H_5)Ru(CO)(P(C\text{-}H_x)_3)CH_3$, 80409-92-3; $(\eta^5\text{-}C_5H_5)Ru(CO)(P(OCH_2)_3CCH_2CH_3)CH_3$, 80409-93-4.

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Reaction of (1-3-η-Vinylcarbene)iron Complexes with Enneacarbonyldiiron. Formation of a (Ferracyclopentadiene)iron(*Fe-Fe*) Complex and a Vinylcarbenediiron(*Fe-Fe*) Complex

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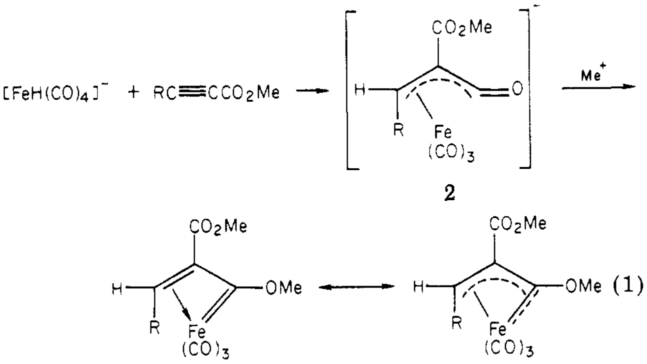
Tricarbonyl[1-3-η-1-methoxy-2-(methoxycarbonyl)prop-2-en-1-ylidene]iron (**1a**) reacts with enneacarbonyldiiron in diethyl ether at 25 °C for 2 h to give a "ferrole" derivative, tricarbonyl[2-5-η-1,1,1-tricarbonyl-5-hydroxy-2-methoxy-3-(methoxycarbonyl)ferracyclopenta-2,4-diene]iron(*Fe-Fe*) (**3**). Methylation of **3** with diazomethane gives a methoxy derivative of **3**, tricarbonyl[2-5-η-1,1,1-tricarbonyl-2,5-dimethoxy-3-(methoxycarbonyl)ferracyclopenta-2,4-diene]iron(*Fe-Fe*) (**4**). Tricarbonyl[1-3-η-*trans*-1-methoxy-2,3-bis(methoxycarbonyl)prop-2-en-1-ylidene]iron (**1b**) reacts with enneacarbonyldiiron in diethyl ether at 35 °C for 1.5 h to give hexacarbonyl-μ-[1-η^1-*anti*,2-bis(methoxycarbonyl)-3-*syn*-methoxy-η^3:η^1-allyl]diiron(*Fe-Fe*) (**5**) by the coordination of the vinylcarbene moiety to two iron atoms: therefore **5** is regarded as a vinylcarbene dinuclear complex. The structure of **5** was determined by single-crystal X-ray diffraction study.

Since the first preparation of a transition-metal-carbene complex by E. O. Fischer in 1964,[1] much attention has been focused on the reactivities of the carbene-metal double bond especially concerning the active species in the catalytic organic reactions such as metatheses of olefins[2] or Fischer-Tropsch synthesis.[3] On the other hand, reactions of acetylenes with transition-metal complexes have led to carbene complexes[4] as well as to various organic syntheses.[5] Recently, the first (η^3-vinylcarbene)tricarbonyliron complexes, **1a** and **1b**, in which the adjacent carbene and olefin are coordinated to one metal have been prepared by methylation of (1-3-η-acryloyl)tricarbonylferrates (**2**) derived from the reaction of acetylenes with hydridotetracarbonylferrate.[6] The highly distorted molecular structure of **1b** was revealed by X-ray analysis.[7] Complexes **1a** and **1b** are highly reactive to nucleophilic reagents such as carbon monoxide or tertiary phosphines, isocyanides, and diazomethane affording (η^4-vinylketene)-,[8] (η^4-vinylketenimine)-,[9] and (η^4-butadiene)-tricarbonyliron[10] derivatives, respectively.



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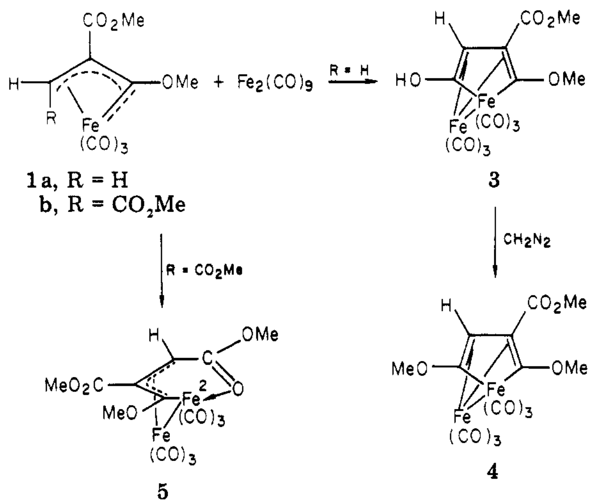
(1)

1a, R = H
b, R = CO$_2$Me

Scheme I



1a, R = H
b, R = CO$_2$Me

3

4

5

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Table I. Infrared Spectral Data (cm^{-1}, KBr)[a]

complex	carbonyl bands: metal carbonyl			carbonyl bands: ester	other bands
3	2075 s	2040 s	1990 s,br	1705 s	3250 br, ν(O-H)
4	2077 s 1987 s	2040 s	1998 s	1735 s	
5	2078 m 1995 m	2035 s 1975 s,br	2006 s	1721 m 1601 m, ν(C=O→Fe)	

[a] s = strong, m = medium, br = broad.

Table II. Hydrogen NMR Spectral Data (δ Relative to $SiMe_4$, *J* (Hz))[a]

complex	olefinic proton (s, 1 H)	CO_2Me (s, 3 H)	COMe (s, 3 H)	others
3[b]	5.36	3.96	3.78	5.98 (s, 1 H, OH)
4[c]	5.35	3.99	3.68 3.81	
5[b]	3.03	3.50 3.83	4.07	

[a] s = singlet, recorded at 100 MHz. [b] Solvent: CD_2Cl_2. [c] Solvent: $CDCl_3$.

This paper deals with the reaction of the η^3-vinylcarbene complexes **1a** and **1b** with enneacarbonyldiiron. The products depend upon the kinds of starting η^3-vinylcarbene complexes; a "ferrole" derivative (**3**) and an (η^3:η^1-allyl)diiron(*Fe–Fe*) complex (**5**) were obtained in the reaction of **1a** and **1b**, respectively.

These results would shed some light on the mechanism of the formation of the "ferrole" complex by the reaction of acetylene with alkali $Fe(CO)_5$ and that of the formation of a methylene species bridged on binuclear metals from a mononuclear carbene–metal species.

Results and Discussion

Reaction of 1a with Enneacarbonyldiiron. Tricarbonyl[1–3-η-1-methoxy-2-(methoxycarbonyl)prop-2-en-1-ylidene]iron (**1a**) readily reacted with enneacarbonyldiiron in diethyl ether at 25 °C for 2 h under an argon atmosphere to give yellow crystals of **3** in 51% yield. Complex **3** is diamagnetic and stable in air for several hours. Analytical data and IR and ^1H and ^{13}C NMR spectral data of **3** are summarized in Tables I–IV. On the basis of the molecular weight, the analytical and spectral data, and its reactivity (see below), **3** has been deduced to be tricarbonyl[2–5-η-1,1,1-tricarbonyl-5-hydroxy-2-methoxy-3-(methoxycarbonyl)ferracyclopenta-2,4-diene]iron(*Fe–Fe*) (Scheme I).

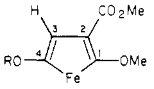
The analytical data of **3** and the molecular weight of **4** which was derived by the methylation of acidic hydroxy group in **3** (see below) with diazomethane show that **3** is a 1:1 adduct of **1a** and a "$Fe(CO)_4$" moiety. The IR spectrum of **3** (Table I) showed three strong absorptions of terminal ν(C≡O) at 2075, 2040, and 1990 (br) cm^{-1} and ester ν(C═O) at 1705 cm^{-1} as well as ν(OH) at 3250 (br) cm^{-1}. The ^1H NMR spectrum of **3** (Table II) exhibited, in addition to signals for two OMe, a signal for the olefinic proton at δ 5.36 and a hydroxylic proton at δ 5.98 which disappeared on addition of D_2O. The ^{13}C NMR spectrum of **3** (Table III) showed four resonances characteristic of a ferracyclopentadiene ring at δ 78.3 (d, *J*(CH) = 162 Hz, C^3 (see Table III)), 85.3 (s, C^2), 221.3, and 227.6 (s, C^1 or C^4).[11]

Table III. Carbon-13 NMR Spectral Data (δ, $SiMe_4$ Internal Reference, $J(^{13}C-H)$ (Hz))[a]

complex	C^1[f]	C^2	C^3	C^4	CO_2*Me*	CO*Me*	*CO*$_2$Me	FeC≡O
3[b]	211.7[e]	85.3 (s)	78.3 (d, 162)	214.5[e]	53.0 (q, 148)	64.8 (q, 146)	168.0 (s)	210.6 (s) 211.4 (s) 211.7 (s)
4[c]	227.6 (br)	81.9 (s)	74.0 (d, 170)	221.3	52.2 (q, 148)	58.9 (q, 147) 64.3 (q, 147)	166.2 (s)	208.6 (s) 209.2 (s) 209.3 (s) 209.6 (s)
5[c]	38.4 (d, 162)	82.0 (s)	221.2 (s)		52.7 (q, 147) 54.6 (q, 149)	63.2 (q, 145)	168.8 (s) 186.3 (s)	205.1 (s)[d] 209.6 (s) 211.4 (s)

[a] At 24.0 °C. s = singlet, d = doublet, q = quartet, br = broad. [b] Solvent: MeOH-d_4. [c] Solvent: $CDCl_3$. [d] Measured at 46 °C. The temperature dependence of Fe(C≡O) is shown in Figure 1. [e] Signals of C^1 and C^4 were tentatively assigned.

[f]



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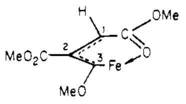

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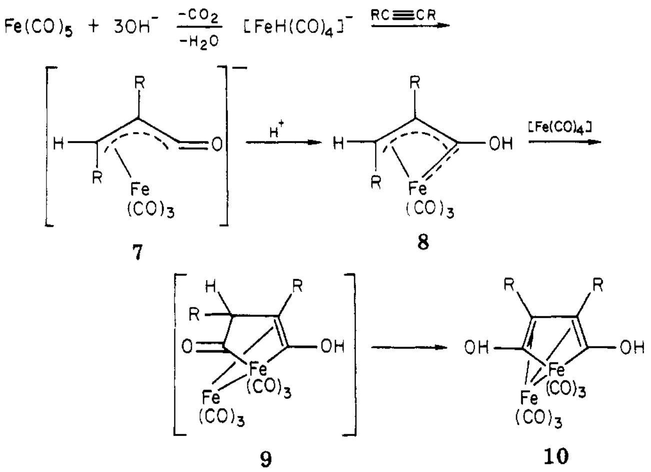
Table IV. Analytical Data

complex	yield, %	color	mol wt[a] (calcd)	Mp, θ_c/°C	% C calcd	% C found	% H calcd	% H found
3	51	yellow		144	35.81	35.63	1.84	1.66
4	64	orange	405 (450)	82	37.38	37.62	2.24	2.41
5	78	red	468 (466)	91 (dec)	36.09	36.10	2.16	2.48

[a] Cryoscopic in benzene.

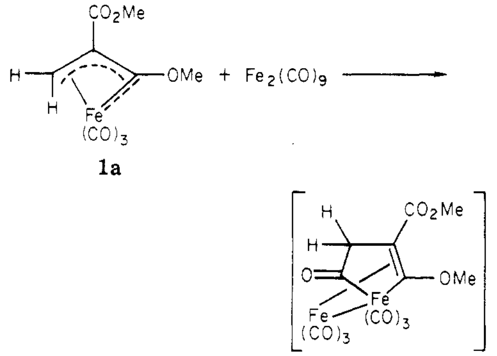
Scheme II



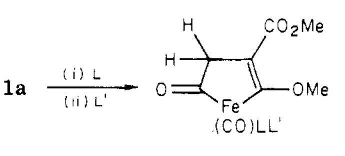
R = H, Me

Treatment of **3** with diazomethane in diethyl ether under nitrogen at room temperature gave orange crystals of **4** in 64% yield. Following observations show that **4** is tricarbonyl[2–5-η-1,1,1-tricarbonyl-2,5-dimethoxy-3-(methoxycarbonyl)ferracyclopenta-2,4-diene]iron(*Fe–Fe*) derived from the methylation of the hydroxyl group in **3** by diazomethane. (i) In the IR spectrum of **4**, the absorption of ν(OH) at 3250 cm^{-1} in **3** disappeared. (ii) In the ^{1}H NMR spectrum of **4**, the signal for the hydroxyl proton in **3** disappeared and a new signal for a methoxy group appeared at δ 3.81 in addition to those for the two methoxy groups. (iii) The ^{13}C NMR spectrum of **4** also exhibited the signal of the introduced methoxy carbon at δ 58.9 (q, *J*(CH) = 147 Hz) in addition to those of the ferracyclopentadiene ring.

The formation of **3** by the reaction of **1a** with $Fe_2(CO)_9$ may be rationalized as follows. The attack of the "$Fe(CO)_4$" moiety on **1a** would induce the insertion of a carbon monoxide into methylene carbon–iron bond of **1a** to give an intermediate, **6**, (2–3-η-ferracyclopentenone)tricarbonyliron(*Fe–Fe*). The keto–enol isomerization would give the product **3** (eq 2). Analogous formation of a ferracyclopentenone complex by the insertion of a carbon monoxide into a methylene–iron bond in **1a** has been observed in the reaction of **1a** with tertiary phosphines and/or carbon monoxide (L or L′) (eq 3).[8,12]



3 (2)



(3)

On the other hand, the ferrole complex **10** (Scheme II) similar to **3** was prepared by the reaction of acetylene with alkali solution of $Fe(CO)_5$[13] and the structure of which was determined by X-ray diffraction.[14] However, the mechanism of the formation of **10** has never been revealed. Taking into account that **1a** is prepared by the methylation of **2** derived from the reaction of the acetylene with $[FeH(CO)_4]^-$ (eq 1), the present result strongly suggests that the mechanism for the formation of **10** is as follows. Acetylene first reacts with $[FeH(CO)_4]^-$ derived from the reaction of alkali with $Fe(CO)_5$ to give (η^3-acryloyl)ferrate (**7**), protonation of which by the protic solvents may give an η^3-vinylhydroxycarbene complex **8**. It is reasonable to explain that **8** then reacts with "$Fe(CO)_4$" which exists in the reaction solution[15] to give the ferrole complex **10** via **9** in a manner similar to **3** being formed from **1a**. Alternatively, it is strongly suggested that this duplicate carbonylation of acetylene affording **10** would proceed via an η^3-vinylcarbene complex.

Reaction of 1b with Enneacarbonyldiiron. Tricarbonyl[1–3-η-*trans*-1-methoxy-2,3-bis(methoxycarbonyl)prop-2-en-1-ylidene]iron (**1b**) reacted with $Fe_2(CO)_9$ in diethyl ether at 35 °C under an argon atmosphere to give red crystals of **5** in 78% yield. Complex **5** is diamagnetic and stable in air for several hours. The structure of **5** was determined by X-ray analysis (see below) to be hexacarbonyl-μ-[1-η^1-*anti*,2-bis(methoxycarbonyl)-3-*syn*-methoxy-η^3:η^1-allyl]-diiron(*Fe–Fe*) (Scheme I) which was fully consistent with the analytical and spectral data. The IR spectrum of **5** (Table I) showed five strong terminal ν(C≡O) absorptions in the 1975–2075-cm^{-1} region in addition to those of ester ν(C=O) at 1721 cm^{-1} and ester ν(C=O) coordinated to iron atom at 1601 cm^{-1}.[16] The ^{1}H NMR spectrum of **5** (Table II) showed a signal of an olefinic proton at a high field [δ 3.03 (s)] in addition to those of the methoxy groups. The ^{13}C NMR spectrum of **5** exhibited the resonances of two olefinic carbons at δ 38.4 (d, *J*(CH) = 162 Hz) and 82.0 (s), and a singlet at δ 221.4 was assigned to C^3 (see footnotes in Table III) since this signal appears at too low of a field for a carbonyl carbon.[17] The signal shifted to higher field by about 50 ppm compared with that of the carbene carbon in **1b**, which would be due to the bond formation between C^3 and Fe^2. The spectrum also exhibited the signals for two ester carbonyl carbons at δ 168.8 and 186.3, the latter signal showing the coordination of the carbonyl group to the iron atom.[18] The variable-temperature ^{13}C NMR spectrum of **5** showed a temperature dependence in the terminal carbonyl region, results of which are shown in Figure 1. Seven resonances appeared in the δ 200–220 region at −68 °C, which can be assigned to six terminal carbonyls and a carbene carbon. Three signals at δ 206.9 (signal f in Figure 1), 207.3 (signal e), and 219.5 (signal b) at −68 °C showed a marked temperature dependence and the peaks coalesced at 46 °C (δ

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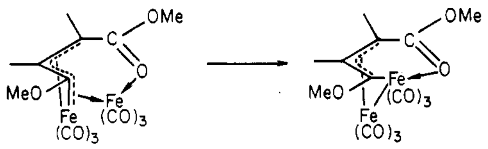
211.3). The other peaks, although two of them (signals c and d) overlapped with increasing the temperature, essentially did not show a significant temperature dependence. These observations show that one of the $Fe(CO)_3$ groups is fluxional near room temperature and the other is not. Probably the $Fe^1(CO)_3$ group coordinated by a π-allyl group would be fluxional.[19]

Comparing the structure of **5** with that of **1b**, the formation of **5** could be explained by the "coordination" of complex **1b** to the $Fe(CO)_3$ moiety as a bidentate ligand through the carbene–iron double bond and the ester group to form an (η^3:η^1-allyl)diiron(*Fe–Fe*) system (eq 4). Although several (η^3:η^1-allyl)dimetal(*M–M*) complexes such as **11–15** similar to **5** have been reported,[20-27] **5** is is the first example derived from a mononuclear carbene complex, and it should be noted that these complexes can be regarded as those which stabilize a vinylcarbene ligand on two metal atoms.



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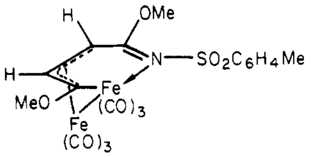

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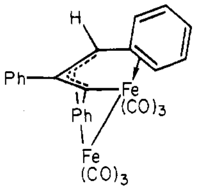

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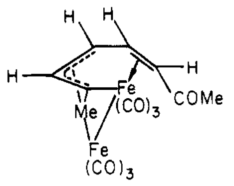

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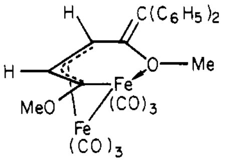

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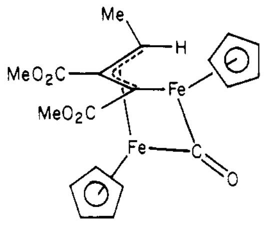

15

As described above, the reactions of $Fe_2(CO)_9$ with **1a** and **1b** gave **3** and **5**, respectively. This difference is due to whether the η^3-vinylcarbene ligand has a methoxycarbonyl group at the "anti" position or not. An η^3-vinylcarbene complex which can "coordinate" to a "Fe(CO)$_3$" moiety as a bidentate chelate ligand such as **1b** gives a binuclear vinylcarbene complex such as **5**, otherwise the insertion of carbon monoxide into the carbene carbon–iron bond is induced, affording **3**.

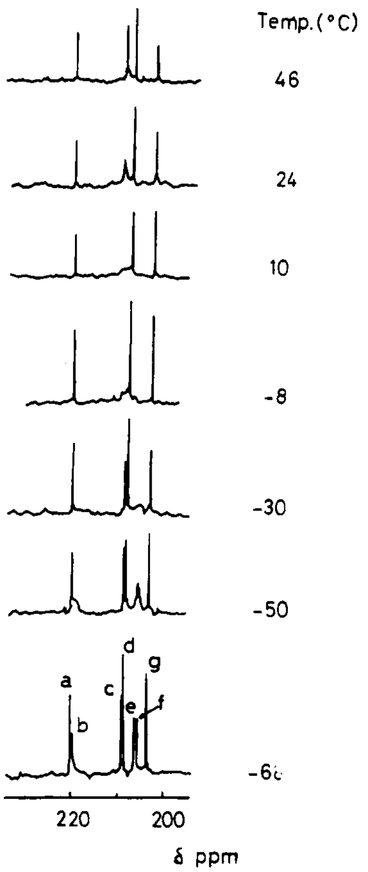

Figure 1. Variable-temperature ^{13}C NMR spectra of terminal carbonyl carbons and a carbene carbon of **5** in $CDCl_3$ solution.

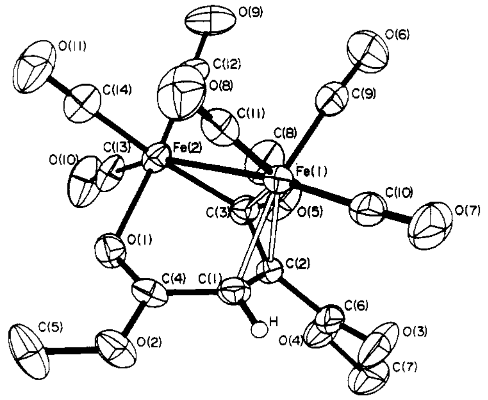

Figure 2. The molecular structure of complex **5**, hexacarbonyl-μ-[1-η^1-*anti*-2-(dimethoxycarbonyl)-3-*syn*-methoxy-η^3:η^1-allyl]-diiron(*Fe–Fe*) viewed perpendicular to the plane defined by the Fe(1), C(1), and C(4) atoms. Thermal ellipsoids enclose at 40% probability except that of H[C(1)], which is drawn by a sphere of an arbitrary radius.

Recently, Weiss et al. reported the preparation of an (η^3:η^1-allyl)diiron complex (**12**) related to **5** in a yield of 6% together with a η^4-vinylketene complex (**17**) in the reaction of cyclopropene derivatives (**16**) with excess enneacarbonyldiiron, and the structure of **12** was determined.[21] Although Weiss did not mention the mechanism of the formation of **12**, the present results would explain the reaction mechanism as follows. First, a vinylcarbene species derived from the fission of the carbon–carbon bond

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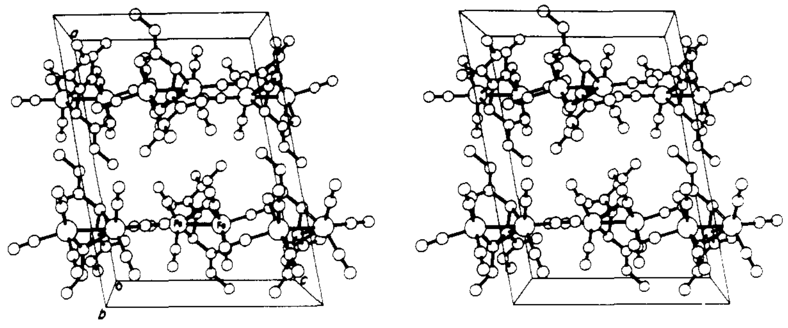
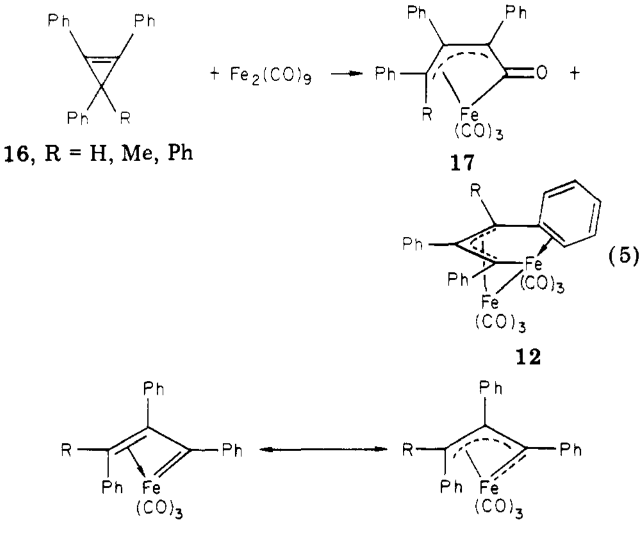


Figure 3. A stereoscopic drawing of the crystal structure of complex **5**, hexacarbonyl-μ-[1-η^1-*anti*-2-(dimethoxycarbonyl)-3-*syn*-methoxy-η^3:η^1-allyl]-diiron(*Fe–Fe*), viewed along the *b* axis.

Table V. Final Atomic Coordinates ($\times 10^4$; $\times 10^3$ for H) for Complex 5 ($(C_8H_{10}O_5)Fe_2(CO)_6$) with Esds in Parentheses

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Fe(1)	2451.3 (4)	3078.6 (5)	4049.6 (5)	C(7)	4276 (4)	−1149 (4)	5594 (5)
Fe(2)	2473.8 (4)	3918.5 (5)	6288.0 (5)	C(8)	4703 (3)	3101 (5)	6915 (5)
O(1)	1446 (2)	2751 (2)	6396 (2)	C(9)	3358 (3)	3979 (4)	3689 (4)
O(2)	426 (2)	1473 (3)	5376 (2)	C(10)	2371 (3)	2343 (4)	2578 (4)
O(3)	3071 (3)	−66 (3)	3857 (3)	C(11)	1537 (3)	4162 (4)	3670 (3)
O(4)	3825 (2)	−5 (2)	5779 (3)	C(12)	3248 (3)	5060 (4)	6078 (4)
O(5)	4121 (2)	2429 (3)	6085 (3)	C(13)	2834 (3)	3842 (4)	7931 (4)
O(6)	3942 (2)	4511 (3)	3414 (3)	C(14)	1606 (3)	5136 (4)	6194 (4)
O(7)	2335 (2)	1929 (3)	1632 (3)	H[C1]	157 (2)	104 (3)	416 (3)
O(8)	949 (2)	4810 (3)	3384 (3)	H[C5]	−67 (3)	147 (4)	590 (4)
O(9)	3743 (2)	5835 (3)	5953 (3)	H′[C5]	−29 (3)	266 (4)	606 (4)
O(10)	3082 (2)	3799 (4)	8957 (3)	H″[C5]	10 (3)	162 (4)	702 (3)
O(11)	1084 (2)	5890 (3)	6131 (3)	H[C7]	446 (3)	−109 (4)	487 (4)
C(1)	1811 (3)	1629 (3)	4714 (3)	H′[C7]	477 (3)	−122 (5)	625 (4)
C(2)	2780 (2)	1577 (3)	5151 (3)	H″[C7]	386 (3)	−172 (4)	553 (4)
C(3)	3209 (2)	2583 (3)	5809 (3)	H[C8]	453 (3)	327 (4)	756 (4)
C(4)	1231 (2)	2008 (3)	5554 (3)	H′[C8]	522 (3)	273 (4)	702 (4)
C(5)	−185 (3)	1840 (5)	6185 (4)	H″[C8]	473 (4)	379 (6)	655 (5)
C(6)	3250 (3)	423 (4)	4832 (3)				

of the cyclopropene derivatives is trapped by the "Fe$(CO)_3$" moiety to give an unstable intermediate, the η^3-vinylcarbene complex **18**. Then the insertion of carbon monoxide gives **17**,[8] and the "coordination" of **18** through the carbon–iron double bond and a phenyl group to another "Fe$(CO)_3$" may give **12** (eq 5).



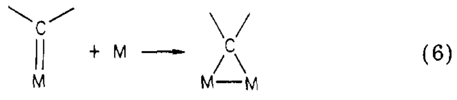
16, R = H, Me, Ph

17

12

18

Although both (η^1-carbene)M (M = metal) (**19**) and μ-carbene-M_2 species (**20**) are regarded to be the possible active species in Fischer–Tropsch reaction,[28] the possibility that **20** is formed from **19** has not yet been pointed out. The present reaction could be considered to be the model reaction that **20** is formed from **19**, suggesting the presence of such a process on the surface of heterogeneous catalysts (eq 6).



19 **20**

X-ray Molecular Structure of 5. The molecular geometry and atom-numbering system are shown in Figure 2 and the crystal packing arrangement in Figure 3, while Tables V and VI summarise the results obtained. These results demonstrated that **5** is an (η^3:η^1-allyl)diiron(*Fe–Fe*) complex in which Fe(1) is coordinated by a 1–3-η-allyl [C(1), C(2), and C(3)] system and Fe(2) is σ bonded with C(3) and coordinated by the ester group. The coordinations about Fe(1) and Fe(2) were both a highly distorted octahedron as has been reported in other (η^3:η^1-allyl)diiron complexes.[20,23] Several (η^3:η^1-allyl)diiron(*Fe–Fe*) complexes such as **11**,[20] **12**,[21] **13**,[22] **14**,[23] and **15**,[24] as well as a dimolybdenum,[25] a dicobalt,[26] and a tetraosmium[27] complex have been reported. To compare the geometry of **5** with those of **11–15**, the bond distances and angles were summarized in Table VII. The Fe(1)–Fe(2) (2.638 Å), Fe(2)–C(3) (1.957 Å), C(2)–C(3) (1.405 Å), and C(1)–C(2) (1.448 Å) lengths in **5** are within the normal range in comparison with those of **11–15**. The Fe(1)–C(3) length of 2.140 Å belongs to the longer region (1.969–2.138 Å in **11–15**). On the other hand, the Fe(1)–C(2) bond (2.047 Å) is rather short as found in **15** (2.042 Å), and the Fe(1)–C(1) length of 2.054 Å is also shorter than those in **11–15** (2.081–2.116 Å). The longer Fe(1)–C(3) length may be due to the substituent effect of the methoxy group attached to C(3) which increases the electron density on C(3) to cause reduced back-donation of electrons from

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[28] E.g., Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.

Table VI. Bond Lengths (Å) and Angles (Deg)

(A) Bond Lengths in Complex 5 ($(C_8H_{10}O_5)Fe_2(CO)_6$)

Fe(1)-Fe(2)	2.638 (1)	O(2)-C(5)	1.450 (6)	C(1)-C(4)	1.445 (5)
Fe(1)-C(1)	2.054 (4)	O(3)-C(6)	1.191 (5)	C(1)-H[C1]	0.91 (3)
Fe(1)-C(2)	2.047 (3)	O(4)-C(6)	1.316 (4)	C(2)-C(3)	1.405 (5)
Fe(1)-C(3)	2.140 (3)	O(4)-C(7)	1.451 (6)	C(2)-C(6)	1.515 (5)
Fe(1)-C(9)	1.780 (4)	O(5)-C(3)	1.357 (4)	C(5)-H1C5	0.842 (38)
Fe(1)-C(10)	1.801 (4)	O(5)-C(8)	1.361 (6)	C(5)-H2C5	0.913 (47)
Fe(1)-C(11)	1.801 (4)	O(6)-C(9)	1.137 (6)	C(5)-H3C5	0.973 (36)
Fe(2)-O(1)	2.019 (3)	O(7)-C(10)	1.133 (5)	C(7)-H1C7	0.893 (46)
Fe(2)-C(3)	1.957 (4)	O(8)-C(11)	1.129 (5)	C(7)-H2C7	0.941 (43)
Fe(2)-C(12)	1.747 (4)	O(9)-C(12)	1.149 (5)	C(7)-H3C7	0.881 (44)
Fe(2)-C(13)	1.804 (4)	O(10)-C(13)	1.131 (5)	C(8)-H1C8	0.826 (50)
Fe(2)-C(14)	1.849 (4)	O(11)-C(14)	1.129 (6)	C(8)-H2C8	0.857 (44)
O(1)-C(4)	1.233 (4)	C(1)-C(2)	1.448 (5)	C(8)-H3C8	0.856 (60)
O(2)-C(4)	1.323 (4)				

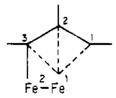
(B) Bond Angles in Complex 5 ($(C_8H_{10}O_5)Fe_2(CO)_6$)

Fe(2)-Fe(1)-C(1)	81.8 (1)	Fe(1)-Fe(2)-C(13)	152.0 (1)	Fe(1)-C(2)-C(3)	74.0 (2)
Fe(2)-Fe(1)-C(2)	75.9 (1)	Fe(1)-Fe(2)-C(14)	107.9 (1)	Fe(1)-C(2)-C(6)	126.6 (3)
Fe(2)-Fe(1)-C(3)	46.9 (1)	O(1)-Fe(2)-C(3)	91.2 (1)	C(1)-C(2)-C(3)	118.7 (3)
Fe(2)-Fe(1)-C(9)	98.0 (1)	O(1)-Fe(2)-C(12)	172.1 (1)	C(1)-C(2)-C(6)	115.9 (3)
Fe(2)-Fe(1)-C(10)	173.1 (1)	O(1)-Fe(2)-C(13)	90.2 (2)	C(3)-C(2)-C(6)	125.4 (3)
Fe(2)-Fe(1)-C(11)	82.6 (1)	O(1)-Fe(2)-C(14)	85.3 (2)	Fe(1)-C(3)-Fe(2)	80.0 (1)
C(1)-Fe(1)-C(2)	41.4 (1)	C(3)-Fe(2)-C(12)	94.1 (2)	Fe(1)-C(3)-O(5)	125.6 (3)
C(1)-Fe(1)-C(3)	71.6 (1)	C(3)-Fe(2)-C(13)	99.1 (2)	Fe(1)-C(3)-C(2)	66.9 (2)
C(1)-Fe(1)-C(9)	158.5 (2)	C(3)-Fe(2)-C(14)	160.8 (2)	Fe(2)-C(3)-O(5)	128.7 (3)
C(1)-Fe(1)-C(10)	91.3 (2)	C(12)-Fe(2)-C(13)	94.8 (2)	Fe(2)-C(3)-C(2)	119.6 (3)
C(1)-Fe(1)-C(11)	101.6 (2)	C(12)-Fe(2)-C(14)	87.8 (2)	O(5)-C(3)-C(2)	111.6 (3)
C(2)-Fe(1)-C(3)	39.1 (1)	C(13)-Fe(2)-C(14)	99.7 (2)	O(1)-C(4)-O(2)	120.6 (3)
C(2)-Fe(1)-C(9)	117.6 (2)	Fe(2)-O(1)-C(4)	117.9 (2)	O(1)-C(4)-C(1)	124.6 (3)
C(2)-Fe(1)-C(10)	98.8 (2)	C(4)-O(2)-C(5)	116.6 (3)	O(2)-C(4)-C(1)	114.7 (3)
C(2)-Fe(1)-C(11)	138.9 (2)	C(6)-O(4)-C(7)	116.5 (3)	O(3)-C(6)-O(4)	124.9 (4)
C(3)-Fe(1)-C(9)	92.4 (2)	C(3)-O(5)-C(8)	125.7 (4)	O(3)-C(6)-C(2)	123.1 (3)
C(3)-Fe(1)-C(10)	130.5 (2)	Fe(1)-C(1)-C(2)	69.1 (2)	O(4)-C(6)-C(2)	111.9 (3)
C(3)-Fe(1)-C(11)	129.4 (2)	Fe(1)-C(1)-C(4)	112.8 (2)	Fe(1)-C(9)-O(6)	176.5 (4)
C(9)-Fe(1)-C(10)	88.3 (2)	Fe(1)-C(1)-H[C1]	117 (2)	Fe(1)-C(10)-O(7)	176.8 (4)
C(9)-Fe(1)-C(11)	99.6 (2)	C(2)-C(1)-C(4)	118.8 (3)	Fe(1)-C(11)-O(8)	176.8 (3)
C(10)-Fe(1)-C(11)	99.1 (2)	C(2)-C(1)-H[C1]	116 (2)	Fe(2)-C(12)-O(9)	178.1 (4)
Fe(1)-Fe(2)-O(1)	87.6 (1)	C(4)-C(1)-H[C1]	115 (2)	Fe(2)-C(14)-O(10)	178.2 (4)
Fe(1)-Fe(2)-C(3)	53.0 (1)	Fe(1)-C(2)-C(1)	69.6 (2)	Fe(2)-C(14)-O(11)	179.0 (4)
Fe(1)-Fe(2)-C(12)	91.0 (1)				

Table VII. Representative Bond Lengths and Angles of Complex 5 and 11-15[a,b]

complex	Fe^1-Fe^2	Fe^2-C_3	C_2-C_3	C_1-C_2	Fe^1-C_3	Fe^1-C_2	Fe^1-C_1	$\angle C_1C_2C_3$	ref
5	2.638	1.957	1.405	1.448	2.140	2.047	2.054	118.7	this work
11	2.636	1.909	1.469	1.447	2.138	2.077	2.116	116	18
12	2.602	1.997	1.414	1.442	2.080	2.079	2.084	112.9	19
13	2.642	2.002	1.404	1.413	2.088	2.078	2.081	115.4	20
14	2.62	1.94	1.38	1.44	2.09	2.07	2.09	118	21
15	2.540	1.968	1.457	1.433	1.969	2.042	2.111	119.3	22

[a]



[b] Lengths in angstroms and angles in degrees.

Fe(1) to C(3). The shorter Fe(1)–C(2) and Fe(1)–C(1) lengths could be explained by the enhanced back-donation due to the electron withdrawing methoxycarbonyl groups at C(2) and C(1).

Considering the substituent effects, Table VII shows that complex 5 is regarded to be an analogue of 11–15. Alternatively, all these complexes consist of a substituted vinylcarbene ligand and the binuclear iron carbonyl. Generally, (η^3:η^1-allyl)dimetal(*M–M*) would be the most stable form of a vinylcarbene–dinuclear metal system.

Experimental Section

All of experimentals were performed in an atmosphere of argon. Infrared spectra were recorded on a JASCO A-302 grating spectrometer, ^1H NMR spectra on a JEOL JNM-FX-100 spectrometer, and ^{13}C NMR spectra on a JEOL JNM-FX-100 spectrometer at 25.05 MHz. Molecular weights were determined by cryoscopy in benzene. Solvents were dried by published techniques and were distilled in an atmosphere of argon before use. Tricarbonyl(1-3-η-vinylcarbene)iron complexes (**1a**,**b**),[6] enneacarbonyldiiron,[29] diazomethane[30] were prepared by the methods described in the literature.

Reaction of 1a with $Fe_2(CO)_9$. To a solution of **1a** (0.80 g, 3 mmol) in diethyl ether (40 cm^3) was added $Fe_2(CO)_9$ (1.09 g, 3 mmol), and the solution was stirred for 2 h at 25 °C. The solution was filtered, and the filtrate was distilled off in vacuo. The residual solid was dissolved in the mixture of methylene dichloride–chloroform (1:1). The solution was concentrated to ca. 5 cm^3 and cooled on dry ice for 12 h to give yellow crystals of **3** (0.67 g, 51%).

Methylation of (3) with Diazomethane. Into the solution of **3** (0.22 g, 0.5 mmol) in dry diethyl ether was bubbled excess

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(29) King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. 1, p 92.

(30) Boer, T. J.; Backer, H. J. "Organic Syntheses"; Wiley: New York, 1963; Coll. Vol. 4, p 250.

(31) Cromer, D. T.; Waber, J. T. "International Table for X-ray Crystallography"; Kynoch Press: Birminham, England, 1974; Vol. IV, Values for iron are taken from p 78 and those for hydrogen, carbon, and oxygen taken from pp 72–73. Anomalous dispersion corrections for Fe, C, and O are taken from p 149.

diazomethane gas in a nitrogen stream at room temperature. After the evaporation of the solvent, the residual solid was dissolved in the mixture of diethyl ether–*n*-hexane (3:2). The solution was concentrated to ca. 2 cm^3 and cooled on dry ice to afford orange crystals of 4 (0.15 g, 64%).

Reaction of 1b with Fe$_2$(CO)$_9$. To a solution of **1b** (0.98 g, 3 mmol) in diethyl ether (20 cm^3) was added Fe$_2$(CO)$_9$ (1.09 g, 3 mmol), and the solution was stirred for 1.5 h at 35 °C. After the evaporation of the solvent, the residual solid was extracted through a glass filter with 30-cm^3 portions of *n*-hexane. The concentration of the filtrate afforded red crystals of **5** (1.09 g, 78%).

Crystal Structure Determination of 5. Recrystallization under nitrogen from a 1:5 chloroform–petroleum ether solution gave reddish brown single crystals. Specimens used for X-ray diffraction studies were sealed into thin-walled glass capillaries under an argon atmosphere. The crystal system and the space group were obtained from preliminary oscillation and Weissenberg photographs about the *c* axis with Cu Kα radiation. Accurate cell parameters were determined by a least-squares treatment of the 2θ angles of the 47 reflections in the range of 20–35° measured on a computer-controlled four-circle diffractometer with Mo Kα radiation (λ = 0.71069 Å).

Crystal Data: C$_{14}$H$_{10}$Fe$_2$O$_{11}$, M_r = 465.9, monoclinic, space group $P2_1/n$; a = 15.006 (2) Å, b = 10.896 (1) Å, c = 11.078 (2) Å, β = 100.48 (1)°, V = 1 781.1 (5) Å^3; D_{measd} = 1.72 g cm^{-3} (by flotation method with sodium iodide aqueous solution), Z = 4, D_{calcd} = 1.7376 (5) g cm^{-3}; $F(000)$ = 936, μ = 17.30 cm^{-1}. A specimen of dimensions ca. 0.28 × 0.28 × 0.25 mm was used for X-ray data collection on the diffractometer. Integrated intensities were collected at 21 °C up to 55 °C in 2θ by the θ–2θ continuous scan mode at a θ scan rate of 2° min^{-1} with graphite-monochromated Mo Kα radiation. Stationary background counts of 10-s duration were made on either side of the scan. Intensities of five standard reflections were monitored before every 50 reflections to check the deteriorations of the specimen. No significant variation was observed for these monitoring intensities during the data collection. The intensities were corrected for the Lorentz and polarization effects but not for absorption and extinction. Of the 4080 independent reflections measured, 2850 with $|F_o| > 3\sigma(|F_o|)$ were accepted as "observed" and used in the subsequent calculations.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom method. Two Fe atoms were located from a Patterson map and the other nonhydrogen atoms located from subsequent Fourier syntheses. The structure was refined by the diagonal least-squares calculations with isotropic thermal factors for all the atoms. At this stage the residual index, $R = \sum|\Delta F|/\sum|F_o|$, where $\Delta F = |F_o| - |F_c|$, was 0.10. The hydrogen atoms were located from a difference Fourier map. The structure was then refined by the block-diagonal least squares with anisotropic thermal factors for the nonhydrogen atoms and isotropic ones for the hydrogen atoms. In the refinement the function minimized was $\sum w(\Delta F)^2$, where the weight $1/w$ was $\sigma^2(|F_o|) + a|F_o|^2$ for the block-diagonal least-squares. The constant a was chosen to give approximately equal distribution of the mean $w(\Delta F)^2$ for several subgroups of increasing $|F_o|$ and was 0.0001 in the final cycles of the refinement. The final residual indices were R = 0.046 and $R_w = [\sum w(\Delta F)^2/\sum|F_o|^2]^{1/2}$ = 0.037. In the final cycle of least-squares refinement no individual parameter except in the hydrogen atoms shifted by more than one-half of its estimated standard deviation. In the final difference map there were no peaks greater than 0.35 e Å^{-3}. Atomic scatterring factors were taken from ref 31, including corrections for the effects of anomalous dispersion. All computations were performed on a FACOM 230/38 computer and a MELCOM 70/30 computer at Kwansei Gakuin University.

Acknowledgment. We thank Professor Y. Takegami for helpful discussions.

Registry No. 1a, 6111-92-0; **1b**, 60941-31-3; **3**, 80485-09-2; **4**, 80485-10-5; **5**, 80485-11-6; Fe$_2$(CO)$_9$, 15321-51-4.

Supplementary Material Available: Tables of fractional coordinates and temperature factors and structure factors for complex **5** (13 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of Dicyclopentenouranocene, U[C$_8$H$_6$(CH$_2$)$_3$]$_2$

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Received July 31, 1981

The title compound **1** was synthesized by the reaction of dipotassium bicyclo[6.3.0]undeca-2,4,6-triene-1,8-diide, **3**, and UCl$_4$, and its crystal and molecular structure was determined by single-crystal X-ray diffraction. The compound crystallizes in the orthorhombic space group *Pbca* with eight molecules in the unit cell with dimensions a = 17.393 (8) Å, b = 22.468 (12) Å, and c = 8.931 (4) Å. The uranium atom is located centrally between the two eight-membered rings with bond distances U–C = 2.64 ± 0.03 Å and C–C = 1.40 ± 0.02 Å. The effects of annulation on the physical properties of uranocene are discussed.

Introduction and Results

As part of a continuing study of annulated derivatives[1,2] of uranocene[3] we report the synthesis and X-ray structure determination of bis[π-(cyclopenteno[8]annulene)]uranium(IV) (dicyclopentenouranocene), **1**.[4] This compound has significance for two reasons. First, it was expected to involve a conformation sufficiently well-defined to assist NMR interpretation. Second, it would be the first X-ray

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diazomethane gas in a nitrogen stream at room temperature. After the evaporation of the solvent, the residual solid was dissolved in the mixture of diethyl ether–*n*-hexane (3:2). The solution was concentrated to ca. 2 cm^3 and cooled on dry ice to afford orange crystals of 4 (0.15 g, 64%).

Reaction of 1b with $Fe_2(CO)_9$. To a solution of **1b** (0.98 g, 3 mmol) in diethyl ether (20 cm^3) was added $Fe_2(CO)_9$ (1.09 g, 3 mmol), and the solution was stirred for 1.5 h at 35 °C. After the evaporation of the solvent, the residual solid was extracted through a glass filter with 30-cm^3 portions of *n*-hexane. The concentration of the filtrate afforded red crystals of 5 (1.09 g, 78%).

Crystal Structure Determination of 5. Recrystallization under nitrogen from a 1:5 chloroform–petroleum ether solution gave reddish brown single crystals. Specimens used for X-ray diffraction studies were sealed into thin-walled glass capillaries under an argon atmosphere. The crystal system and the space group were obtained from preliminary oscillation and Weissenberg photographs about the *c* axis with Cu Kα radiation. Accurate cell parameters were determined by a least-squares treatment of the 2θ angles of the 47 reflections in the range of 20–35° measured on a computer-controlled four-circle diffractometer with Mo Kα radiation ($\lambda = 0.71069$ Å).

Crystal Data: $C_{14}H_{10}Fe_2O_{11}$, $M_r = 465.9$, monoclinic, space group $P2_1/n$; $a = 15.006$ (2) Å, $b = 10.896$ (1) Å, $c = 11.078$ (2) Å, $\beta = 100.48$ (1)°, $V = 1\,781.1$ (5) Å^3; $D_{measd} = 1.72$ g cm^{-3} (by flotation method with sodium iodide aqueous solution), $Z = 4$, $D_{calcd} = 1.7376$ (5) g cm^{-3}; $F(000) = 936$, $\mu = 17.30$ cm^{-1}. A specimen of dimensions ca. 0.28 × 0.28 × 0.25 mm was used for X-ray data collection on the diffractometer. Integrated intensities were collected at 21 °C up to 55 °C in 2θ by the θ–2θ continuous scan mode at a θ scan rate of 2° min^{-1} with graphite-monochromated Mo Kα radiation. Stationary background counts of 10-s duration were made on either side of the scan. Intensities of five standard reflections were monitored before every 50 reflections to check the deteriorations of the specimen. No significant variation was observed for these monitoring intensities during the data collection. The intensities were corrected for the Lorentz and polarization effects but not for absorption and extinction. Of the 4080 independent reflections measured, 2850 with $|F_o| > 3\sigma(|F_o|)$ were accepted as "observed" and used in the subsequent calculations.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom method. Two Fe atoms were located from a Patterson map and the other nonhydrogen atoms located from subsequent Fourier syntheses. The structure was refined by the diagonal least-squares calculations with isotropic thermal factors for all the atoms. At this stage the residual index, $R = \sum|\Delta F|/\sum|F_o|$, where $\Delta F = |F_o| - |F_c|$, was 0.10. The hydrogen atoms were located from a difference Fourier map. The structure was then refined by the block-diagonal least squares with anisotropic thermal factors for the nonhydrogen atoms and isotropic ones for the hydrogen atoms. In the refinement the function minimized was $\sum w(\Delta F)^2$, where the weight $1/w$ was $\sigma^2(|F_o|) + a|F_o|^2$ for the block-diagonal least-squares. The constant a was chosen to give approximately equal distribution of the mean $w(\Delta F)^2$ for several subgroups of increasing $|F_o|$ and was 0.0001 in the final cycles of the refinement. The final residual indices were $R = 0.046$ and $R_w = [\sum w(\Delta F)^2/\sum|F_o|^2]^{1/2} = 0.037$. In the final cycle of least-squares refinement no individual parameter except in the hydrogen atoms shifted by more than one-half of its estimated standard deviation. In the final difference map there were no peaks greater than 0.35 e Å^{-3}. Atomic scatterring factors were taken from ref 31, including corrections for the effects of anomalous dispersion. All computations were performed on a FACOM 230/38 computer and a MELCOM 70/30 computer at Kwansei Gakuin University.

Acknowledgment. We thank Professor Y. Takegami for helpful discussions.

Registry No. 1a, 6111-92-0; **1b**, 60941-31-3; **3**, 80485-09-2; **4**, 80485-10-5; **5**, 80485-11-6; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Tables of fractional coordinates and temperature factors and structure factors for complex 5 (13 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of Dicyclopentenouranocene, $U[C_8H_6(CH_2)_3]_2$

Allan Zalkin,* David H. Templeton,* Wayne D. Luke, and Andrew Streitwieser, Jr.*

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The title compound 1 was synthesized by the reaction of dipotassium bicyclo[6.3.0]undeca-2,4,6-triene-1,8-diide, 3, and UCl_4, and its crystal and molecular structure was determined by single-crystal X-ray diffraction. The compound crystallizes in the orthorhombic space group *Pbca* with eight molecules in the unit cell with dimensions $a = 17.393$ (8) Å, $b = 22.468$ (12) Å, and $c = 8.931$ (4) Å. The uranium atom is located centrally between the two eight-membered rings with bond distances U–C = 2.64 ± 0.03 Å and C–C = 1.40 ± 0.02 Å. The effects of annulation on the physical properties of uranocene are discussed.

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Scheme I

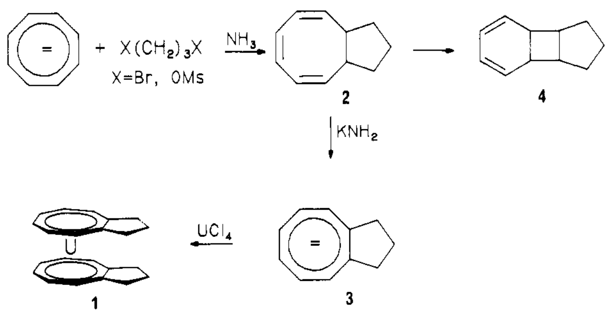

Table I. Infrared Spectrum (cm^{-1}) in Nujol[a]

$(C_8H_8)_2U$[c]	$[C_8H_6\text{-}(CH_2)_3]_2U$, 1	$(C_8H_8)_2U$[c]	$[C_8H_6\text{-}(CH_2)_3]_2U$, 1
	1870 (w)	1018 (s)[b]	1020 (m)[b]
1730 (w)	1765 (w)		900 (s)
	1320 (m)	799 (s)	790 (m)
1262 (s)	1260 (m)		745 (s)
1095 (s)[b]	1090 (m)[b]	720 (s)	700 (vs)

[a] w = weak; m = medium; s = strong; vs = very strong. [b] References 11, 12, and 22–25. [c] Very Broad.

structure of an unstrained uranocene in which the ring–U axis is not a C_2 symmetry axis; the position of the uranium was therefore expected to provide a significant indication of the relative roles of covalent and ionic bonding. The title compound was synthesized in a manner similar to dicyclobutenouranocene,[2] shown in Scheme I. The bicyclotriene 2 was prepared by ether addition of 1,3-dibromopropane, or the dimethanesulfonate of 1,3-propanediol, to a solution of dilithium cyclooctatrienediide in liquid ammonia, affording distilled yields of 46.8% and 58.4%, respectively. This compound was contaminated by the tricyclic isomer 4; on standing, 2 rearranged completely to 4. Dideprotonation of 2 with potassium amide in THF/liquid ammonia formed a red solution of the dianion 3 which could be isolated as an impure tan solid. Subsequent reaction of 3 with UCl_4 in THF produced the desired uranocene 1 in 15.9% yield. The visible spectrum of this green air-sensitive material exhibited the typical uranocene cascade of four principal absorptions at 632, 656, 663, and 680 nm. The principal IR absorption bands are compared with those of uranocene in Table I.

The ^1H NMR (toluene-d_8) spectrum of 1 at 30 °C showed six sharp well-resolved resonances upfield from Me_4Si, −8.3 (m, 2 H), −18.8 (m, 4 H), −23.1 (s, 4 H), −32.6 (m, 2 H), −34.2 (s, 4 H), −41.2 ppm (s, 4 H), and one resonance downfield from Me_4Si, +24.4 ppm (m, 4 H). The ^{13}C NMR spectrum (dioxane-d_8) at 39 °C showed four broad peaks at 308.0, 296.9, 279.0, and 268.5 ppm downfield from Me_4Si and two sharp peaks at 13.4 and −32.5 ppm.

Magnetic susceptibility measurements on the bulk solid from 2.4 to 95.6 K are shown in Figure 1. Above 20 K the magnetic susceptibility follows the Curie–Weiss Law with $C = 0.743 \pm 0.005$ emu K mol^{-1}, $\mu = 2.4 \pm 0.1\ \mu_B$, and $\theta = 16.6° \pm 0.5°$. Below 10 K the magnetic moment was independent of temperature with $\chi_m = (2.56 \pm 0.03) \times 10^{-2}$ csu/mol. With use of a diamagnetic correction of -187×10^{-6} emu mol^{-1}, the corrected values are $C = 0.714 \pm 0.005$ emu K mol^{-1}, $\mu = 2.4 \pm 0.1\ \mu_B$, and $\theta = 16.1° \pm 0.5°$.[5]

The compound crystallizes in the orthorhombic space group *Pbca* with eight molecules in the unit cell with dimensions $a = 17.393$ (8) Å, $b = 22.468$ (12) Å, and $c = 8.931$ (4) Å. With a molecular weight of 526.46 the calculated density is 2.004 g cm^{-3}. The structure was determined by conventional single-crystal X-ray methods and was refined by full-matrix least squares to an R factor of 0.04 for 1000 data where $F^2 > 3\sigma$. Final positional parameters are given in Table II. Tables of calculated positional parameters for the hydrogen atoms, carbon–carbon distances, thermal parameters, and observed structure factors amplitudes are given in the supplementary material. Uranium–carbon distances are listed in Table III. The atom numbering is seen in Figures 2 and 3.

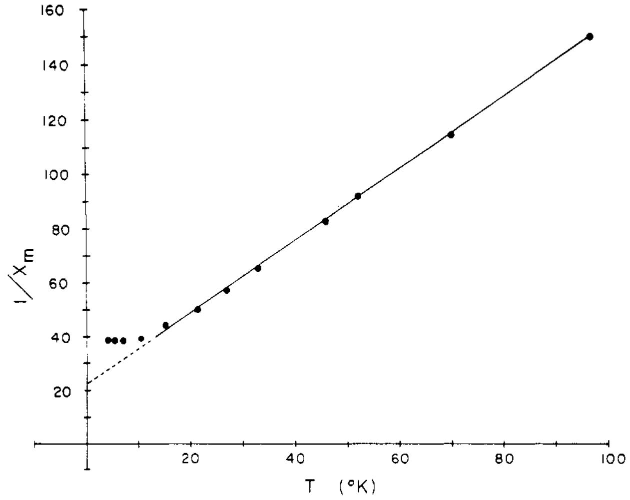

Figure 1. Plot of $1/\chi$ vs. absolute temperature for dicyclopentenouranocene, 1.

Table II. Positional Parameters[a]

atom	x	y	z
C (1)	0.047 (2)	0.163 (1)	0.159 (3)
C(2)	0.077 (2)	0.122 (1)	0.264 (3)
C(3)	0.147 (2)	0.109 (2)	0.329 (4)
C(4)	0.218 (2)	0.138 (1)	0.309 (3)
C(5)	0.254 (2)	0.182 (2)	0.225 (4)
C(6)	0.228 (2)	0.220 (2)	0.115 (4)
C(7)	0.153 (2)	0.2305 (9)	0.061 (3)
C(8)	0.079 (2)	0.209 (1)	0.074 (3)
C(9)	0.014 (2)	0.230 (1)	−0.032 (3)
C(10)	−0.051 (3)	0.205 (3)	0.029 (6)
C(11)	−0.038 (2)	0.152 (2)	0.122 (6)
C(12)	0.285 (1)	0.098 (1)	−0.160 (3)
C(13)	0.222 (2)	0.116 (1)	−0.245 (3)
C(14)	0.142 (2)	0.111 (2)	−0.258 (4)
C(15)	0.099 (2)	0.067 (2)	−0.184 (4)
C(16)	0.105 (2)	0.022 (1)	−0.078 (4)
C(17)	0.168 (2)	−0.003 (1)	−0.004 (3)
C(18)	0.245 (1)	0.014 (1)	0.016 (2)
C(19)	0.294 (1)	0.054 (1)	−0.052 (2)
C(20)	0.378 (1)	0.058 (2)	0.005 (3)
C(21)	0.407 (2)	0.111 (2)	−0.061 (5)
C(22)	0.361 (2)	0.132 (1)	−0.182 (4)
U	0.17237 (5)	0.11510 (4)	0.0369 (1)

[a] Here and in the following tables the number in parentheses is the estimated standard deviation in the least significant figure. The estimated standard deviations are a result of least-squares refinement on a model in which C–C distances were restrained as described in the text. Hydrogen atoms were included but not refined.

Table III. Uranium–Carbon Distances (Å)

U–C(1)	2.66 (3)	U–C(12)	2.66 (2)
-C(2)	2.63 (3)	-C(13)	2.66 (3)
-C(3)	2.65 (4)	-C(14)	2.68 (4)
-C(4)	2.60 (3)	-C(15)	2.58 (3)
-C(5)	2.66 (3)	-C(16)	2.61 (3)
-C(6)	2.64 (3)	-C(17)	2.67 (2)
-C(7)	2.62 (2)	-C(18)	2.61 (2)
-C(8)	2.68 (2)	-C(19)	2.66 (2)

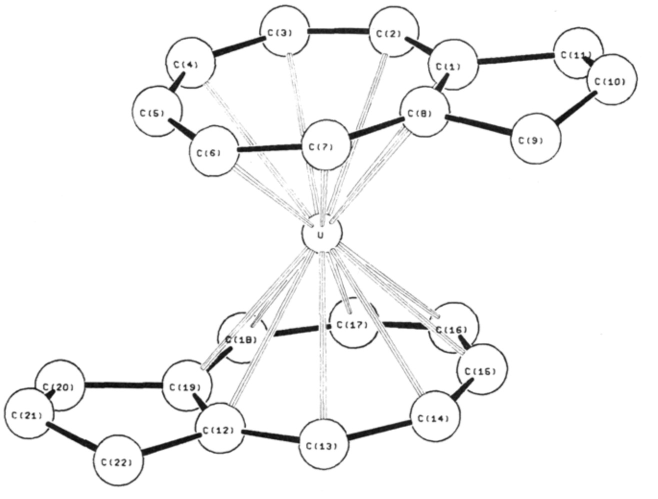

Figure 2. ORTEP ball and spoke view of the molecule. Hydrogen atoms are omitted for clarity.

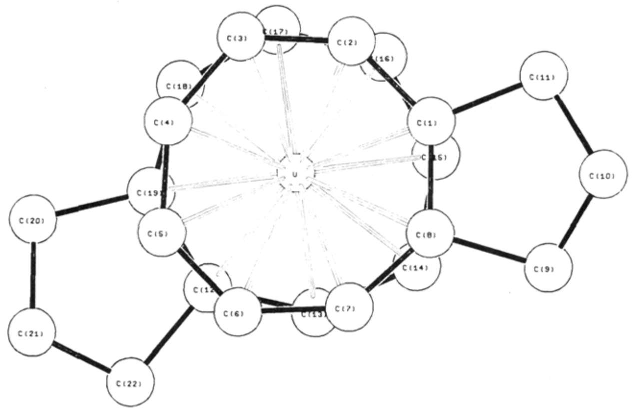

Figure 3. Ball and spoke view of the molecule perpendicular to the cyclooctatetraene rings. Hydrogen atoms omitted.

Discussion

The title compound exists as discrete molecules in the solid state. All atoms are in the general positions, and no symmetry is imposed on the molecule by the space group; however, the molecule does have approximate C_2 symmetry (see Figure 3). The uranium atom is centrally sandwiched between the two eight-membered rings with a U–ring distance of 1.92 Å, in good agreement with other uranocenes.[1,6-8] The COT rings of the molecule are rotated about 8° from a staggered configuration (see Figure 3). In other uranocenes both staggered[11,12] and eclipsed[1,10,11] configurations have been reported. As in ferrocenes, the relative orientation of the rings in uranocene crystals results from crystal packing and not from significant steric interactions between the rings which are 3.85 Å apart. Bond angles and distances for the uranocene part of the molecule are similar to those reported for other uranocenes.[1,6-8] The mean planes of carbons, (C_{11}, C_9, C_1, C_8) and (C_{20}, C_{22}, C_{12}, C_{19}), are bent slightly inward toward the uranium atom from the plane of the 8-membered ring as has been found in dicyclobutenouranocene[1] and in 1,3,5,7,1′,3′,5′,7-octamethyluranocene.[7] Similar convex distortions in the carbocyclic rings have been observed in ferrocenes and chromacene[9] and in a variety of organometallic compounds with planar five-, six- and eight-membered rings.[10]

Unrealistic bond distances (1.38–1.46 Å) and very large and anisotropic thermal parameters in the five-membered rings indicate that we are observing the mean positions of atoms which have disorder up and down from the mean planes, a situation which is commonplace for aliphatic five-membered rings.

The bending appears to be a general feature in sandwich structures where steric interactions between rings is small. Two possible explanations have been offered to account for this bending:[7] (1) bending the substituent toward the metal makes each carbon slightly more pyramidal with the π orbital of the C_nH_n ring bent inward toward the metal and providing greater directionality for overlap between π orbitals and metal orbitals; (2) contraction in volume of the electron density on the side of the ring adjacent to the highly charged metal ion. Nonbonding interaction between the substituted bond and the more diffuse electron density on the uncomplexed side of the ring would result in an inward bend of the substituent. This latter explanation suggests that the inward bending should be independent of ring size. However, it appears that for three- and four-membered rings the substituents bend outward away from the metal.[10] Theoretical calculations on d transition-metal compounds attribute this bending to the former explanation and predict an outward bend for three- and four-membered ring and an inward bend in the substituent for rings larger than five.[10] This bending of the substituent in toward the metal appears to be a general feature in all substituted uranocenes in the absence of steric effects and may reflect the proposed covalency in ligand–metal bonding in these systems.[11]

An especially important point in this regard is the central position with respect to the C_8 rings of uranium in all uranocene structures thus far studied. This result is expected for a model involving important covalent ring–metal bonding. If ionic character dominated we would expect some deviations from C_8 centrosymmetry, particularly in a case such as the present where the overall structure is so lacking in symmetry. This result makes the present structure an especially significant one.

The spectral properties of 1 show no significant differences from those of other uranocenes. In the visible spectrum the shift in λ_{max} from that of uranocene (λ_{max} 616 nm) is between that of 1,1′-dialkyl substituted uranocenes (λ_{max} 610–625 nm) and 1,3,5,7,1′,3′,5′,7′-octamethyluranocene (λ_{max} 650 nm), in accord with the proposed charge-transfer model for the visible spectrum.[12,13]

The paramagnetic shifts of the ^{1}H NMR resonances of 1 are similar to those reported for other substituted uranocenes.[11] Due to the paramagnetic center, the endo and exo protons in the α- and β-positions of the annulated rings are nonequivalent. The three nonequivalent ring proton positions could be assigned to the resonances at −32.1, −34.2, and −41.2 ppm, from the lack of splitting due to J–J coupling and their larger line widths (ca. 30 Hz). The remaining four resonances were partially resolved multiplets and could be easily differentiated into α (+24.4, −18.8 ppm) and (−8.3, −32.6 ppm) sets by integration. Further assignment into endo and exo sets was made in the following manner.

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In uranocene[14] and 1,3,5,7,1′,3′,5′,7′-octamethyluranocene[15] the paramagnetic shifts have been factored into contact and pseudocontact components.[11] The contact component affords an upfield shift to ring protons, and an alternating pattern of upfield and downfield shifts to substituent protons such that protons on the β, δ, etc. carbons are shifted upfield and protons on the α, γ, etc. carbons are shifted downfield, with the magnitude of the contact interaction rapidly diminishing to zero along the substituent chain. Variable-temperature studies on uranocene and octamethyluranocene have established that the total paramagnetic shift is linear with $1/T$. Consequently, the pseudocontact contribution can be expressed by eq 1. Where symmetry requires $\chi_x = \chi_y$, the latter term is zero.[16]

$$\Delta_{\text{pseudocontact}} = \frac{(\chi_z - \frac{1}{2}\chi_x - \frac{1}{2}\chi_y)}{3}\,\frac{(3\cos^2\theta - 1)}{R^3} - \frac{(\chi_x - \chi_y)}{2}\,\frac{(\sin^2\theta\cos 2\psi)}{R^3} \quad (1)$$

For a number of unsymmetrical uranocenes it appears that $\chi_x = \chi_y$ and that the last term in eq 1 can be generally neglected.[11] With this assumption, the sign of the pseudocontact shift will be controlled by θ. Similar to dicyclobutenouranocene we expect the contact shift of the α_{exo} and α_{endo} protons to be approximately the same; calculation from the observed structure gives $\theta < 54.74°$ for the α_{exo} protons, and thus, the pseudocontact shift is downfield. Hence, the α-proton resonances are assigned as α_{exo} + 24.4 ppm and α_{endo} −18.8 ppm; by analogy, the β-proton resonances are β_{exo} 8.3 ppm and β_{endo} −32.6 ppm.

For ^{13}C NMR the contact shift model for uranocene[15] predicts that the contact shifts for carbons should be just opposite those of the corresponding protons. Ring carbons are shifted to low field and are assigned tentatively to the four resonances at 308.0, 296.9, 297.0, and 268.5 ppm. Correspondingly, the α-carbon is assigned to the upfield resonance (−32.5 ppm) and the β-carbon to the 13.4-ppm resonance.

The similarity of the ^{1}H and ^{13}C resonances in 1 with those of other substituted uranocenes[12,13] and the parent compound[12] itself suggest that the electronic factors giving rise to the paramagnetic shifts are similar in all uranocenes. Further support for this generalization comes from the magnetic susceptability data which show that the magnetic moment of 1 is equal within experimental error to that of uranocene.[5,17] Further analysis of the NMR spectra of 1 and related annulated uranocenes, their temperature dependences and dissection into contact and pseudocontact components will be detailed in another paper now in preparation.

Experimental Section

All reactions requiring air-free anhydrous conditions were conducted under an Ar atmosphere or in a Vacuum Atmospheres recirculating glovebox. Solvents were distilled from CaH_2 and degassed prior to use. Visible spectra were obtained on a Cary 118 spectrometer, infrared spectra on a Perkin-Elmer 297 spectrometer, ^{1}H and NMR on Varian T-60 (60 MHz) or the V.C. Berkeley FT-NMR system (180 MHz), and ^{13}C NMR on a Brucker TT-23 spectrometer. Mass spectra and elemental analysis were performed by the Analytical Services Laboratory, University of California, Berkeley, CA. Magnetic susceptability measurements were measured on a vibrating-sample magnetometer previously described in the literature.[17]

X-ray Diffraction. Single crystals suitable for X-ray analysis were grown from hot hexane in an Ar atmosphere glovebox. A crystal fragment approximately 0.10 × 0.15 × 0.35 mm was placed on a Picker FACS-I automated diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.709 30 Å). The setting angles of 12 manually centered reflections (35° < 2θ < 40°) were used to determine the cell parameters by least squares.

Intensity data were collected by using the θ–2θ scan technique with a scan speed of 2°/min on 2θ. Each reflection was scanned from 0.65° before the Kα_1 peak to 0.65° after the Kα_2 peak, and backgrounds were counted for 4 s at each end of the scan range, offset by 0.5°. The temperature during data collection was 22 ± 1 °C. Three standard reflections (6,0,0; 0,0,$\bar{4}$; 0,10,0) were measured after every 200th scan. At the beginning of the data collection ω scans of the 400, 060, and 002 reflections showed half-widths of 0.09°, 0.07°, and 0.09° respectively; at the end of the data collection the values were 0.18, 0.12, and 0.11, indicating significant deterioration of the crystal. Although 6043 scans were collected, only the first 3010 were used; the remaining half of the data, based on the declining intensities of the standards, were rejected. The decay was anisotropic with the largest amount recorded by the 600 standard reflection. An isotropic decay correction varying from 0.91 to 1.06 was applied to the 3010 data used. An absorption correction[18] was estimated, and corrections between 1.5 and 1.8 were applied to the data. Because the crystal had an irregular shape with indistinct faces, a shape and size were estimated, and the dimensions were tailored to fit the intensity variations obtained from three azimuthal scans taken after the data collection was concluded. The 3010 scans resulted in 2312 unique data 1000 of which have $F^2 > 3\sigma$.

A three-dimensional Patterson function calculation revealed the uranium position, and subsequent least-squares calculations and Fourier maps revealed all of the carbon atoms. A series of least squares in which the function $\sum w(|F_o| - |F_c|)^2/\sum wF_o^2$ was minimized converged rapidly to the final structure. The expressions that were used in processing the data and estimating the weights are given in the supplementary material; the "ignorance factor", p, was set to 0.06. Scattering factors from Doyle and Turner[19] were used, and anomalous dispersion corrections[20] were applied. The positions of all of the hydrogen atoms were estimated and included in the calculations with isotropic temperature factors but were not refined. Anisotropic thermal parameters were applied to U and all of the carbon atoms.

Because of the low quality of the data, the cyclooctatetraene (COT) ring was not well resolved, and some of the C–C bond distances deviated from the expected values by as much as 0.2 Å. Restraints were imposed on the bond distances in the COT ring and the cyclopenteno group adjacent to the ring in the following manner.[21] Interatomic distances between selected atoms were introduced into the least-squares calculations and treated as observations; estimated standard deviations of these distances were also introduced and used to calculate the weights. The derivatives of these distances with respect to the positional parameters were calculated by a special patch, and these "observations" were not included in the least-squares calculation in the same manner as the observed structure factors. This procedure allows the structure to adjust to the electron density

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with a flexibility governed by the weighting. The C–C bond distances within the ring were restrained to 1.40 ± 0.02 Å, and the C–C bonds from the cyclopento carbon to the ring carbons were restrained to 1.54 ± 0.02 Å.

The discrepancy indices for 1000 data where $F^2 > 3\sigma$ are

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.040$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2} = 0.046$$

R for all 2332 data is 0.14. The error in an observation of unit weight is 1.07. In the last cycle no parameter changed more than 0.13σ. The top three peaks in the final difference Fourier map are 1.0–1.3 e A^{-3} and are all ripples about the uranium atom.

***cis*-Bicyclo[6.3.0]undeca-2,4,6-triene, 2.** Under an Ar atmosphere, 1.4 g (0.2 mol) of lithium wire (1% sodium) was added to 300 mL of anhydrous liquid ammonia in a 500-mL round-bottom flask. To this deep blue solution was added 10.4 g (0.1 mol) of freshly distilled cyclooctatetraene (33 °C (14mmHg)) (BASF), at −40 °C via syringe. The resulting yellow suspension of dianion was stirred for 1.5 h at −40 °C followed by dropwise addition (1 drop every 2 s) of 20.2 g (0.1 mol) of 1,3-dibromopropane (Aldrich) in 20 mL of ether. The reaction mixture was stirred for 4.5 h at ca. −40 °C followed by overnight evaporation of ammonia to afford a red brown solid which was suspended in 200 mL of saturated ammonia chloride and extracted with ether (4 × 100 mL). The ether extracts were washed with water (3 × 100 mL) and dried over $MgSO_4$. Removal of solvent followed by vacuum distillation (25 °C (0.1mmHg)) yielded 6.83 g (46.8%) of a clear yellow liquid: mass spectrum parent *m/e* 156. The ^1H and ^{13}C NMR ($CDCl_3$) of this material indicated that it was mixture of both the bicyclic (**2**) and tricyclic (**4**) valence isomers: bicyclic ^1H NMR δ 5.80 (s, 6 H, vinyl), 2.77 (br m, 1.4 H, bridgehead), and 1.65 (complex m, 5.3 H cyclopentyl); ^{13}C NMR δ 135.4, 127.7, 126.2 (vinyl), 43.5 (bridgehead), 32.3, 19.5 (cyclopentyl); tricyclic ^1H NMR ($CDCl_3$) δ 5.57 (s, 4 H, vinyl), 2.77 and 2.43 (br m, 2 H, bridgehead), 1.67 (complex multiplet, 5.3 H, cyclopentyl); ^{13}C NMR: δ 126.6, 120.3 (vinyl), 51.0, 35.6 (bridgehead), 32.9, 24.7 (cyclopentyl). After standing for 4 days at room temperature, the material had rearranged completely to the tricyclic isomer **4**.

Following the same procedure but using 23.2 g (0.1 mol) of **5** in 100 mL of THF instead of 1,3-dibromopropane in 10 mL of ether gave the same product in 58.4% yield.

$AgNO_3$ Adduct of *cis*-Bicyclo[6.3.0]undeca-2,4,6-triene. To a boiling solution of 3.4 g (0.02 mol) of silver nitrate and 15 mL of absolute ethanol was added 2.9 g (0.02 mol) of **2**. Most of the silver nitrate dissolved upon addition of the hydrocarbon. Cooling of the solution in a refrigerator for several hours afforded off-white crystals which were recrystallized from absolute ethanol; mp 135–136 °C dec.

Anal. Calcd for $C_{11}H_{14}NO_3Ag$: C, 41.79; H, 4.46; N, 4.43. Found: C, 41.48; H, 4.35; N, 4.29.

1,3-Bis((methylsulfonyl)oxy)propane. To a stirred 0 °C solution of 15.22 g (0.2 mol) of 1,3-propanediol (Aldrich), 70 mL (0.5 mol) of triethylamine, and 1 L of CH_2Cl_2 in a 2-L round-bottom flask was added dropwise 32.5 mL (0.42 mol) of methanesulfonyl chloride (Eastman) over 5 min. The resulting reaction mixture was stirred for 0.5 h during which time a white precipitate formed. After sequential extractions with 200 mL of ice water, 200 mL of cold 10% HCl, 200 mL of saturated sodium bicarbonate, and 200 mL of brine, the organic layer was dried over $MgSO_4$ and stripped of solvent to afford a white solid which was recrystallized from hot methanol: yield 38.4 g (82.7%); mp 40.5–41.5 °C; NMR ($CDCl_3$) δ 4.37 (t, 4 H, OCH_2), 3.07 (s, 6 H, CH_3), 2.19 (p, 2 H, CH_2).

Anal. Calcd for $C_5H_{12}O_6S_2$: C, 25.85; H, 5.21; S, 27.61. Found: C, 26.04, H, 5.26, S, 27.42.

Dipotassium Bicyclo[6.3.0]undeca-2,4,6-triene-1,8-diide, 3. Under Ar a suspension of potassium amide in liquid ammonia was prepared by distilling 300 mL of ammonia from a lithium metal–ammonia solution into a 500-mL round-bottom flask containing several milligrams of anhydrous $FeCl_3$. Subsequent addition of 2.14 g (0.055 mol) of potassium metal at −40 °C afforded a blue solution which was stirred (ca. 5 min) until the blue color disappeared, indicating formation of the amide. A 4.0-g (0.027-mol) aliquot of **2** was added via syringe, and the resulting red brown solution was stirred for 1.5 h at −35 °C. The solution was slowly warmed to room temperature, and the ammonia was swept out with a steady Ar purge overnight, affording 4.66 g of the crude dianion as a highly air-sensitive gray-brown solid: ^1H NMR (THF-d_8) δ 5.67, 1.3, 0.93 (br s); ^{13}C NMR δ 99.9 (quat), 96.9, 89.8, 87.0 (ring), 46.4 (α-CH_2), 27.2 (β-CH_2). No attempt was made to purify this material.

Dicyclopentenouranocene, 1. In an Ar atmosphere glovebox 2.56 g (0.0068 mol) of UCl_4 in 25 mL of THF was added to a solution of 3.0 g (0.0135 mol) of **3** in 100 mL of THF in a 500-mL round-bottom glask, and the resulting green solution was stirred for 18 h. Removal of the solvent by vacuum transfer afforded a green solid which was purified by Soxhlet extraction with hexane: yield 0.57 g (15.9%); mass spectrum, parent peak *m/e* 526; visible spectrum in hexane, nm ($\epsilon \times 10^3$) 632 (2.1), 656 (0.9), 663 (0.9), 680 (0.7). The IR spectrum is given in Table I, and NMR spectra are discussed in the text.

The NMR spectra showed that the bulk sample was substantially pure (>95%) although a good combustion analysis could not be obtained. The results were always about 1% low in carbon, even with added oxidant. This pattern is not uncommon in attempted combustion analyses of uranocenes, apparently because of the formation of carbides. Anal. Calcd for $C_{22}H_{24}U$: C, 50.2; H, 4.6. Found: C, 48.8; H, 4.8.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract No. W-7405-ENG-48.

Registry No. **1**, 80287-59-8; **2**, 64924-30-7; **3**, 80263-15-6; **4**, 36093-17-1; 1,3-dibromopropane, 109-64-8; 1,3-bis((methylsulfonyl)oxy)propane, 15886-84-7; UCl_4, 10026-10-5.

Supplementary Material Available: Data processing formulas, calculated positional parameters for the hydrogen atoms, anisotropic thermal parameters, carbon–carbon distances, a table of selected angles, and a list of observed structure factors (14 pages). Ordering information is given on any current masthead page.

Reactions of (Silylamino)phosphines with Some Organic Halides[1,2]

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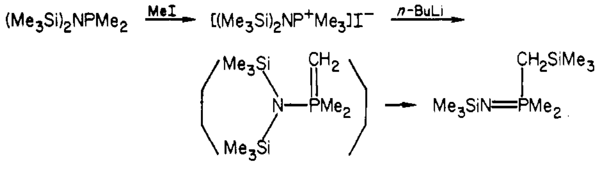
(Silylamino)phosphines including $(Me_3Si)_2NPR_2$ (**1a**, R = Me; **1b**, R = Et), $\overline{Me_2SiCH_2CH_2SiMe_2N}PMe_2$ (**2**), and $Me_3SiN(R)PMe_2$ (**3a**, R = *t*-Bu; **3b**, R = Me) react readily with organic halides to give a variety of products. Treatment of **1a**, **1b**, or **3a** with ethyl bromoacetate yields the structurally rearranged phosphonium salts $[R'N(H){-}P^+R_2{-}CHSiMe_3{-}CO_2Et]Br^-$ (**4a**, R = Me, R′ = $SiMe_3$; **4b**, R = Et, R′ = $SiMe_3$; **10**, R = Me, R′ = *t*-Bu) while the cyclic compound **2** gives the simple phosphonium salt $[\overline{Me_2SiCH_2CH_2SiMe_2N}{-}P^+Me_2{-}CH_2CO_2Et]Br^-$ (**9**). The salts **4a** and **4b** react with alkyl lithium reagents to give the *N*-silylphosphinimines $Me_3SiN{=}PR_2{-}CH_2CO_2Et$ (**8a**, R = Me; **8b**, R = Et). With allyl bromide phosphine **1a** reacts to form a mixture of the isomeric phosphonium salts $[(Me_3Si)_2N{-}P^+Me_2R]Br^-$ (**11**, R = $CH_2CH{=}CH_2$; **12**, R = $CH{=}CHCH_3$) which readily eliminate Me_3SiBr, yielding the phosphinimines $Me_3SiN{=}PMe_2R$ (**13**, R = $CH_2CH{=}CH_2$; **14**, R = $CH{=}CHCH_3$). Traces of atmospheric moisture catalyze the isomerizations of **11** to **12** and **13** to **14**. Phosphine **2** again affords a simple phosphonium salt **15** with allyl bromide. Phosphine **1a** reacts smoothly with chloroformates to give the alkoxycarbonyl-substituted phosphinimines $Me_3SiN{=}PMe_2{-}C(O)OR$ (**16a**, R = Me; **16b**, R = Et). The *N*-*tert*-butyl analogue (**18**), from **3a** and methyl chloroformate, was obtained as a mixture with other unidentified products, and the cyclic compound **2** gave only a low yield of the P–N cleavage product **17**. The *N*-methyl phosphine **3b**, however, reacts cleanly via Si–N bond cleavage to afford the aminophosphine $MeOC(O)N(Me){-}PMe_2$ (**19**) in high yield. Proton, ^{13}C, and ^{31}P NMR spectroscopic data for this new series of compounds are reported.

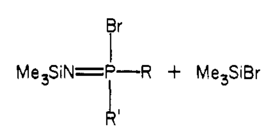
Introduction

As reported in earlier papers,[3-5] the chemistry of (silylamino)phosphines such as $(Me_3Si)_2NPMe_2$ usually involves participation of both phosphorus and silicon as reactive sites. For example, while salt formation occurs readily with MeI, subsequent dehydrohalogenation (eq 1) results in a [1,3]-silyl shift rather than simple ylide formation.[3]



(1)

Elimination of silyl halides from (silylamino)phosphonium salts is another mode of reactivity as illustrated by the bromination reaction (eq 2) which yields the synthetically important *P*-bromophosphinimines.[4]

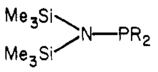


(2)

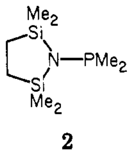
We report here the reactions of some (silylamino)phosphines with a representative group of reactive organic halides: ethyl bromoacetate, allyl bromide, and chloroformates. Silyl halide elimination from the resulting phosphonium salts yields phosphinimines bearing organic functional groups on phosphorus.

Results and Discussion

As in the related study,[5] the (silylamino)phosphines used in this work included the [bis(trimethylsilyl)amino]dialkylphosphines **1**, the cyclic analogue **2**, and the (*N*-alkyl-*N*-silylamino)phosphines **3**.



1a, R = Me
b, R = Et



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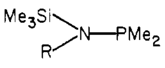
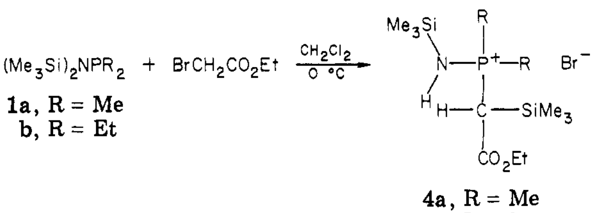


3a, R = *t*-Bu
b, R = Me

Reactions with Ethyl Bromoacetate. Treatment of phosphine **1a** or **1b** with 1 equiv of ethyl bromoacetate in dichloromethane solution yields, quite surprisingly, the structurally rearranged phosphonium salts **4a** and **4b**, respectively (eq 3). The structure of **4**, in which a proton and a $SiMe_3$ group have exchanged positions, was confirmed by ^{13}C and ^1H NMR spectroscopy. Most notably, the carbon to which both phosphorus and silicon are bonded appears as a doublet of doublets in the off-resonance decoupled ^{13}C spectrum. Furthermore, the Me_3Si groups are nonequivalent in both the ^{13}C and ^1H NMR spectra, and the N–H proton is clearly visible in the ^1H spectrum (Table I).



(3)

1a, R = Me
b, R = Et

4a, R = Me
b, R = Et

A possible pathway for the formation of these phosphonium salts is proposed in eq 4. Phosphonium salt **5** is assumed to be the initial product; however, it could not be observed in the reaction mixture by NMR spectroscopy. It seems reasonable to suggest that the N–H proton in **4**

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[1] Presented in part at the International Conference on Phosphorus Chemistry, Durham, NC, June 1981, Abstr. 176.

[2] Taken in part from the Ph.D. Dissertation of D. W. Morton, Texas Christian University, Fort Worth, TX, 1981.

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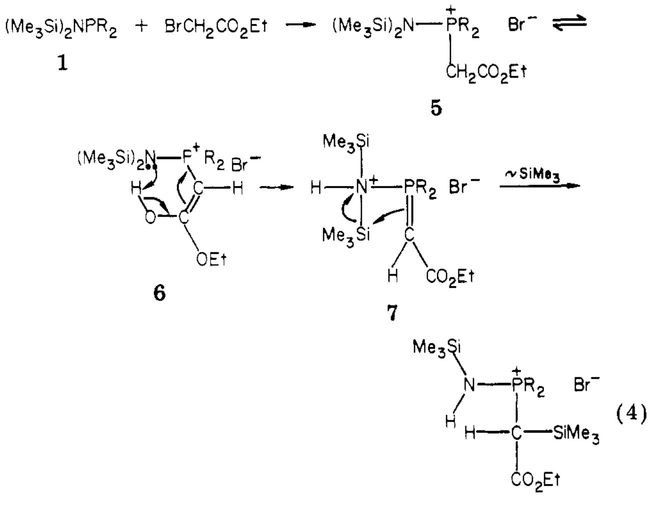
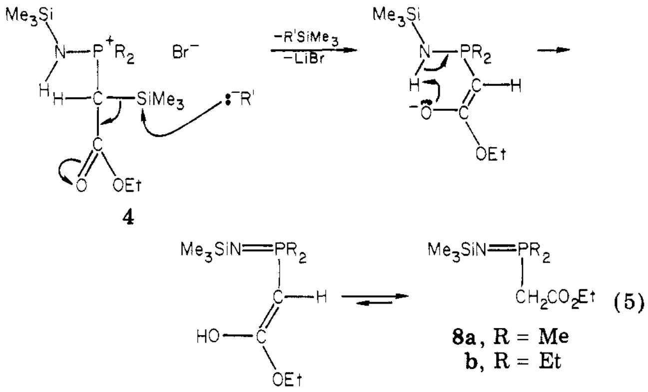


(4)

may be transferred via the enol **6** to give **7**. The formation of **4** from **7** could then occur by a [1,3]-silyl migration from nitrogen to carbon.[3]

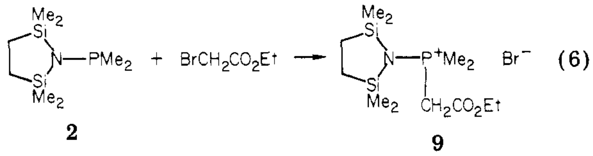
Another rather unexpected result was obtained when the phosphonium salts **4** were treated with either *n*-butyl- or *tert*-butyllithium (eq 5). Instead of removing an N–H or C–H proton, the alkyl anion apparently attacks the C-bonded silyl group to afford, after proton transfer back to carbon, the *N*-silylphosphinimines **8**.



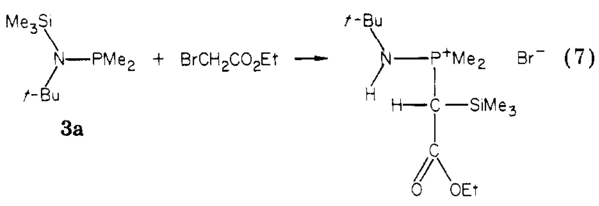
(5)

R′ = *n*-Bu, *t*-Bu

The cyclic (disilylamino)phosphine **2** also forms a salt (**9**) with ethyl bromoacetate, but no silyl migration to carbon occurs (eq 6). The (*N*-*tert*-butyl-*N*-silylamino)phosphine **3a**, however, reacts in the same manner as **1** to yield **10** (eq 7). The phosphonium salts **9** and **10** both react vigorously with *n*-butyllithium but none of the reaction products could be identified by NMR spectroscopy.

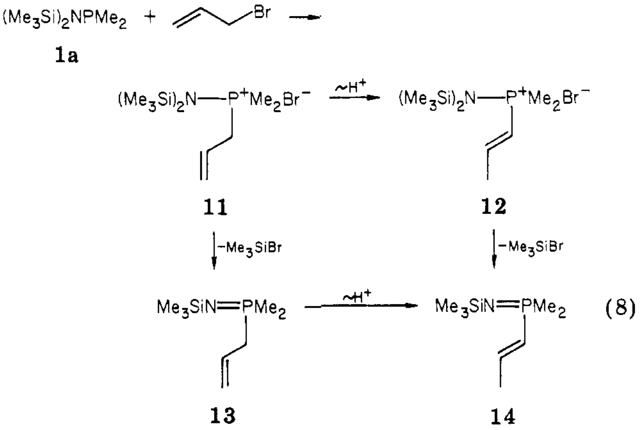


(6)



(7)

Reactions with Allyl Bromide. Phosphine **1a** reacts exothermically with allyl bromide to produce a mixture of compounds **11–14** (eq 8). When the reactants were combined under rigorously anhydrous conditions in dichloromethane at −78 °C in an NMR tube and the probe temperature was raised gradually, the following observations were made. At −78 °C, much of **1a** remained unreacted, but signals due to **11** and **13** could be discerned. By −40 °C, practically all of **1a** had reacted, and by +2 °C the mixture consisted of about 50% of **11** and 50% of **13**. At +30 °C the spectrum showed that all of **11** had decomposed to **13**.

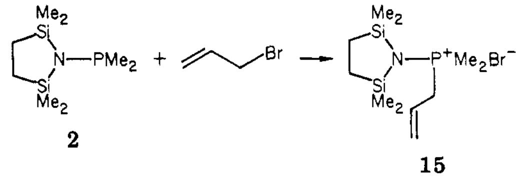


(8)

If a trace amount of water is introduced by briefly opening the reaction vessel to air, however, **13** is observed to slowly convert into **14**. This is probably an acid-catalyzed isomerization caused by HBr from the hydrolysis of Me_3SiBr. If moisture is introduced before the salt **11** has completely decomposed to **13**, then the isomeric phosphonium salt **12** can be observed by ^1H NMR. Compound **12** can, of course, eliminate Me_3SiBr directly to form **14**.

On a preparative scale, mixtures of **13** and **14** are usually observed, but nearly pure **13** is obtained if moisture is carefully excluded. When left standing for several days, **13** gradually rearranges to the conjugated isomer **14** which, based on the large vinylic coupling of 16.5 Hz, is assigned the *E* configuration.

Phosphine **2** also reacts with allyl bromide to form the stable phosphonium salt **15** (eq 9) which does not give a phosphinimine at room temperature. Compound **15** exhibits no tendency toward double-bond migration, which is most likely a result of the fact that there is no halosilane formation (and no acid catalyst) as in eq 8.

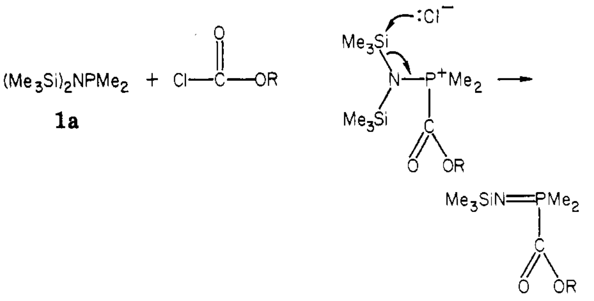


(9)

Reactions with Chloroformates. The course of the reaction of (silylamino)phosphines with methyl or ethyl chloroformate was found to vary markedly depending upon the electronic and steric effects of the nitrogen substituents in the starting phosphine. Thus, different types of products were obtained from similar reactions of phosphines **1**, **2**, or **3** with the chloroformates.

Phosphine **1a** reacts via nucleophilic attack by phosphorus on the carbonyl carbon followed by loss of Me_3SiCl (eq 10) to give the alkoxycarbonyl-substituted phosphinimines **16** in ca. 70% yields. In contrast, however, to the reactions with ethyl bromoacetate (eq 4) or allyl bromide (eq 8), the intermediate phosphonium salt could not be observed by NMR spectroscopy.

The cyclic analogue **2** reacted quite differently with methyl chloroformate. In this case, only a P–N cleavage

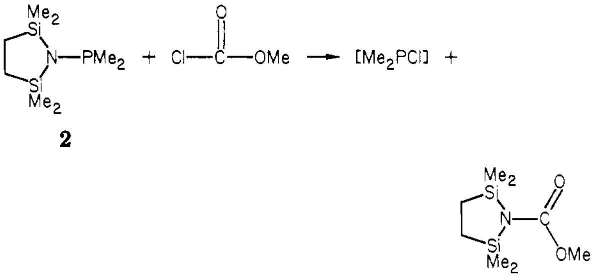


1a

(10)

16a, R = Me
b, R = Et

product, **17**, (eq 11) was obtained in low yield (ca. 15%).



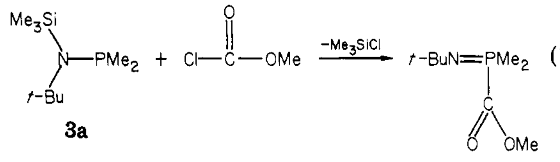
2

(11)

17

Although it was not identified in the product mixture, the other initial product was probably Me_2PCl which could have reacted[6,7] with **2** to form other unidentified products, thus accounting for the low yield of **17**.

When phosphine **3a** was treated with methyl chloroformate (eq 12), a mixture of products was formed, being



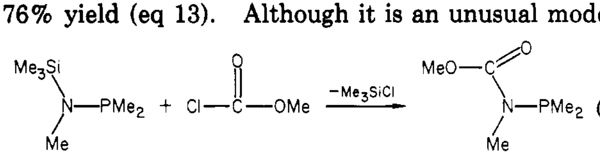
3a

(12)

18

comprised of about 50% of **18**. The other components of the mixture could not be identified and **18** was not obtained in sufficient purity for elemental analysis.

The (*N*-methyl-*N*-silylamino)phosphine **3b**, in which nitrogen is less sterically crowded, reacts in yet a different manner with methyl chloroformate. In this case, simple Si–N bond cleavage occurs, leading to formation of the *N*-methoxycarbonyl-substituted aminophosphine **19** in 76% yield (eq 13). Although it is an unusual mode of reactivity for (silylamino)phosphines, nucleophilic attack by nitrogen in compounds bearing the $Me_3SiN(Me)$– group has been previously observed when strong electrophiles such as acid halides are involved.[6-8]



(13)

3b **19**

Conclusion

The results reported here and in the related paper[5] demonstrate that the reactions of (silylamino)phosphines with electrophilic organic substrates are useful for the preparation of a variety of new functionalized phosphinimines. In addition, some consistent reactivity trends in these systems are apparent: (1) (disilylamino)phosphines such as **1** react via nucleophilic attack by phosphorus followed by silyl group migration[5] or silyl halide elimination; (2) the cyclic compound **2** reacts similarly although Si–N bond cleavage is much less likely to occur in the initially formed products (see, for example, phosphonium salts **9** and **15**); (3) the *N*-*tert*-butyl derivative **3a** usually reacts like the (disilylamino)phosphines **1** but, quite often, side reactions and/or unstable products are obtained; and (4) when relatively strong electrophiles (e.g., methyl chloroformate) are used, the (*N*-methyl-*N*-silylamino)phosphine **3b** can react via nucleophilic attack by nitrogen rather than phosphorus.

Experimental Section

Materials and General Procedures. The (silylamino)phosphines were prepared according to the published procedures.[3,9] Dichloromethane was distilled and stored over molecular sieves prior to use. Ethyl bromoacetate, allyl bromide, and the chloroformates were obtained from commercial sources and used without further purification. All reactions were performed under an atmosphere of dry nitrogen with reagents being transferred by syringe. Proton NMR spectra were obtained on a Varian EM390 or JEOL MH-100 spectrometer. Carbon-13 and ^{31}P NMR spectra were obtained on a JEOL FX-60 spectrometer operating in the FT mode. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Reaction of 1 with Ethyl Bromoacetate. Typically, phosphine **1a** (ca. 10–20 mmol) was dissolved in CH_2Cl_2 (ca. 10–15 mL) in a 25-mL flask equipped with a magnetic stirrer and an adapter with a gas inlet side arm and a rubber septum. One equivalent of ethyl bromoacetate was then added via syringe to the stirred phosphine solution at 0 °C. The reaction was complete instantaneously. Evaporation of solvent left the phosphonium salt **4a** as a white, hygroscopic solid (mp 56–58 °C dec) which was identified by NMR spectroscopy (Table I). Anal. Calcd: C, 37.11; H, 8.04. Found: C, 37.10; H, 7.87. The salt **4b** was prepared from phosphine **1b** by using the same procedure.

Preparation of Phosphinimines 8. One equivalent of *n*-butyllithium or *tert*-butyllithium (1.6 M in hexane or 2.1 M in pentane, respectively) was added via syringe to a stirred CH_2Cl_2 solution of freshly prepared phosphonium salt **4a** (ca. 15 mmol) at 0 °C. The mixture was allowed to warm to room temperature while stirring for ca. 20 min. Filtration, solvent removal, and distillation afforded **8a** as a colorless liquid (50% yield, bp 42.5–44.5 °C (0.02 mm)). Anal. Calcd: C, 45.93; H, 9.42. Found: C, 46.17; H, 9.61. With use of the same procedure, the phosphinimine **8b** was prepared from **4b** (65% yield, bp 50.5 °C (0.02 mm)). Anal. Calcd: C, 50.16; H, 9.95. Found: C, 50.40; H, 9.98.

Reactions of 2 or 3a with Ethyl Bromoacetate. With use of the procedure described above for compound **1**, treatment of phosphines **2** or **3a** with ethyl bromoacetate gave the phosphonium salts **9** and **10**, respectively, which were identified by NMR spectroscopy (Table I). Anal. Calcd for compound **9**: C, 37.30; H, 7.56. Found: C, 37.02; H, 7.85 (mp 127–130 °C dec).

Reaction of 1a with Allyl Bromide. With use of the same procedure, phosphine **1a** was treated with 1 equiv of allyl bromide. If ice bath cooling is used and moisture is rigorously excluded, then only phosphonium salt **11** is observed. However, if allyl bromide is added at room temperature, causing the solvent to reflux, and a trace amount of moisture is introduced by briefly exposing the mixture to air, then some of the isomeric salt **12** can be observed by ^1H NMR.

Preparation of Phosphinimines 13 and 14. The solvent was removed from the reaction mixture in the preparation of salts **11** and **12** described above. The flask containing the remaining white solid was attached to a fractional distillation assembly. A vacuum of about 4 mm was applied and the flask was heated to ca. 70 °C at which point the solid liquefied and the products distilled. This procedure gave a mixture (84% yield, bp 54.5–55

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[7] Keat, R. *J. Chem. Soc. A* **1970**, 1795.

[8] Pudovik, M. A.; Kibardina, L. K.; Medvedeva, M. D.; Pudovik, A. N. *J. Gen. Chem. USSR (Engl. Trans.)* **1979**, *49*, 855.

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Table I. NMR Spectroscopic Data[a]

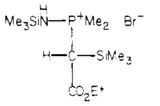
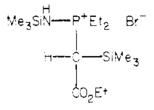
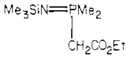
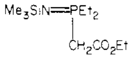
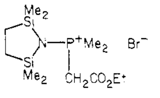
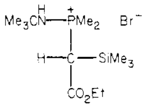
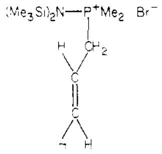
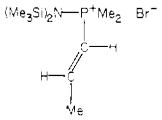
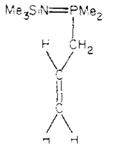
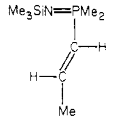
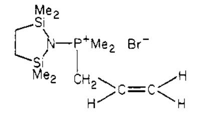
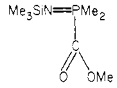
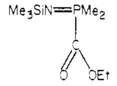
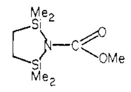
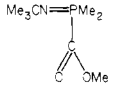
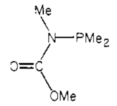
		^{1}H NMR			^{13}C NMR		^{31}P NMR
compd	signal	δ	J_{PH}	J_{HH}	δ	J_{PC}	δ
 **4a**	Me$_3$SiN	0.09			−0.45		35.89
	Me$_3$SiC	0.01			−1.56		
	Me$_2$P	1.75	14.0		14.62	72.3	
	PCH	3.94	11.4		56.11	120.1	
	NH	5.59					
	OCH$_2$*CH*$_3$	1.12		6.9	11.95		
	O*CH*$_2$CH$_3$	3.89		6.9	64.91		
	C=O				164.90	5.9	
 **4b**	Me$_3$SiN	0.45[b]			0.43	1.8	47.96
	Me$_3$SiC	0.42			−0.93		
	PCH$_2$*CH*$_3$	1.27	19.2	7.3	4.47	4.9	
	P*CH*$_2$CH$_3$	2.36	12.8	7.3	18.60	50.1	
	PCH	3.55	8.3		51.80	115.4	
	NH	5.63					
	OCH$_2$*CH*$_3$	1.50		7.0	12.70		
	O*CH*$_2$CH$_3$	4.18		7.0	65.70		
	C=O				167.62	6.7	
 **8a**	Me$_3$SiN	−0.06	0.4		3.31	3.9	2.35
	Me$_2$P	1.46	12.6		18.49	71.3	
	PCH$_2$	2.78	14.4		41.32	52.7	
	OCH$_2$*CH*$_3$	1.21		7.0	13.58		
	O*CH*$_2$CH$_3$	4.09		7.0	60.36		
	C=O				166.76	4.9	
 **8b**	Me$_3$SiN	−0.06	0.4		3.61	2.9	11.78
	PCH$_2$*CH*$_3$	0.9–1.3[c]			5.43	4.9	
	P*CH*$_2$CH$_3$	1.4–1.8[c]			22.42	70.3	
	P*CH*$_2$CO$_2$	2.70	13.5		36.74	47.9	
	OCH$_2$*CH*$_3$	1.22		7.4	13.64		
	O*CH*$_2$CH$_3$	4.07		7.4	60.36		
	C=O				167.05	3.9	
 **9**	Me$_2$Si	0.46[b]			1.18		48.25
	SiCH$_2$	0.91			7.57	6.7	
	PMe$_2$	2.44	13.5		14.88	65.3	
	PCH$_2$	4.12	14.1		36.02	63.5	
	OCH$_2$*CH*$_3$	1.29		7.0	13.28		
	O*CH*$_2$CH$_3$	4.16		7.0	61.48		
	C=O				162.53	5.5	
 **10**	Me$_3$Si	0.32			−2.01		31.04
	Me$_3$C	1.28			29.04	3.9	
	Me$_3$*C*				50.74	3.9	
	PMe$_2$	1.91	13.0		13.51	72.3	
	PCH	3.87	12.0		56.37	116.2	
	NH	5.62					
	OCH$_2$*CH*$_3$	1.29		7.6	11.44		
	O*CH*$_2$CH$_3$	3.97		7.6	64.32		
	C=O				164.06	5.9	
 **11**	Me$_3$Si	0.44[b]					30.73
	Me$_2$P	2.35	12.6				
	PCH$_2$	3.54	13.4	5.9			
	PCCH	~5.8[d]		5.9			
	PCCCH$_2$	~5.0					
		~5.2					
 **12**	Me$_3$Si	0.44[b]					
	Me$_2$P	2.35	12.6				
	PCH	~5.7	*e*	16.7			
				1.4			
	PCCH	~6.7	*e*	16.7			
				6.3			
	PCCMe	2.03	2.6	6.1			
				1.4			
 **13**	Me$_3$Si	0.04[b]	0.4		3.51	4.3	7.08
	Me$_2$P	1.34	12.0		17.01	68.4	
	PCH$_2$	2.49	15.0	7.1	39.57	64.1	
	PC*CH*	5.5–6.0[d]		7.1	128.89	8.5	
	PCC*CH*$_2$	4.9–5.1		1.4	118.35	11.6	
		5.1–5.2		1.3			

Table I (*Continued*)

compd	signal	^{1}H NMR			^{13}C NMR		^{31}P NMR
		δ	J_{PH}	J_{HH}	δ	J_{PC}	δ
 **14**	Me_3Si	0.04 [b]	0.4		3.51	4.3	0.08
	Me_2P	1.38	12.3		19.00	70.8	
	PCH	5.74	24.6	16.5 1.5	127.63	96.4	
	PC*CH*	6.46	20.0	16.5 6.3	141.74	1.8	
	PCC*Me*	1.86	1.6	6.3 1.5	19.00	18.3	
 **15**	Me_2Si	0.44			1.22		50.09
	$SiCH_2$	0.90			7.17	6.7	
	Me_2P	2.22	13.2		13.26	64.1	
	PCH_2	3.42	15.4	6.1	33.42	59.8	
	PC*CH*	5.3-6.0 [d]		6.1	123.57	9.8	
	PCCCH_2	5.3-6.0			123.25	13.4	
 **16a**	Me_3Si	−0.13	0.4		2.34	3.9	−3.41
	Me_2P	1.47	13.5		16.93	73.2	
	OMe	3.67	0.8		51.00	2.0	
	C=O				172.37	117.2	
 **16b**	Me_3Si	−0.07	0.4		2.60	3.9	−3.41
	Me_2P	1.50	13.3		16.99	73.2	
	OCH_2CH_3	1.06	1.0	7.1	13.32		
	OCH_2CH_3	4.16	0.7	7.1	60.56	2.0	
	C=O				172.18	117.2	
 **17**	Me_2Si	0.18					
	$SiCH_2$	0.71					
	OMe	3.54					
 **18**	*Me*$_3$C	1.28	0.9		26.76	30.94	
	Me$_3$*C*				49.79	4.9	
	PMe_2	1.55	13.6		14.17	69.6	
	OMe	3.68	0.8		51.31	3.1	
	C=O				170.88	134.8	
 **19**	Me_2P	1.15	7.8		13.95	17.7	38.06
	NMe	2.72	3.9		29.99	3.1	
	OMe	3.53			51.67	1.8	
	C=O				157.44	12.2	

[a] Chemical shifts downfield from Me_4Si for ^{1}H and ^{13}C spectra and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^{1}H, CH_2Cl_2; ^{13}C and ^{31}P, $CDCl_3$. [b] Benzene/$CDCl_3$ solution used for ^{1}H NMR. [c] PEt_2 protons give a complex ABC_3X pattern. [d] Protons of allyl group give a complex $ABCM_2X$ pattern. [e] J_{PH} values could not be extracted from complex signals.

°C (2.1 mm)) of phosphinimines **13** and **14** consisting mainly of **14**. In order to obtain nearly pure **13**, we conducted the preparation of the salt **11** in a flask already attached to a distillation assembly and cooled to −78 °C. The reaction mixture was warmed to 0 °C, volatiles were removed at 0.2 mm, and almost pure **13** was distilled at 30–31 °C (0.2 mm). A gradual isomerization to **14** occurred over a period of several days. Anal. Calcd: C, 50.76; H, 10.65. Found: C, 50.79; H, 10.80.

Reaction of 2 with Allyl Bromide. Addition of 1 equiv of allyl bromide to a stirred solution of phosphine **2** (ca. 15 mmol) in CH_2Cl_2 (ca. 10 mL) at 0 °C gave phosphonium salt **15** which was identified by NMR spectroscopy (Table I). Anal. Calcd: C, 38.81; H, 7.99. Found: C, 37.72; H, 7.51 (mp 80–83 °C dec).

Preparation of Phosphinimines 16. In the same manner, a solution of phosphine **1a** in CH_2Cl_2 was treated with methyl chloroformate at 0 °C. Solvent was removed after a few minutes and distillation gave phosphinimine **16a** as a colorless liquid (67% yield, bp 54.5 °C (0.5 mm)). Anal. Calcd: C, 40.56; H, 8.75. Found: C, 40.78; H, 8.73. With use of the same procedure, **1a** and ethyl chloroformate gave phosphinimine **16b** (72% yield, bp 54.5 °C (0.3 mm)). Anal. Calcd: C, 43.42; H, 9.11. Found: C, 43.22; H, 9.04.

Reaction of 2 with Methyl Chloroformate. Phosphine **2** was treated with 1 equiv of methyl chloroformate in CH_2Cl_2 at 0 °C. Solvent was removed after 1 h. From the residual mixture, compound **17** was distilled as a colorless liquid (15% yield, bp 42–45 °C (0.7 mm)) which was identified by ^{1}H NMR spectroscopy. No phosphorus-containing products could be identified.

Reaction of 3a with Methyl Chloroformate. Similarly, phosphine **3a** was treated with methyl chloroformate. Solvent was removed after 30 min. Distillation gave a fraction (bp 50 °C (0.4 mm)) which contained about 50% of **18** as evidenced by ^{1}H NMR spectroscopy. Other products could not be identified. Approximate yield of **18**: 25%.

Preparation of Phosphine 19. Similarly, phosphine **3b** was treated with methyl chloroformate. Solvent was removed after a few minutes and distillation gave phosphine **19** as a colorless liquid (76% yield, bp 51.5 °C (3.3 mm)). Anal. Calcd: C, 40.27; H, 8.11. Found: C, 40.28; H, 8.04.

Acknowledgment. We thank The Robert A. Welch Foundation and the U.S. Army Research Office for generous financial support of this research.

Registry No. 1a, 63744-11-6; **1b**, 73270-05-0; **2**, 68437-96-7; **3a**, 68437-82-1; **3b**, 68437-84-3; **4a**, 80448-20-0; **4b**, 80448-21-1; **8a**, 80448-22-2; **8b**, 80448-23-3; **9**, 80448-24-4; **10**, 80448-25-5; **11**, 80448-26-6; **12**, 80448-27-7; **13**, 80448-28-8; **14**, 80448-29-9; **15**, 80448-30-2; **16a**, 80448-31-3; **16b**, 80448-32-4; **17**, 80448-33-5; **18**, 80448-34-6; **19**, 80448-35-7.

Synthesis and Characterization of Cationic Iron Vinylidene Compounds. Formation of C–H, C–N, and C–P Bonds and the X-ray Crystal Structure of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(PPh_3)=CH_2\}]^+BF_4^-$

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Received November 23, 1981

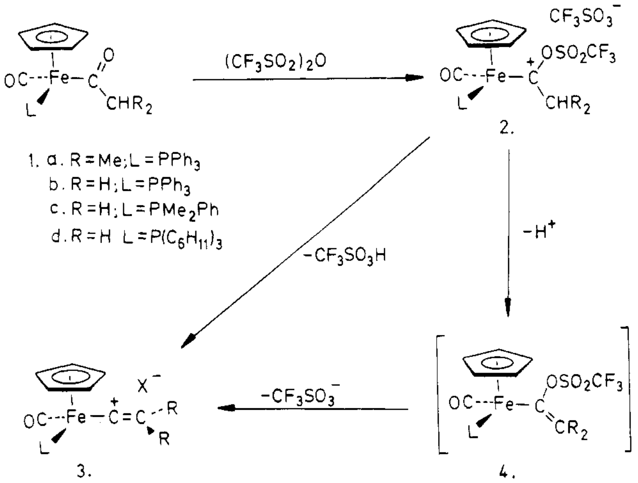
The syntheses and spectroscopic characterization of the vinylidene complexes $[Fe(\eta\text{-}C_5H_5)(CO)(L)(C{=}CR_2)]^+BF_4^-$ {L = PPh_3, R = Me, H; L = PMe_2Ph, $P(C_6H_{11})_3$, R = H}, from the acyl precursors $[Fe(\eta\text{-}C_5H_5)(CO)(L)\{C(O)CHR_2\}]$ and trifluoromethanesulfonic anhydride in the presence of $HBF_4{\cdot}Et_2O$, are described. An upper limit to the barrier for rotation about the Fe–C bond in $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CMe_2)]^+$ of 8.6 kcal·mol^{-1} is calculated. Reaction of $Li^+[Mn(\eta\text{-}C_5H_5)(CO)_2\{C(O)CH_3\}]^-$ with $(CF_3SO_2)_2O$ and 1,8-bis(dimethylamino)naphthalene affords $[Mn_2(\eta\text{-}C_5H_5)_2(CO)_4(\mu\text{-}C{=}CH_2)]$. Thermal decomposition of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ in CH_2Cl_2 solution affords the vinyl phosphonium compound $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(PPh_3){=}CH_2\}]^+BF_4^-$, whose molecular structure has been determined by X-ray crystallography (space group C_i^1–$P\bar{1}$, a = 9.517 (4) Å, b = 11.038 (3) Å, c = 18.965 (4) Å, α = 99.81 (2)°, β = 94.41 (3)°, γ = 102.54 (3)°, Z = 2). Other vinyl derivatives $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(Y){=}CH_2\}]^+BF_4^-$ (Y = PMe_2Ph, pyridine, 4-methylpyridine) have also been characterized. Deprotonation of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ with t-BuO$^-$ affords $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{\equiv}CH)]$, while reduction with BH_4^- leads to $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(CH{=}CH_2)]$.

Introduction

The stabilization of carbene ligands by coordination to a transition-metal center is a well-established phenomenon in organometallic chemistry. While numerous examples of neutral and cationic complexes containing carbene ligands with stabilizing heteroatoms α to the carbene carbon atom were synthesized after Fischer's pioneering work,[2] it was not until the discovery of $Ta(\eta\text{-}C_5H_5)_2(CH_3)(CH_2)$[3] and $W(CO)_5(CPh_2)$[4] that carbenes without such heteroatom stabilization became recognized as viable ligands. An even more recent development has seen the synthesis and characterization of a number of complexes containing unsaturated carbene, or vinylidene, ligands.

Chisholm and Clark initially proposed the intermediacy of a reactive cationic vinylidene complex of Pt, obtained by rearrangement of a coordinated terminal alkyne,[5] and almost concurrently the first reports of stable neutral complexes of Fe, Mo, and W containing bridging and terminal dicyanovinylidene ligands appeared.[6,7] Since that time a series of neutral and cationic mononuclear complexes of Cr,[7] Mn,[8-11,24] Re,[12] Fe,[13-17] Ru,[18-21] and Os[20-22] containing terminal vinylidene ligands has been reported; almost invariably the vinylidene ligand results either from

Scheme I



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[1] (a) Dartmouth College. (b) SUNY Buffalo. (c) Alfred P. Sloan Research Fellow 1980–1982. (d) Department of Chemistry, University of Delaware, Newark, DE 19711.

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$$\overset{+}{M}=C=CR_2 \longleftrightarrow M-\overset{+}{C}=CR_2$$

Figure 1. Canonical forms representing (A) a cationic metal vinylidene complex and (B) a metal-substituted vinyl cation.

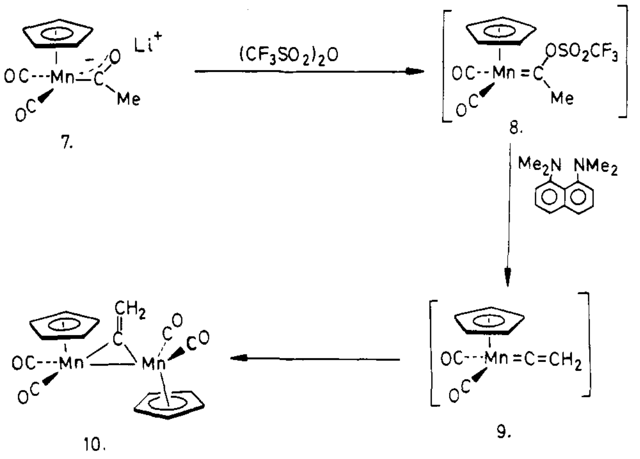
the rearrangement of a coordinated terminal alkyne or by the electrophilic protonation or alkylation of the β-carbon atom of an alkynylmetal complex. Examples of substituted allenylidene complexes of Cr,[7,23] W,[23] Ru,[24] and Mn[25] have also been reported.

Cationic transition-metal vinylidene complexes can be regarded as metal stabilized vinyl cations (Figure 1). A particularly useful route to organic vinyl cations has involved dissociation of the super leaving group triflate ($CF_3SO_3^-$, OTf^-) from vinyl triflates; the vinyl triflate precursors are readily available by the reaction of the oxygen atom of enolate anions with triflic anhydride [$(CF_3SO_2)_2O$, Tf_2O].[26,27] The known nucleophilicity of the acyl oxygen atom in neutral[28,29] and anionic[2] transition-metal acyl complexes suggested a similar route to cationic and neutral organometallic vinylidene complexes. This paper presents the results of our synthetic and spectroscopic studies, together with some characteristic reaction chemistry. A preliminary account of some of these results has already appeared,[30a] and further reaction chemistry of cationic vinylidene complexes of Fe is presented in the following paper.[30b]

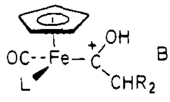
Results and Discussion

Synthesis and Spectroscopic Characterization of Vinylidene Complexes. In a preliminary communication[30a] we reported IR and ^1H NMR observations of the reactions of the acyl complexes **1a–c** with Tf_2O in either CH_2Cl_2 or $CDCl_3$ solution. The spectroscopic evidence clearly indicated the clean, quantitative and rapid formation of the cationic carbene complexes **2**, followed by a relatively slow, spontaneous elimination of the elements of triflic acid to produce the vinylidene complexes **3**. Analogous observations have since been made by using the tricyclohexylphosphine complex **1d**. It is not known whether the elimination of HOTf from **2** occurs by sequential loss of H^+, to give the vinyl triflates **4**, followed by loss of triflate anion to give the final product, or whether a concerted elimination occurs. Generation of **3b** by this route in $CDCl_3$ solution allowed a $^{13}C\{^1H\}$ NMR spectrum of this complex to be recorded. The α-vinylidene carbon resonance was observed as a doublet at δ 372.38 (J_{P-C} = 29.3 Hz), corresponding well with the reported chemical shifts of δ 363.0 (t, J_{P-C} = 33.3 Hz) and δ 358.9 (t, J_{P-C} = 24 Hz) for the corresponding α-carbon resonances in $[Fe(\eta\text{-}C_5H_5)(dppe)(C{=}CMe_2)]^{+}$ [15] and $[Ru(\eta\text{-}C_5H_5)(PPh_3)_2(C{=}CHPh)]^{+}$ [20], respectively.

Scheme II



While the methodology outlined in Scheme I allowed the characterization of the vinylidene complexes **3** (X = $CF_3SO_3^-$) as stable solution species, it proved impossible to obtain crystalline materials upon evaporation of solutions of these triflate salts; only oily solids were obtained. However, a modification of the reaction procedure did allow for the isolation of clean tetrafluoroborate salts **3** (X = BF_4^-). Addition of excess $HBF_4{\cdot}Et_2O$ to diethyl ether solutions of the acyl precursors **1** caused immediate precipitation of oils, which are presumably the hydroxycarbene complexes **5**;[28] subsequent addition of triflic anhydride to these reaction mixtures effected slow dissolution of the oils and subsequent precipitation of the vinylidene complexes **3a–d** (X = BF_4^-) as microcrystalline solids. These compounds were spectroscopically identical with those previously characterized in solution, except for the presence of strong IR bands at 1050–1100 cm⁻¹ and ^{19}F NMR singlet resonances at ca. δ 154 (upfield from internal $CFCl_3$), characteristic of the BF_4^- anion.[31] No ^{19}F NMR resonances at δ 78 due to the $CF_3SO_3^-$ anion were observed.[32]



5.

A low-temperature ^1H NMR study of complex **3a** failed to freeze out rotation of the dimethylvinylidene ligand around the Fe–C bond axis at −100 °C, the lowest temperature which could be reached before freezing of the solution or crystallization of the solute occurred. Theoretical calculations[33] indicate that the ground state of the cationic vinylidene complexes **3** should be as depicted in Scheme I, with nonequivalent R substituents. The observation of a single sharp methyl resonance for **3a** at −100 °C can only mean that rotation is fast even at this tem-

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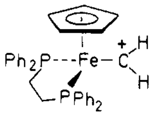
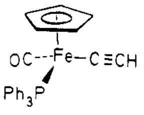
perature, in accord with the predictions of theory.[33] An upper limit to the free energy of activation for vinylidene rotation of between 8 and 9 kcal·mol^{-1} can be calculated.[34] In comparison, $\Delta G^{\ddagger}$ for methylene rotation in cation **6** has been observed to be 10.4 ± 0.1 kcal·mol^{-1}.[35,36]



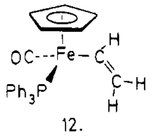
6.

Modification of the synthetic methodology already outlined provided a useful new route to a neutral vinylidene complex as shown in Scheme II. An ether suspension of the anionic manganese acyl **7**[37] reacted with triflic anhydride to give an orange solution of a compound presumed to have structure **8**, on the basis of two strong IR bands at 1960 and 1897 cm^{-1} characteristic of alkoxycarbene complexes of manganese.[37] This compound was too unstable to be isolated but reacted in situ with the non-nucleophilic base 1,8-bis(dimethylamino)naphthalene[40] to eliminate CF_3SO_3H and produce as the final product the μ-vinylidene complex **10**, presumably via the intermediacy of the mononuclear complex **9**. The facile thermal conversion of terminal vinylidene complexes of manganese to the corresponding μ-vinylidene compounds has already been documented.[9,11] Complex **10** produced in this manner was spectroscopically identical (IR, ^{1}H NMR) with that reported in the literature.[11]

Deprotonation and Reduction of [Fe(η-C_5H_5)(CO)(PPh_3)(C=CH_2)]$^+$$BF_4^-$. The unsubstituted vinylidene ligand of complex **3b** was readily deprotonated by treatment with a solution of *t*-BuOK in *t*-BuOH to afford good yields of the previously unknown alkynyl complex **11**.[41] This compound exhibited a medium intensity IR band at 1933 cm^{-1} ($\nu_{C\equiv C}$) and a doublet resonance in the ^{1}H NMR spectrum at δ 2.35 (J_{P-H} = 2.7 Hz); these data are entirely compatible with those reported for the closely related compound [Fe(η-C_5H_5)(dppe)(C≡CH)].[15] A similar deprotonation of [Ru(η-C_5H_5)(PPh_3)$_2$(C=CHPh)]$^+$ to afford the corresponding alkynylruthenium complex has been reported.[20] In our particular system the overall conversion of the acyl complex **1b** to **11** represents the net dehydration of a ketone.



11.



12.

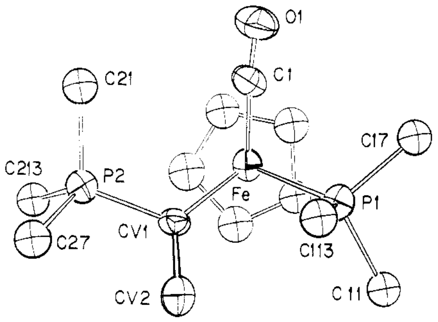
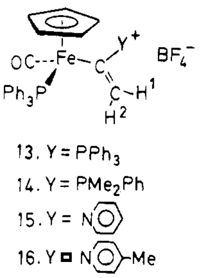


Figure 2. View of the structure of the cation [Fe(η-C_5H_5)(CO)(PPh_3){C(PPh_3)=CH_2}]$^+$ with numbering scheme.

Treatment of **2b** with $NaBH_4$ in CH_2Cl_2 solution at −78 °C afforded the known vinyl complex **12**[42] resulting from hydride addition to the cationic α-carbon atom.[43] Notably the related cationic compound [Fe(η-C_5H_5)(dppe)(C=CMe_2)]$^+$ is reported to be reactive toward BH_4^-[44] although cleaner reduction to give the corresponding substituted vinyl derivative was achieved by using $BH(OMe)_3^-$.[44,45]

Thermal Decomposition of [Fe(η-C_5H_5)(CO)(PPh_3)(C=CH_2)]$^+$$BF_4^-$ and Formation of Tertiary Phosphine and Pyridine Adducts. Gentle warming (40 °C) of CH_2Cl_2 solutions of **3b** led to partial decomposition and formation of the vinylphosphonium compound **13**; the molecular structure of this complex was verified by an X-ray crystallographic investigation described below. Analogous adducts **14**–**16** were prepared in high yields by the reaction of **3b** with the appropriate donor molecule. Notably the ^{1}H NMR spectra of the adducts **13** and **14** exhibited vinylic proton signals, coupled to a single phosphorus center, with coupling constants very similar to those reported for the vinylphosphonium derivative (Ph_3PCD=CH_2)$^+$Br$^-$.[46] Clearly, compound **3b** is thermally labile in solution and decomposes to release PPh_3 which is trapped by the carbonium ion center of a further molecule of **3b**. The observed reactions of PMe_2Ph, pyridine, and 4-methylpyridine add credence to this hypothesis. Reactions of **3b** with other amines are described separately.[30b]



13. Y = PPh_3
14. Y = PMe_2Ph
15. Y =
16. Y =

A compound [Fe(η-C_5H_5)(CO)$_2${C(PPh_3)=CHPh}]$^+$$BF_4^-$, analogous to **13**, has been synthesized by the low-temperature protonation of [Fe(η-C_5H_5)(CO)$_2$(C≡CPh)] in the presence of PPh_3.[47] The authors proposed that an intermediate vinylidene compound [Fe(η-C_5H_5)(CO)$_2$(C=CHPh)]$^+$ was formed and was trapped with PPh_3 at the α-carbon atom; our results clearly substantiate this proposal.

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(34) For the coalescence formula used see: Anet, F. A. L.; Brown, A. J. R. *J. Am. Chem. Soc.* **1967**, *89*, 760. The coalescence temperature was assumed to be 173 K, the separation of methyl resonances at the slow exchange limit was assumed to be 53 Hz (the methyl resonance separation in the acyl complex **1a**) and the frequency factor *A* was taken as 10^{12} (see ref 35).

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(36) Theory predicts a lower $\Delta G^{\ddagger}$ for vinylidene rotation than for methylene rotation in analogous systems.[33]

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(38) The alternative formulation of **8** as the triflate salt of the cationic carbyne complex [Mn(η-C_5H_5)(CO)$_2$(CMe)]$^+$ was discounted due to its solubility in Et_2O and the absence of ν_{CO} bands above 2000 cm^{-1} which are characteristic of cationic carbyne complexes of this type.[39]

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(41) This deprotonation can also be carried out cleanly by using Me_3N.[30b]

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(43) This reduction cannot be carried out in THF solution since **2b** reacts with this solvent.[30b]

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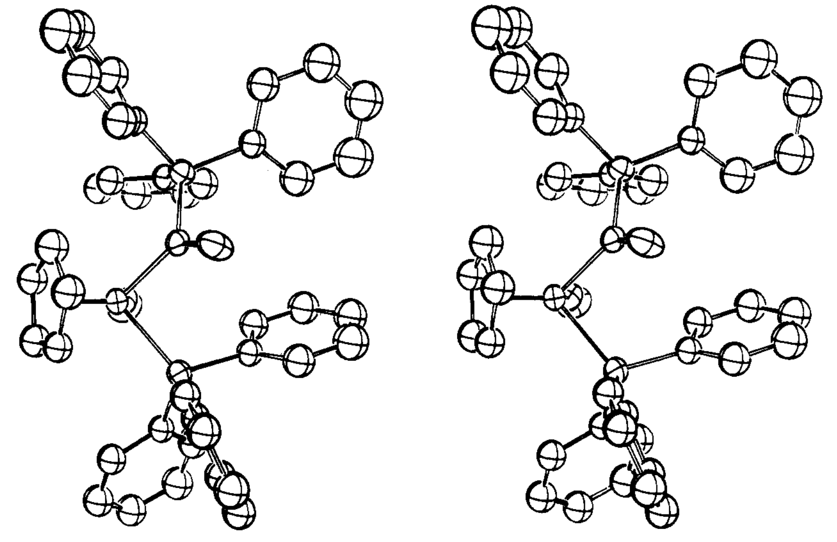

Figure 3. Stereoview of the structure of the cation $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(PPh_3){=}CH_2\}]^+$.

Molecular Structure of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(PPh_3){=}CH_2\}]^+BF_4^-$ (13). Final positional parameters appear in Table I, and final anisotropic thermal parameters are listed in Table II. Interatomic distances and their estimated standard deviations (esd's) are shown in Table III, and interatomic angles are presented in Table IV. The labeling scheme and stereoviews of the cation $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(PPh_3){=}CH_2\}]^+$ are shown in Figures 2 and 3, respectively.

The structure of the cation $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(PPh_3){=}CH_2\}]^+$ is similar in most respects to that determined by Kolobova et al. for $[Fe(\eta\text{-}C_5H_5)(CO)_2\{C(PPh_3){=}CHPh\}]^+$[47] and differs significantly only in the absence of the 2-vinylphenyl group and the replacement of one of the CO ligands by PPh_3. These differences do not result in any major changes in the molecular framework. In both structures the vinyl group is exclusively σ bonded; for the present structure, Fe–CV(1) = 2.014 (7) and Fe···CV(2) = 2.992 (8) Å. Neither structure reveals clear indication for localization of positive charge at a site other than the phosphonium phosphorus atom. In both structures the average P–C distance in the phosphonium group is 1.800 (8) Å, a value similar to that found in simpler phosphonium salts (e.g., $[Ph_3PCH_2Ph]^+Cl^-$, P–C(av) = 1.790 Å)[48] and 0.04 Å shorter than normally found in tertiary phosphines.[49]

Experimental Section

General Remarks. Infrared spectra were recorded on a Perkin-Elmer 257 instrument and calibrated against the 1601-cm^{-1} band of polystyrene. ^1H NMR (59.75 MHz), ^{13}C NMR (15.00 MHz) and ^{19}F NMR (56.20 MHz) spectra were recorded on a JEOL FX-60Q Fourier Transform spectrometer. Certain ^1H NMR spectra (270 MHz) were recorded on a Brüker HX-270 instrument at the NSF-NMR Regional Facility at Yale University. All NMR spectra were run in $CDCl_3$ solution. Cation mass spectra of organometallic salts were obtained by field desorption or fast atom bombardment techniques at the Middle Atlantic Mass Spectrometry Regional Facility at Johns Hopkins University School of Medicine. Microanalyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI, or Atlantic Microlab, Inc., Atlanta, GA.

Reaction solvents were distilled from sodium benzophenone ketyl, except for CH_2Cl_2 and $CDCl_3$ which were distilled from P_4O_{10}. All reactions were performed under an atmosphere of dry nitrogen.

Trifluoromethanesulfonic anhydride (Tf_2O) were prepared by the method of Stang and Duebner.[50] $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)CHMe_2\}]$ (**1a**), $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)Me\}]$ (**1b**), $[Fe(\eta\text{-}C_5H_5)(CO)(PMe_2Ph)\{C(O)Me\}]$ (**1c**), and $[Fe(\eta\text{-}C_5H_5)(CO)\{P(C_6H_{11})_3\}\{C(O)Me\}]$ (**1d**) were prepared by literature procedures.[51]

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CMe_2)]^+BF_4^-$ (3a). To a stirring solution of **1a** (0.10 g, 0.21 mmol) in Et_2O (25 mL) was added $HBF_4{\cdot}Et_2O$ (Aldrich, 0.06 mL, 0.53 mmol) in a dropwise fashion. A yellow oil precipitated. Dropwise addition of Tf_2O (0.10 mL, 0.62 mmol) caused the oil to slowly redissolve and a peach-colored solid to precipitate. After the solution was stirred (3 h, 20 °C), the solid was allowed to settle and the supernatant liquid was removed by using a cannula. The solid was washed with Et_2O (2 × 20 mL), the washings being removed by cannula, and dried under vacuum to give pure product: 0.104 g 90%; mp 135–136 °C dec; IR (Nujol) ν_{CO} 2030 (vs), $\nu_{C=C}$ 1621 (m), $\nu_{BF_4^-}$ 1030–1100 (vs) cm^{-1}; ^1H NMR δ 5.30 (d, J_{PH} = 1.2 Hz, C_5H_5), 7.50 (m, PPh_3), 1.66 (s, CMe_2); ^{19}F NMR δ 153.3 (s, BF_4^-). Anal. C, H. The ^1H NMR spectrum of **3a** was invariant down to −100 °C in a 1:1 $CDCl_3/Tf_2O$ solution.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ (3b) was prepared similarly from **1b** (0.10 g, 0.22 mmol), $HBF_4{\cdot}Et_2O$ (0.07 mL, 0.55 mmol), and Tf_2O (0.11 mL, 0.66 mmol) in Et_2O (25 mL), as a yellow-gold solid: 0.10 g, 90%; mp 154–155 °C dec; IR (Nujol) ν_{CO} 2035 (vs), $\nu_{C=C}$ 1630 (m), $\nu_{BF_4^-}$ 1035–1110 (vs) cm^{-1}; ^1H NMR δ 5.25 (d, J_{PH} = 2.0 Hz, C_5H_5), 7.50 (m, PPh_3), 5.30 (s, CH_2); ^{19}F NMR δ 149.5 (BF_4^-); ^{13}C NMR δ 92.03 (C_5H_5), 107.14 ($C{=}\mathit{C}H_2$), 128–134 (Ph), 209.40 (d, J_{PC} = 26.9 Hz, CO), 372.38 (d, J_{PC} = 29.3 Hz, $\mathit{C}{=}CH_2$). Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)(PMe_2Ph)(C{=}CH_2)]^+BF_4^-$ (3c) was prepared similarly from **1c** (0.10 g, 0.30 mmol), $HBF_4{\cdot}Et_2O$ (0.10 mL, 0.75 mmol), and Tf_2O (0.15 mL, 0.90 mmol) in Et_2O (25 mL), as a lime-green solid: 0.09 g, 70%; mp 130–134 °C dec; IR (Nujol) ν_{CO} 2030 (vs), $\nu_{C=C}$ 1633 (m), $\nu_{BF_4^-}$ 1030–1100 (vs) cm^{-1}; ^1H NMR δ 5.20 (d, J_{PH} = 2.0 Hz, C_5H_5), 7.40 (m, Ph), 2.08 (d, J_{PH} = 11.0 Hz, P-Me), 1.98 (d, J_{PH} = 11.0 Hz, P-Me), 5.41 (s, $C\mathit{H}_2$); ^{19}F NMR δ 154.0 (BF_4^-). Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)\{P(C_6H_{11})_3\}(C{=}CH_2)]^+BF_4^-$ (3d) was prepared similarly from **1d** (0.10 g, 0.18 mmol), $HBF_4{\cdot}Et_2O$ (0.06 mL, 0.45 mmol), and Tf_2O (0.09 mL, 0.54 mmol) in Et_2O (30 mL), as a lime-green solid: 0.09 g, 88%; mp 170 °C dec; IR (Nujol) ν_{CO} 2020 (vs), $\nu_{C=C}$ 1629 (m), $\nu_{BF_4^-}$ 1020–1110 (vs) cm^{-1}; ^1H NMR δ 5.46 (d, J_{PH} = 2.0 Hz, C_5H_5), 1.50 (m, C_6H_{11}), 5.36 (s, CH_2); ^{19}F NMR δ 153.5 (BF_4^-). Anal. C, H.

$[Mn_2(\eta\text{-}C_5H_5)_2(CO)_4(\mu\text{-}C{=}CH_2)]$ (10). A suspension of $Li[Mn(\eta\text{-}C_5H_5)(CO)_2\{C(O)Me\}]$[37] (3.16 g, 14 mmol) in Et_2O (50 mL) was cooled to −78 °C, and Tf_2O (3.70 mL, 21 mmol) was added dropwise. The resultant mixture was warmed to 20 °C to afford

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Table I. Positional Parameters (and Esd's) for $Fe(CP)(CO)PPh_3\{C(PPh_3)=CH_2\}^2$

atom	x	y	z	B, Å^2
Fe	0.763 92 (11)	0.289 23 (10)	0.315 49 (6)	
P1	0.869 56 (21)	0.192 73 (19)	0.391 76 (11)	
P2	0.705 02 (20)	0.118 92 (20)	0.145 91 (11)	
C1	0.598 27 (91)	0.191 22 (78)	0.325 68 (41)	
O1	0.490 49 (64)	0.139 14 (59)	0.340 05 (31)	
Cp1	0.725 08 (94)	0.455 60 (77)	0.377 33 (46)	
Cp2	0.654 97 (89)	0.434 74 (76)	0.306 54 (52)	
Cp3	0.758 4 (10)	0.435 98 (72)	0.258 59 (42)	
Cp4	0.896 24 (90)	0.460 29 (74)	0.299 36 (56)	
Cp5	0.874 22 (89)	0.470 81 (72)	0.371 66 (46)	
CV1	0.821 90 (74)	0.184 35 (69)	0.229 84 (37)	
CV2	0.954 92 (88)	0.170 43 (84)	0.221 29 (41)	
C11	1.063 46 (74)	0.255 23 (70)	0.427 99 (39)	2.86 (15)
C12	1.157 20 (77)	0.327 17 (72)	0.391 61 (40)	3.25 (16)
C13	1.305 78 (82)	0.363 19 (78)	0.415 76 (43)	3.76 (17)
C14	1.356 15 (85)	0.325 77 (80)	0.476 47 (45)	4.05 (18)
C15	1.264 54 (84)	0.268 27 (78)	0.513 79 (44)	3.85 (17)
C16	1.116 26 (81)	0.220 99 (76)	0.490 42 (42)	3.57 (17)
C17	0.786 30 (76)	0.189 31 (71)	0.474 79 (39)	3.01 (15)
C18	0.786 70 (83)	0.304 60 (78)	0.520 53 (43)	3.73 (17)
C19	0.728 04 (87)	0.305 80 (83)	0.585 77 (46)	4.39 (19)
C110	0.666 85 (91)	0.196 68 (88)	0.605 54 (48)	4.60 (19)
C111	0.663 66 (93)	0.081 98 (91)	0.562 57 (50)	5.07 (20)
C112	0.724 75 (89)	0.079 39 (84)	0.497 32 (47)	4.42 (19)
C113	0.860 91 (77)	0.025 00 (72)	0.356 86 (39)	3.05 (15)
C114	0.726 64 (84)	−0.057 12 (80)	0.330 01 (44)	3.93 (17)
C115	0.715 76 (92)	−0.184 31 (87)	0.301 10 (48)	4.63 (19)
C116	0.841 0 (10)	−0.225 74 (91)	0.296 99 (50)	5.08 (20)
C117	0.974 4 (10)	−0.147 68 (94)	0.321 07 (52)	5.34 (21)
C118	0.985 94 (86)	−0.019 96 (82)	0.351 31 (45)	4.27 (19)
C21	0.519 04 (77)	0.065 68 (74)	0.159 67 (48)	3.18 (16)
C22	0.461 18 (93)	−0.058 88 (88)	0.162 13 (48)	4.76 (20)
C23	0.316 6 (11)	−0.093 6 (10)	0.179 39 (55)	6.11 (24)
C24	0.240 1 (10)	−0.004 0 (10)	0.193 49 (52)	5.47 (22)
C25	0.296 1 (10)	0.118 55 (92)	0.191 58 (50)	5.11 (20)
C26	0.437 47 (85)	0.155 46 (80)	0.174 41 (43)	3.98 (18)
C27	0.762 41 (77)	−0.013 22 (74)	0.095 87 (41)	3.25 (16)
C28	0.794 14 (95)	−0.104 29 (92)	0.131 35 (50)	4.95 (20)
C29	0.840 0 (11)	−0.208 0 (10)	0.094 30 (59)	6.55 (25)
C210	0.853 7 (10)	−0.214 9 (10)	0.023 49 (55)	5.92 (23)
C211	0.829 3 (10)	−0.125 43 (94)	−0.011 98 (52)	5.40 (21)
C212	0.780 39 (87)	−0.022 10 (83)	0.023 86 (46)	4.22 (18)
C213	0.714 78 (80)	0.235 11 (74)	0.089 82 (40)	3.33 (16)
C214	0.596 73 (93)	0.233 17 (88)	0.040 29 (40)	4.83 (20)
C215	0.609 7 (11)	0.322 7 (10)	−0.004 56 (55)	5.99 (23)
C216	0.735 9 (11)	0.410 8 (10)	−0.000 16 (57)	6.26 (24)
C217	0.852 5 (10)	0.414 71 (94)	0.048 33 (52)	5.44 (21)
C218	0.842 00 (88)	0.325 90 (83)	0.092 50 (46)	4.38 (19)
F1	0.382 7 (14)	0.604 9 (12)	0.206 45 (81)	
F2	0.282 5 (10)	0.456 3 (10)	0.258 34 (42)	
F3	0.202 8 (16)	0.435 3 (14)	0.149 54 (67)	
F4	0.180 9 (14)	0.574 2 (12)	0.202 87 (94)	
F5	0.384 1 (21)	0.451 1 (21)	0.163 6 (10)	
B	0.285 64 (0)	0.510 89 (0)	0.191 22 (0)	7.64 (62)
HCV21	1.029 78 (0)	0.200 00 (0)	0.260 52 (0)	6.0000 (0)
HCV22	0.975 32 (0)	0.130 90 (0)	0.175 93 (0)	6.0000 (0)
HCp1	0.680 28 (0)	0.458 76 (0)	0.420 47 (0)	6.0000 (0)
HCp2	0.553 61 (0)	0.421 95 (0)	0.293 74 (0)	6.0000 (0)
HCp3	0.740 02 (0)	0.422 88 (0)	0.207 58 (0)	6.0000 (0)
HCp4	0.986 97 (0)	0.467 98 (0)	0.280 74 (0)	6.0000 (0)
HCp5	0.948 08 (0)	0.485 85 (0)	0.410 91 (0)	6.0000 (0)
HC12	1.121 26 (0)	0.352 77 (0)	0.349 79 (0)	6.0000 (0)
HC13	1.370 94 (0)	0.412 88 (0)	0.390 50 (0)	6.0000 (0)
HC14	1.457 15 (0)	0.347 91 (0)	0.492 31 (0)	6.0000 (0)
HC15	1.301 16 (0)	0.235 73 (0)	0.556 50 (0)	6.0000 (0)
HC16	1.052 06 (0)	0.172 82 (0)	0.516 78 (0)	6.0000 (0)
HC18	0.827 41 (0)	0.382 31 (0)	0.506 71 (0)	6.0000 (0)
HC19	0.731 29 (0)	0.384 18 (0)	0.616 47 (0)	6.0000 (0)
HC110	0.625 44 (0)	0.198 87 (0)	0.649 62 (0)	6.0000 (0)
HC111	0.620 60 (0)	0.005 33 (0)	0.576 89 (0)	6.0000 (0)
HC112	0.723 64 (0)	0.000 17 (0)	0.468 06 (0)	6.0000 (0)
HC114	0.641 27 (0)	−0.025 81 (0)	0.331 45 (0)	6.0000 (0)
HC115	0.623 97 (0)	−0.240 58 (0)	0.284 73 (0)	6.0000 (0)
HC116	0.834 86 (0)	−0.311 82 (0)	0.276 66 (0)	6.0000 (0)
HC117	1.059 16 (0)	−0.179 56 (0)	0.317 41 (0)	6.0000 (0)
HC118	1.078 29 (0)	0.035 14 (0)	0.367 81 (0)	6.0000 (0)
HC22	0.516 57 (0)	−0.120 52 (0)	0.152 49 (0)	6.0000 (0)

Table I (*Continued*)

atom	*x*	*y*	*z*	*B*, Å^2
HC23	0.274 19 (0)	−0.179 27 (0)	0.180 99 (0)	6.0000 (0)
HC24	0.143 86 (0)	−0.028 14 (0)	0.205 10 (0)	6.0000 (0)
HC25	0.239 90 (0)	0.179 37 (0)	0.201 85 (0)	6.0000 (0)
HC26	0.477 60 (0)	0.241 48 (0)	0.172 80 (0)	6.0000 (0)
HC28	0.785 07 (0)	−0.097 30 (0)	0.181 33 (0)	6.0000 (0)
HC29	0.860 90 (0)	−0.271 66 (0)	0.118 61 (0)	6.0000 (0)
HC210	0.881 71 (0)	−0.285 94 (0)	−0.002 05 (0)	6.0000 (0)
HC211	0.844 74 (0)	−0.131 31 (0)	−0.061 22 (0)	6.0000 (0)
HC212	0.760 12 (0)	0.040 63 (0)	−0.001 37 (0)	6.0000 (0)
HC214	0.508 45 (0)	0.171 54 (0)	0.037 15 (0)	6.0000 (0)
HC215	0.529 94 (0)	0.321 72 (0)	−0.038 16 (0)	6.0000 (0)
HC216	0.743 70 (0)	0.470 54 (0)	−0.031 10 (0)	6.0000 (0)
HC217	0.939 59 (0)	0.477 77 (0)	0.051 58 (0)	6.0000 (0)
HC218	0.923 46 (0)	0.327 34 (0)	0.125 16 (0)	6.0000 (0)

[a] Esd's are right-justified to the least significant figure of the parameter.

Table III. Selected Interatomic Distances (Å) with Esd's for $[Cp(CO)(PPh_3)FeC(PPh_3){=}CH_2]^+BF_4^-$

(A) $[Cp(CO)(PPh_3)FeC(PPh_3){=}CH_2]^+$

Fe-P (1)	2.237 (2)	P(1)-C(17)	1.819 (8)
Fe-C(1)	1.752 (9)	P(1)-C(113)	1.839 (8)
Fe-Cp(av)	2.112 (9)	P(2)-CV(1)	1.811 (7)
Fe-CV(1)	2.014 (7)	P(2)-C(21)	1.794 (8)
Fe···CV(2)	2.992 (8)	R(2)-C(27)	1.811 (8)
C(1)-O(1)	1.139 (11)	P(2)-C(213)	1.793 (8)
P(1)-C(11)	1.856 (8)	CV(1)-CV(2)	1.327 (11)

(B) BF_4^-

B-F(1)	1.206 (13)	B-F(4)	1.346 (14)
B-F(2)	1.498 (9)	B-F(5)	1.347 (21)
B-F(3)	1.156 (14)	B-F(av)	1.311 (14)

Table IV. Selected Interatomic Angles (Deg) with Esd's for $[Cp(CO)(PPh_3)FeC(PPh_3){=}CH_2]^+BF_4^-$

(A) $[Cp(CO)(PPh_3)Fe\text{-}C(PPh_3){=}CH_2]^+$

P(1)-Fe-CV(1)	91.6 (2)	Fe-CV(1)-P(2)	123.8 (4)
C(1)-Fe-CV(1)	100.9 (4)	Fe-CV(1)-CV(2)	125.9 (6)
P(1)-Fe-C(1)	87.4 (3)	P(2)-CV(1)-CV(2)	109.4 (6)
Fe-C(1)-O(1)	171.0 (8)		

(B) BF_4^-

F(1)-B-F(2)	104.2 (8)	F(2)-B-F(4)	97.6 (7)
F(1)-B-F(3)	151 (1)	F(2)-B-F(5)	95 (1)
F(1)-B-F(4)	94.1 (9)	F(3)-B-F(4)	88 (1)
F(1)-B-F(5)	86.7 (1)	F(3)-B-F(5)	85 (1)
F(2)-B-F(3)	103.8 (8)	F(4)-B-F(5)	167 (1)

an orange, homogeneous solution. This solution was recooled to −78 °C, a solution of 1,8-bis(dimethylamino)naphthalene (2.98 g, 14 mmol) in Et_2O (10 mL) was added dropwise, and the resultant mixture was warmed slowly to 20 °C. After being stirred for 1 h, the mixture was filtered by using filter aid to give a solid, characterized as the hydrotriflate salt of 1,8-bis(dimethylamino)naphthalene by IR comparison with an authentic sample prepared from the naphthalene derivative and HOTf. Ether was removed from the filtrate under vacuum, to afford a red-purple residue which was chromatographed on a 150 × 2 cm alumina (activity III)/hexane column. Hexane eluted $[Mn(\eta\text{-}C_5H_5)(CO)_3]$ (0.85 g) and a 1:1 hexane/Et_2O mixture eluted a purple band, which upon removal of the solvent yielded **10** (1.11 g, 42%). The IR and ^1H NMR data for **10** corresponded exactly with those reported in the literature.[11]

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{\equiv}CH)]$ (11). A suspension of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ (0.350 g, 0.66 mmol) in *t*-BuOH (10 mL) was treated with a solution of *t*-BuO^-K^+ (0.230 g, 1.98 mmol) in *t*-BuOH (16 mL), and the resultant mixture was stirred for 0.5 h to give an orange solution. The solvent was removed under vacuum, and the residue was extracted with toluene (3 × 50 mL). The extracts were filtered and concentrated to ca. 20 mL under vacuum. Hexane (50 mL) was added, and the solution was set aside overnight at −20 °C to afford red-brown crystals of **11**: 0.19 g, 65%; mp 160 °C dec; IR (CCl_4) ν_{CO} 1957 (s), $\nu_{C{\equiv}C}$ 1933 (m) cm^{-1}; ^1H NMR δ 7.40 (m, Ph), 4.38 (d, J_{PH} = 1.2 Hz, C_5H_5), 2.35 (d, J_{PH} = 2.7 Hz, $C{\equiv}CH$). Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(CH{=}CH_2)]$ (12). A solution of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ (1.15 g, 2.2 mmol) in CH_2Cl_2 (25 mL) was cooled to −78 °C and solid $NaBH_4$ (0.50 g, 13.8 mmol) was added. The yellow slurry was stirred at −78 °C for 2 h and then allowed to warm to 20 °C, at which point gas evolution was observed and the solution became yellow-orange. The solvent was removed under vacuum, and the residue was extracted with benzene (20 mL) and filtered. The filtrate was reduced in volume to ca. 5 mL and applied to a 40 × 3 cm silica gel/hexane column. Hexane produced a yellow eluate, which was concentrated to ca. 15 mL and cooled to −50 °C to afford **12** as a yellow solid (0.38 g, 40%). The IR and ^1H NMR spectra of **12** were identical with those reported in the literature.[42]

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(PPh_3){=}CH_2\}]^+BF_4^-$ (13). A solution of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ (1.15 g, 2.2 mmol) in CH_2Cl_2 (50 mL) was refluxed for 24 h, cooled, and filtered. The resultant orange solution was reduced in volume to ca. 5 mL and applied to a 50 × 6 cm deactivated silica gel/Et_2O column. Elution with Et_2O produced traces of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)Me\}]$, and subsequent elution with CH_2Cl_2 developed a bright orange band, which afforded a dark orange residue on evaporation. Recrystallization from CH_2Cl_2/Et_2O gave **13** as large, bright orange crystals: 0.34 g, 40%; mp 174 °C dec; IR (CH_2Cl_2) ν_{CO} 1937 (s) cm^{-1}; ^1H NMR (numbering shown in text) δ 7.40 (m, Ph), 4.33 (d, J_{PH} = 1.2 Hz, C_5H_5), 6.47 (d, J_{PH} = 23.0 Hz, H^1), 6.63 (d, J_{PH} = 45.8 Hz, H^2); ^{13}C NMR δ 125–135 (Ph), 84.70 (C_5H_5), 120.18 ($C{=}\mathit{C}H_2$), 158.00 ($\mathit{C}{=}CH_2$), 215.60 (CO); mass spectrum (field desorption) *m/e* 671 $[Fe(\eta\text{-}C_5H_5)(PPh_3)\{C(PPh_3){=}CH_2\}]^+$. Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(PMe_2Ph){=}CH_2\}]^+BF_4^-$ (14). A solution of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ (1.15 g, 2.2 mmol) in CH_2Cl_2 (20 mL) was cooled to −78 °C, and PMe_2Ph (0.31 mL, 2.2 mmol) was added. The resultant red-orange solution was warmed to 20 °C and treated with Et_2O (100 mL) to precipitate an orange solid. The supernatant liquid was decanted off, and the solid was washed with Et_2O (2 × 20 mL). The product was purified by chromatography on a deactivated silica gel column, eluting with CH_2Cl_2, followed by recrystallization from CH_2Cl_2/Et_2O to give **14** as red orange crystals: 1.12 g, 80%; mp 165 °C dec; IR (CH_2Cl_2) ν_{CO} 1937 (s) cm^{-1}; ^1H NMR δ 7.40 (m, Ph), 4.38 (d, J_{PH} = 1.2 Hz, C_5H_5), 6.27 (d, J_{PH} = 23.2 Hz, H^1), 6.47 (d, J_{PH} = 53.0 Hz, H^2), 1.83 (d, J_{PH} = 11.0 Hz, PMe), 1.79 (d, J_{PH} = 11.0 Hz, PMe); ^{13}C NMR δ 125–135 (Ph), 85.10 (C_5H_5), 121.00 ($C{=}\mathit{C}H_2$), 150.80 ($\mathit{C}{=}CH_2$), 200.85 (CO), 10.17 (PMe), 9.53 (PMe). Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(NC_5H_5){=}CH_2\}]^+BF_4^-$ (15). Pyridine (15 mL) was added to $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ (1.15 g, 2.2 mmol), and the resultant dark orange solution was stirred for 3 h. Excess pyridine was removed under vacuum, and the residue was chromatographed on deactivated silica gel. A 1/1 mixture of $CH_2Cl_2/(CH_3)_2CO$ eluted an orange band. Removal of the solvents under vacuum and recrystallization of the residue twice from CH_2Cl_2/Et_2O afforded **15** as orange crystals: 1.04 g, 79%; mp 165 °C dec; IR (CH_2Cl_2) ν_{CO} 1937 (s)

Table V. Crystal and Refinement Data

formula	$FeP_2F_4OC_{45}BH_{37}$
fw	798.40
space group	C_i^1–$P\bar{1}$
a, Å	9.517 (4)
b, Å	11.038 (3)
c, Å	18.965 (4)
α, deg	99.81 (2)
β, deg	94.41 (3)
γ, deg	102.54 (3)
V, Å^3	1902.9
Z	2
ρ(obsd), ρ(calcd)^a	1.37, 1.39 g·cm^{-3}
temp.	23 °C
crystal dimension	0.26 × 0.30 × 0.35 mm
radiation	graphite-monochromated Mo $K\bar{\alpha}$ (λ = 0.710 73 Å)
diffractometer	Syntex $P2_1$
abs coeff, cm^{-1}	μ = 5.5
scan speed	3.0° in 2θ/min (fixed)
scan range, deg	$3.0 < 2\theta < 42$
scan technique	$\theta - 2\theta$
data collected	$h, \pm k, \pm l$
scan width, deg	[2θ (Mo $K\bar{\alpha}_1$) – 0.9] to [2θ(Mo $K\bar{\alpha}_2$) + 0.9]
ignorance factor	0.02
unique data	4107 rflns (4426 collected)
unique data with $(F_o)^2 > 3\sigma(F_o)^2$	3269

^{a} By flotation, CH_2I_2/cyclohexane.

cm^{-1}; ^{1}H NMR δ 7.50 (m, Ph, meta and para protons of C_5H_5N), 4.79 (d, J_{PH} = 1.3 Hz, C_5H_5), 5.50 (m, br, CH_2), 8.20 (m, ortho protons of C_5H_5N); ^{13}C NMR δ 130–133 (Ph), 87.9 (C_5H_5), 125.0 ($C{=}CH_2$), 162.0 (d, J_{PC} = 19.0, $C{=}CH_2$), 210.0 (CO), 127.5, 135.0, 141.0 (C_5H_5N). Anal. C, H, N (the molecules crystallize with 0.25 molecules CH_2Cl_2 of crystallization).

[Fe(η-C_5H_5)(CO)(PPh_3){C(4-MeC_5H_4N)=CH_2}]$^+BF_4^-$ (16) was prepared similarly from [Fe(η-C_5H_5)(CO)(PPh_3)(C=CH_2)]$^+BF_4^-$ (1.15 g, 2.2 mmol) and 4-methylpyridine (10 mL), as orange crystals: 1.11 g, 82%; mp 104 °C dec; IR (CH_2Cl_2) ν_{CO} 1937 (s) cm^{-1}; ^{1}H NMR δ 7.50 (m, Ph, meta protons of 4-MeC_5H_4N), 4.73 (d, J_{PH} = 1.3 Hz, C_5H_5), 5.43 (m, br, CH_2), 8.00 (m, ortho protons of 4-MeC_5H_4N), 2.48 (s, Me); ^{13}C NMR δ 132–134 (Ph), 85.5 (C_5H_5), 131.2 (d, J_{PC} = 4.0 Hz, $C{=}CH_2$), 155.1 (d, J_{PC} = 19.0 Hz, $C{=}CH_2$), 21.6, 127.6, 139.4, 141.0 (4-MeC_5H_4N). Anal. C, H, N (the molecules contain 0.75 molecules CH_2Cl_2 of crystallization).

X-ray Diffraction Measurements. Collection and Reduction. Specific details concerning crystal characteristics and X-ray diffraction methodology are shown in Table V. The crystal selected for study was an irregularly shaped fragment cleaved from a larger crystal and mounted on a glass fiber with "Crazy Glue". The crystal was centered on the diffractometer using 25 Friedel-related reflections with 20° < 2θ < 30°, and the cell dimensions were refined on these reflections to give the values shown in Table V.

Data were placed on an approximately absolute scale via a Wilson plot which provided the average overall thermal parameter ($\bar{B}$ = 2.95 Å^2).

Intensity data were collected and corrected for Lp effects and absorption as previously described.[52] The intensities of three reflections located along the reciprocal lattice axes were measured every 97 reflections to check crystal stability and alignment. No decay correction was required. Diffractometer examination of the reciprocal lattice revealed no systematic absences.

Solution and Refinement of the Structure. The structure was solved by the SHELEX direct methods routine and the heavy atoms located from the E map based on the phase solution of highest internal consistency. The remaining nonhydrogen atoms with the exception of the boron atom were located from a series of difference-Fourier syntheses, each being phased by an increasing number of atoms. All nonhydrogen atoms with the exceptions of the phenyl carbon atoms and the boron atom were refined with anisotropic thermal parameters.[53] Neutral atom scattering factors were used, and anomalous dispersion corrections were applied to all nonhydrogen atoms.[54]

Full-matrix least-squares refinement for all nonhydrogen atoms, except boron, of the scale factor and positional and thermal parameters led to convergence with R = 12.5% and R_w = 14.3%. A difference-Fourier map at this stage of refinement revealed a peak in the vicinity of the anion which was located in a position inconsistent with its identity being the still unlocated boron atom and more consistent with its being a "fifth" fluorine atom. Further refinement of all "five" fluorine atoms with variable occupancy led to the postulation of a model for the apparent disorder in the anion: two BF_4^- tetrahedra are oriented with parallel, shared interpenetrating bases and eclipsed vertices. Incorporation of this model in which the shared fluorine atoms, F(1)–F(3), were refined at unit occupancy, the apical fluorines, F(4) and F(5), at half occupancy, and the boron atom in an idealized, centered and fixed position (see Figure 4) lowered the discrepancy indices to R = 8.0% and R_w = 8.3%. The final refinement cycles included all hydrogen atoms at calculated positions with the C–H bond lengths fixed at 0.95 Å, the H–CV(1)–H bond angle fixed at 120°, and B = 6.0 Å^2.[55] At convergence, R = 7.4%, R_w = 7.6%, and GOF = 2.157. A final difference map showed a general background of approximately 0.2 e/Å^3 and a peak (0.84 e/Å^3) associated with the anion, and the residual $\sum w(|F_o| - |F_c|)^2$ showed no significant variation against $|F_o|$, (sin θ)/λ, or identity or parity of index or sequence number.

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Registry No. 1a, 32661-71-5; **1b**, 12101-02-9; **1c**, 32993-87-6; **1d**, 32610-55-2; **3a**, 80642-54-2; **3b**, 80642-55-3; **3c**, 80642-56-4; **3d**, 80642-58-6; **10**, 71616-07-4; **11**, 80642-59-7; **12**, 79292-33-4; **13**, 80658-43-1; **14**, 80642-61-1; **15**, 80642-63-3; **16**, 80642-65-5; Li[Mn(η-C_5H_5)$(CO)_2${C(O)Me}], 12082-24-5.

Supplementary Material Available: Observed and calculated structure factor tables, Table II, anisotropic thermal parameters, a full list of bond lengths, and Figure 4, the disordered BF_4^- ion (35 pages). Ordering information is given on any current masthead page.

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Organometallics 1982, *1*, 635–639

Reactions of the Cationic Iron Vinylidene Compound $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ with O–H, N–H, S–H, Cl–H, and C≡C Bonds

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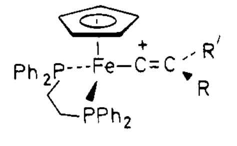
The cationic vinylidene compound $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)^+BF_4^-$, 1, reacts with a variety of alcohols (ROH) to produce cationic alkoxycarbene compounds $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(OR)Me\}]^+BF_4^-$ (R = Me, Et, *i*-Pr, $CH_2CH{=}CH_2$). The reaction of 1 with H_2S or MeSH affords analogous carbene compounds $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(SR)Me\}]^+BF_4^-$ (R = H, Me). While reaction of 1 with benzylamine yields only the aminocarbene compound $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(NHCH_2Ph)Me\}]^+BF_4^-$, the corresponding reactions with $MeNH_2$ or Me_2NH afford both the carbene complexes $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(NR'R)Me\}]^+BF_4^-$ (R = H, R' = Me; R = R' = Me) and the alkynyl complex $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{\equiv}CH)]$; reaction of 1 with Me_3N affords only this latter product. Dry HCl also adds across the vinylidene double bond of 1 to yield the chloromethylcarbene complex $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(Cl)Me\}]^+BF_4^-$. In tetrahydrofuran (THF) solution 1 reacts spontaneously to produce the μ-cyclobutenylidene complex $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(PPh_3)_2(\mu\text{-}C_4H_3)]^+BF_4^-$ as a 3:1 mixture of diastereoisomers, the meso form being dominant. In contrast, the related vinylidene complex $[Fe(\eta\text{-}C_5H_5)(CO)\{P(C_6H_{11})_3\}(C{=}CH_2)]^+BF_4^-$ reacts in THF to give only the *R,R:S,S* pair of enantiomers of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{P(C_6H_{11})_3\}_2(\mu\text{-}C_4H_3)]^+BF_4^-$.

Introduction

Previously, we have described a convenient synthetic procedure for the isolation of cationic vinylidene complexes of iron, $[Fe(\eta\text{-}C_5H_5)(CO)(L)(C{=}CR_2)]^+BF_4^-$ {L = PPh_3, R = H, Me; L = PMe_2Ph, $P(C_6H_{11})_3$, R = H}, by the reaction of the appropriate acyl precursor $[Fe(\eta\text{-}C_5H_5)(CO)(L)\{C(O)CHR_2\}]$ with $(CF_3SO_2)_2O$ in the presence of $HBF_4\cdot Et_2O$.[2] A separate communication described the solution characterization of these molecules.[3] The α-carbon atom of the vinylidene ligand in $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$, 1, was shown to be extremely reactive toward pyridine and tertiary phosphine nucleophiles, affording the vinyl derivatives $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(Y){=}CH_2\}]^+BF_4^-$ (Y = pyridine, 4-methylpyridine, PPh_3, PMe_2Ph); the molecular structure of one such complex was also determined.[2] Other workers have described related cationic vinylidene compounds 2 and 3 [M = Fe, Ru, Os] containing a variety of ligands L and L′ and a number of different vinylidene substituents R and R′.[4-8] The only previously reported example of a cationic complex containing the parent, unsubstituted vinylidene ligand was 2 (R = R′ = H).[4]



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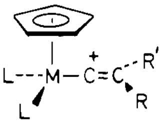


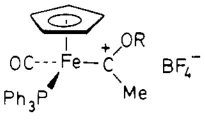
3.

Classic methods for trapping unstable intermediate organic vinyl cations have involved reactions with alcohols or water.[9] While complexes 2 (R = R′ = H, Me; R = Me, R′ = H) are reported to be unreactive toward water and alcohols,[4] as is the cationic vinylidene complex *trans*-$[Fe(dppe)_2Cl(C{=}CHPh)]^+$,[10] the corresponding compounds 3 (M = Fe, L = PPh_3, L′ = CO, R = H, R′ = Ph;[8] M = Ru, L′ = PPh_3, L = PPh_3, CO, *t*-BuNC, PMe_3, $P\{OMe\}_3$, R = H, R′ = Ph;[7] M = Ru, L = L′ = PPh_3, R = H, R′ = Me, CO_2Me)[7] have been shown to react with water and methanol to give respectively the neutral acyl compounds $[M(\eta\text{-}C_5H_5)LL'\{C(O)CHRR'\}]$ or the cationic alkoxycarbene compounds $[M(\eta\text{-}C_5H_5)LL'\{C(OMe)CHRR'\}]^+$. The rates of these reactions appear to be dependent upon both the steric and electronic properties of the ligands L and L′;[7] sterically demanding ligands block the reactive α-carbon site while good electron-donor ligands serve to enhance the ability of the metal to stabilize the α-carbonium ion center and result in slower reactions.

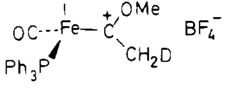
This paper presents results which demonstrate that $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$, 1, is highly reactive toward addition of OH, NH, SH, ClH, and C≡C functionalities across the double bond of the vinylidene ligand.

Results and Discussion

Reactions With O–H Bonds. Compound 1 reacted rapidly with water, or in moist organic solvents, to give the acetyl complex $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)Me\}]$. Similarly 1 dissolved in alcohols, ROH, to give bright yellow solutions from which the cationic alkoxycarbene complexes 5–8 could be isolated in high yields. Compound 1 was unreactive toward *t*-BuOH at 20 °C. An analogous reaction of 1 with CH_3OD afforded 9. The spectroscopic data



5. R = Me
6. R = Et
7. R = ^{i}Pr
8. R = $CH_2CH{=}CH_2$



9.

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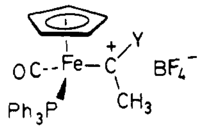
Table I. IR, ^{1}H NMR, and ^{19}F NMR Data for Cationic Carbene Compounds of Iron



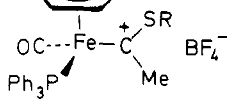
compd	ν_{CO},[a] cm^{-1}	δ(^{1}H)[b] PPh$_3$	C$_5$H$_5$[c]	Me	Y	δ(^{19}F)[d] (BF$_4^-$)
5	1985	7.57 (m)	4.89 (d, 1.5)	2.84 (s)	3.98 (s)	153.3 (s)
6	1983	7.54 (m)	4.88 (d, 1.5)	2.83 (s)	4.25 (m, CH$_2$) 1.40 (t, J = 7 Hz, Me)	153.6 (s)
7	1973	7.53 (m)	4.80 (d, 1.5)	2.95 (s)	3.40 (m, C*H*Me$_2$) 1.40 (d, J = 6 Hz, CH*Me*$_2$) 1.05 (d, J = 6 Hz, CH*Me*$_2$)	154.0 (s)
8	1977	7.55 (m)	4.88 (d, 1.3)	2.88 (s)	5.77 (m, C*H*=CH$_2$) 5.51 (m, CH=C*H*$_2$) 5.31 (m, CH=CH$_2$) 4.65 (d, J = 6 Hz, OCH$_2$)	154.0 (s)
9	1985	7.57 (m)	4.90 (d, 1.5)	2.83 (t)[e]	3.98 (s)	153.3 (s)
10	1975	7.55 (m)	4.90 (d, 1.2)	2.60 (s)	4.32 (s, br)	[f]
11	1975	7.55 (m)	4.95 (d, 1.2)	2.61 (s)	3.19 (s)	154.0 (s)
12	1975 (3450)[g]	7.50 (m)	4.82 (d, 1.3)	2.34 (s)	10.81 (s, br, NH) 4.67 (d, J = 5 Hz, CH$_2$) 7.50 (m, Ph)	153.6 (s)
13	1950 (3450)[g]	7.60 (m)	4.77 (d, 1.3)	2.14 (s)	9.90 (s, br, NH) 2.98 (d, J = 5 Hz, Me)	153.9 (s)
14	1950	7.60 (m)	4.79 (d, 1.3)	2.37 (s)	3.34 (s, Me) 3.94 (s, Me)	153.8 (s)
16	1990	7.55 (m)	4.70 (s)	2.55 (s)		[f]

[a] CH$_2$Cl$_2$ solution. [b] Ppm downfield from internal Me$_4$Si, CDCl$_3$ solution. [c] J_{PH} (Hz) in parentheses. [d] Ppm upfield from internal CFCl$_3$. [e] This resonance integrates to 2 protons, J_{HD} = 2 Hz. [f] Not recorded. [g] ν_{NH}.

for **5** and **6** were identical with those previously reported,[11] and the structures of **7**–**9** were established clearly by comparison of their IR and ^{1}H NMR spectra (Table I) with those of **5** and **6**. No iron analogues of **7** and **8** exist, although the closely related ruthenium compound [Ru(η-C$_5$H$_5$)(CO)(PPh$_3$){C(O-*i*-Pr)CH$_2$Ph}]$^+$PF$_6^-$ has been reported;[7] while the ^{1}H NMR signal for the isopropyl group of this latter compound could not be observed due to a solvent impurity,[7] the ^{1}H NMR spectrum of **7** clearly shows the presence of two doublets corresponding to the diastereotopic methyl groups.

Compounds **5**–**9** arise by initial nucleophilic attack at the α-carbon of the vinylidene ligand by the alcohol oxygen atom, in a manner analogous to that already demonstrated for pyridine and tertiary phosphine nucleophiles.[2] Subsequent prototropic shifts afford the observed products, as shown by the formation of **9** from CH$_3$OD. When water is the nucleophile, this sequence would afford the unstable hydroxycarbene compound [Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(OH)Me}]$^+$BF$_4^-$, which, as expected,[12] spontaneously deprotonates to give the acetyl product.

Reactions with S–H Bonds. In contrast, the reaction of **1** with liquid H$_2$S afforded an isolable sulfhydrylcarbene complex **10**, and a similar reaction using liquid CH$_3$SH yielded the methylthiocarbene analogue **11**. ^{1}H NMR spectroscopy (Table I) located the SH proton reasonance of **10** at δ 4.32.[13] The ^{1}H NMR resonances of the methyl(methylthio)carbene ligand of **11** were entirely compatible with those reported for the same ligand in [Ir(η-C$_5$H$_5$)I(PPh$_3$){C(SMe)Me}]$^+$I$^-$.[14] Compound **10** was quite unstable in solution; attempted deprotonation of the sulfhydryl group, using the hindered base NEt-*i*-Pr$_2$, produced a very unstable orange material which could only be characterized by its IR spectrum. The presence of strong bands at 1937 (ν_{CO}) and 1260 cm^{-1} ($\nu_{C=S}$?) suggested that the neutral thioacyl complex [Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(S)Me}] might have been formed; no thioacyl compounds appear to have been reported in the literature, although a thioformyl compound of osmium has been characterized.[15]



10. R=H
11. R=Me

Reactions with N–H Bonds. We have already established that **1** reacts cleanly with pyridine, or 4-methylpyridine, to yield vinyl compounds resulting from nucleophilic attack of the amine nitrogen atom at the vinylidene α-carbon atom.[2] Compound **1** dissolved slowly in benzylamine at room temperature to yield, on workup, the single yellow cationic methyl(benzylamino)carbene complex **12** in high yield. The IR and ^{1}H NMR spectral

12. R = CH$_2$Ph; R′=H
13. R = Me; R′=H
14. R = R′ = Me

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Table II. IR and NMR Spectroscopic Data for Cationic Cyclobutenylidene Complexes

compd	ν_{CO},[b] cm^{-1}	nucleus	δ[a] L	δ[a] C_5H_5	δ[a] α-C	δ[a] CH	δ[a] CH_2	δ[a] CO
17	1954	^1H	7.40 (m)	4.51 (s)		7.80 (s)	3.20 (d, J = 14.4 Hz) 3.29 (d, J = 14.4 Hz)	
18	1954	^1H	7.40 (m)	4.65 (s)		7.80 (s)	3.30 (s)	
19	1954	^1H	1.59 (m)	4.91 (s)		8.32 (s)	3.72 (s)	
17		^{13}C	127-132	87.8	304.0	286.0	21.6	209.9
18		^{13}C	127-132	87.5	*c*	*c*	*c*	*c*
19		^{13}C	28.5 (br)	85.8	330.6	290.0	24.9	218.0

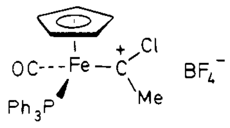
[a] Ppm downfield from internal Me_4Si, $CDCl_3$ solution. [b] CH_2Cl_2 solution. [c] These resonances could not be observed for the minor isomer in solution.

properties of **12** agree well with those reported for the product of the reaction of [Fe(η-C_5H_5)(CO)(PPh_3){C(OEt)Me}]$^+BF_4^-$ with benzylamine;[16] similar compounds [Fe(η-C_5H_5)(CO)(PPh_3){C(NRR′)Me}]$^+BF_4^-$ (R = R′ = H; R′ = H, R = (−)-CHMePh) have been obtained by an analogous route,[16,17] though secondary amines are reported to be unreactive.[17] Similarly **1** reacted smoothly with liquid $MeNH_2$ or Me_2NH to produce the corresponding compounds **13** and **14**; in these latter two reactions some deprotonation to produce [Fe(η-C_5H_5)(CO)(PPh_3)(C≡CH)], **15**, was also observed. This metal alkynyl complex was the sole product of the reaction of **1** with liquid Me_3N.[18]

The carbene compounds **12–14** clearly arise via nucleophilic attack at the vinylidene α-carbon by the amine, followed by proton transfer. Notably this is the exclusive mode of reaction for the weakly basic benzylamine (pK_a = 9.33),[19] which behaves like pyridine (pK_a = 5.25),[19] but the more basic amines $MeNH_2$ (pK_a = 10.66)[19] and Me_2NH (pK_a = 10.77)[19] act both as nucleophiles and bases. While Me_3N (pK_a = 9.81)[19] is a weaker base in aqueous solution than either $MeNH_2$ or Me_2NH, it is a stronger base in the absence of solvent,[20] and it is not surprising, therefore, that under these reaction conditions Me_3N acts exclusively as a base and cleanly deprotonates the vinylidene complex to give **15**. It has been noted that the more hindered amine, Et_2NH, will deprotonate [Fe(η-C_5H_5)(CO)(PPh_3)(C=CHPh)]$^+BF_4^-$ to give the corresponding alkynyl iron complex.[8]

Two pieces of evidence point to the presence of considerable double-bond character between the nitrogen and α-carbon atoms of **12–14**. The value of ν_{CO} is significantly lower for these compounds than for the alkoxycarbene compounds **5–8** (Table I), indicating that the aminocarbene ligand is a weaker π acceptor than the alkoxycarbene ligand, due to increased heteroatom stabilization of the carbene carbon atom. The observation of two ^1H NMR resonances for the Me_2N group of **14** at 25 °C clearly substantiates this proposal.

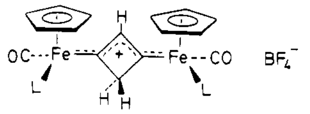
Reaction with HCl. At −78 °C, **1** reacted swiftly with dry HCl in CH_2Cl_2 solution to give, on workup, an air- and moisture-sensitive brick-red solid formulated as the chloromethylcarbene complex **16**. The value of ν_{CO} for this compound (Table I) is consistent with this formulation, but unfortunately samples of **16** prepared in this fashion could not be freed of paramagnetic impurities in order to allow NMR spectra to be recorded. Recrystallization attempts led invariably to further decomposition, and attempted chromatography on deactivated silica gel led to rapid hydrolysis to give [Fe(η-C_5H_5)(CO)(PPh_3){C(O)Me}]. To circumvent this problem, **16** was generated in $CDCl_3$ solution by adding one equivalent each of CF_3SO_3H and [Ph_3P=N=PPh_3]$^+Cl^-$ to **1**; the resultant red-purple solution exhibited an identical IR band at 1990 cm^{-1} (see Table I). The ^1H NMR spectrum of this sample of **16** exhibited only PPh_3 resonances, a cyclopentadienyl peak at δ 4.70 and a methyl singlet at δ 2.55; the $^{13}C\{^1H\}$ NMR spectrum exhibited a resonance at δ 344.50, characteristic of the α-carbon atom of such carbene complexes,[21] as well as a methyl peak at δ 13.40 and a cyclopentadienyl peak at δ 86.76. We feel that these data provide good evidence for the formulation of **16** as a chloromethylcarbene complex.



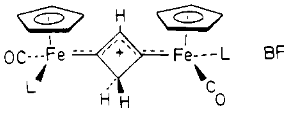
16.

Formation of μ-1,3-Cyclobutenylidene Complexes. While **1** dissolved in dry CH_2Cl_2 or $CDCl_3$ without change and was insoluble in Et_2O,[2] it dissolved readily in dry THF to afford a bright orange solution which yielded deep orange crystals on workup. Although the crystals exhibited a single CO stretching band in the IR spectrum (Table II) together with bands characteristic of BF_4^-, the ^1H NMR spectrum (60 MHz) was more complex and clearly indicated the presence of two isomeric species in solution. Two cyclopentadienyl resonances were observed (ratio 3:1), and the methylene region contained an AB quartet and a singlet, also in a 3:1 ratio. At 270 or 360 MHz the AB quartet simplified to an AX pattern with a coupling constant (14.4 Hz) characteristic of geminally coupled protons.[13b] A further singlet peak was observed at δ 7.80. A fast atom bombardment (FAB)[22] mass spectrum indicated that the molecular weight of the cationic portion of the molecule was 872.6.

These data are only compatible with the formation of a binuclear complex containing a cyclobutenylidene ligand, and the most reasonable conclusion appears to involve the formation of two diastereoisomeric pairs of enantiomers **17** and **18**. The major component must be the meso-



17. L = PPh_3



18. L = PPh_3

19. L = $P(C_6H_{11})_3$

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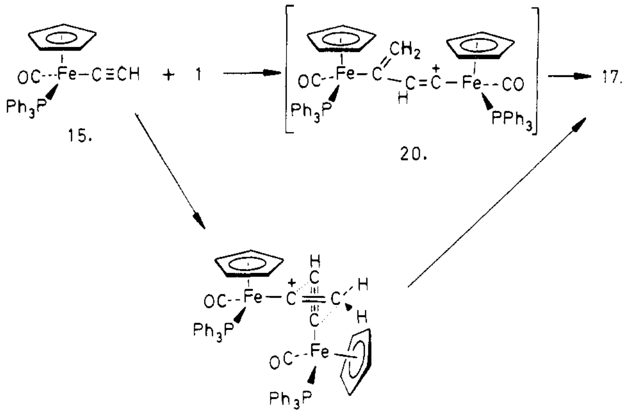
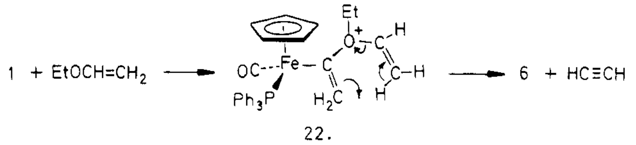
(22) A discussion of fast atom bombardment (FAB) mass spectrometry has appeared recently: Williams, D. H.; Bradley, C.; Bojesen, G.; Santikarn, S.; Taylor, L. C. E. *J. Am. Chem. Soc.* **1981**, *103*, 5700–5704.

compound **17**, in which the methylene protons are symmetrically nonequivalent, and the minor component must be the *R,R:S,S* pair **18** in which the methylene protons are related by a twofold rotation axis. Surprisingly it was not possible to alter the 3:1 ratio of **17**/**18** either by repeated recrystallization or by chromatography on deactivated silica gel. A further curious observation was made when an analogue of **1**, $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})\{\mathrm{P(C_6H_{11})_3}\}(\mathrm{C{=}CH_2})]^+\mathrm{BF_4}^-$ was dissolved in THF. The ^{1}H NMR spectrum of the product (Table II) showed it to consist of a single isomer **19** which corresponds structurally to the minor isomer **18**; only a singlet peak was observed for the methylene protons at 360 MHz. Supporting evidence was provided by ^{13}C NMR spectra (Table II) which clearly showed two cyclopentadienyl resonances for the mixture of **17** and **18** but only one for **19**. A FAB mass spectrum of **19** confirmed the molecular weight of the cation as 908.6.

Similar cationic cyclobutenylidene complexes have been reported by two groups of workers,[8,23] from the protonation of $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{C{\equiv}CPh})]$ in the absence of nucleophiles. Formation of an intermediate cationic vinylidene complex $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{C{=}CHPh})]^+$, followed by a cycloaddition reaction of this molecule with more acetylide, was proposed as a mechanism for this reaction.[8,23] It seems reasonable to suppose that partial deprotonation of **1** occurs in THF solution, to produce the alkynyl complex **15**, which is then trapped in a cycloaddition reaction with **1**, as shown below for the formation of the meso-compound **17**. In agreement with this hypothesis, addition of 0.5 equiv of $\mathrm{HBF_4{\cdot}Et_2O}$ to solutions of **15** afforded an identical 3:1 mixture of **17** and **18**. It has been suggested that this mechanism may involve a stepwise cyclization via the intermediate **20**,[8] although a concerted $[{}_\pi 2_s + {}_\pi 2_a]$ cycloaddition should also be feasible. Indeed, the vinyl cation would be a superb antarafacial component for such a cycloaddition, which should occur via the bisected transition state **21**.[24] It is not clear where the origins of the preference for selective formation of the meso-diastereomer **17** lie or why an inversion of this preference occurs for the $\mathrm{P(C_6H_{11})_3}$ analogue of **1** to give **19**. A possible explanation, which also accounts for our lack of success in separating **17** and **18**, or even altering their ratio, would be that **17** and **18** were in equilibrium in solution. This would require a complete retrocycloaddition to regenerate **1** and **15** in solution and seems extremely implausible since the mixture of **17** and **18** can be chromatographed unchanged on water saturated silica gel, conditions under which immediate hydrolysis of free **1** would occur. No traces of the expected product of hydrolysis, $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})(\mathrm{PPh_3})\{\mathrm{C(O)Me}\}]$, or of **15**, both of which can be chromatographed unchanged under these conditions, were ever detected. It seems likely, therefore, that the selectivity which occurs in cyclobutenylidene formation is kinetic rather than thermodynamic in origin.



Reaction with $\mathrm{EtOCH{=}CH_2}$. In view of the ability of certain electrophilic carbene complexes to effect the cyclopropanation of electron rich olefins,[25] the reaction of **1** with ethyl vinyl ether was examined. No cyclopropanation was observed, but instead a surprisingly clean conversion of **1** to the ethoxymethylcarbene complex **6** was observed. A speculative mechanism for this transformation utilizes the demonstrated affinity of the α-carbon atom of **1** for oxygen nucleophiles to give **22**, followed by an elimination reaction to give **6**. No attempts were made to identify any organic byproduct(s).



22.

Experimental Section

General Remarks. IR spectra were run on a Perkin-Elmer PE 257 instrument and calibrated against the 1601-cm^{-1} band of polystyrene. ^{1}H (60 MHz), ^{13}C (15 MHz), and ^{19}F (56 MHz) NMR spectra were run on a JEOL FX-60Q instrument; certain ^{1}H NMR spectra were run at 270 MHz on a Bruker HX-270 spectrometer or at 360 MHz on a Nicolet NT-360 spectrometer at the NSF-NMR Regional facilities at Yale University or Colorado State University, respectively. Fast atom bombardment cation mass spectra were obtained at the Middle Atlantic Mass Spectrometry Facility at the Johns Hopkins School of Medicine. Spectroscopic data are reported in Tables I and II or in the text.

Alcohols were obtained as spectrograde solvents and were used as received, with the exception of allyl alcohol which was distilled before use. Methylamine, dimethylamine, trimethylamine, $\mathrm{H_2S}$, and methyl mercaptan were obtained from Matheson and were used as received. Benzylamine was dried over BaO before use. Organometallic reaction solvents were distilled from sodium benzophenone ketyl except for $\mathrm{CH_2Cl_2}$ and $\mathrm{CDCl_3}$ which were distilled from $\mathrm{P_4O_{10}}$. All reactions were run under an atmosphere of dry nitrogen or on a vacuum line.

$[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})(\mathrm{PPh_3})(\mathrm{C{=}CH_2})]^+\mathrm{BF_4}^-$, **1**, and $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})\{\mathrm{P(C_6H_{11})_3}\}(\mathrm{C{=}CH_2})]^+\mathrm{BF_4}^-$ were prepared as previously described.[2]

Reaction of 1 with $\mathrm{H_2O}$. A solution of **1** (0.10 g, 0.19 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was shaken vigorously with $\mathrm{H_2O}$ (5 mL). The organic layer was separated, dried ($\mathrm{MgSO_4}$), filtered, and evaporated to afford $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})(\mathrm{PPh_3})\{\mathrm{C(O)Me}\}]$ as orange crystals (0.070 g, 80%). IR and ^{1}H NMR spectra were identical with literature data.[26]

$[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})(\mathrm{PPh_3})\{\mathrm{C(OMe)Me}\}]^+\mathrm{BF_4}^-$ (5). The vinylidene compound **1** (0.10 g, 0.19 mmol) was dissolved in $\mathrm{CH_3OH}$ (20 mL). After 0.25 h the pale yellow solution was evaporated and the crude residue recrystallized from $\mathrm{CH_2Cl_2/Et_2O}$ to give **5** as yellow crystals (0.074 g, 70%; mp 164 °C). IR and ^{1}H NMR spectra were identical with literature data.[11]

$[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})(\mathrm{PPh_3})\{\mathrm{C(OEt)Me}\}]^+\mathrm{BF_4}^-$ (6) was prepared in similar fashion from **1** (0.10 g, 0.19 mmol) and EtOH (20 mL), as yellow crystals (0.070 g, 65%; mp 108 °C dec). IR and ^{1}H NMR spectra were identical with literature data.[11]

$[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})(\mathrm{PPh_3})\{\mathrm{C(O\text{-}\mathit{i}\text{-}Pr)Me}\}]^+\mathrm{BF_4}^-$ (7) was similarly prepared from **1** (0.10 g, 0.19 mmol) and *i*-PrOH (15 mL),

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as yellow crystals (0.079 g, 72%; mp 173 °C). For IR and ^1H NMR data, see Table I. Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(OCH_2CH{=}CH_2)Me\}]^+BF_4^-$ (8) was similarly prepared from 1 (0.10 g, 0.19 mmol) and allyl alcohol (15 mL), as dark yellow crystals (0.067 g, 61%; mp 130 °C). For IR and ^1H NMR data, see Table I. Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(OMe)CH_2D\}]^+BF_4^-$ (9) was likewise prepared from 1 (0.10 g, 0.19 mmol) and CH_3OD (Aldrich, 15 mL), as pale yellow crystals (0.080 g, 75%; mp 108 °C). For IR and ^1H NMR data see Table I.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(SH)Me\}]^+BF_4^-$ (10). A Schlenck flask (100 mL) containing 1 (0.50 g, 0.95 mmol) was evacuated and cooled to −196 °C. Hydrogen sulfide was condensed on to solid 1 until the flask was about half-full. The flask was warmed to −78 °C to liquify the H_2S, and the reaction mixture was stirred for 1 h. Excess H_2S was removed under vacuum, and the flask was warmed to room temperature. The crude product was chromatographed on a 15 × 2 cm deactivated silica gel/Et_2O column. Et_2O eluted $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)Me\}]$ (0.050 g, 11%), and acetone eluted an orange band which yielded 10, after evaporation and recrystallization from CH_2Cl_2/Et_2O, as orange crystals (0.34 g, 65%; mp 104 °C). For IR and ^1H NMR data see Table I. Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(SMe)Me\}]^+BF_4^-$ (11) was likewise prepared from 1 (0.50 g, 0.95 mmol) and MeSH (20 mL), by maintaining the reaction mixture at −24 °C using a CCl_4/N_2 (liquid) slush bath. Recrystallization of the crude product from acetone/Et_2O yielded 11 as yellow crystals (0.43 g, 79%; mp 141 °C dec). For IR and ^1H NMR data see Table I. Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(NHCH_2Ph)Me\}]^+BF_4^-$ (12). Compound 1 (1.00 g, 1.91 mmol) was dissolved in benzylamine (20 mL) and stirred for 8 h. Excess benzylamine was removed under vacuum, and the crude residue was recrystallized from CH_2Cl_2/Et_2O (−30 °C) to give 12 as yellow crystals (0.89 g, 74%; mp 203 °C). For IR and ^1H NMR data, see Table I. Anal. C, H, N.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(NHMe)Me\}]^+BF_4^-$ (13). $MeNH_2$ (ca. 25 mL) was condensed on to 1 (1.00 g, 1.91 mmol) at −196 °C, and the reaction mixture was warmed to −24 °C (CCl_4/N_2 (liquid) slush bath) and stirred for 1 h. Excess amine was removed under vacuum, and the crude residue was chromatographed on a 15 × 2 cm deactivated silica gel/Et_2O column. Ether eluted $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)Me\}]$ (0.017 g, 2%) followed by $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{\equiv}CH)]$,[2] 15 (0.092 g, 11%), and CH_2Cl_2 eluted a bright orange band, which on evaporation and recrystallization, afforded 13 as orange crystals (0.80 g, 75%; mp 137 °C). For IR and ^1H NMR data, see Table I. Anal. C, H, N.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(NMe_2)Me\}]^+BF_4^-$ (14) was prepared in a similar reaction using 1 (1.00 g, 1.91 mmol) and Me_2NH (25 mL). Chromatography as described above yielded $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)Me\}]$ (0.07 g, 8%), and 15 (0.11 g, 13%), eluting with Et_2O. Acetone eluted an orange band, which was evaporated and recrystallized from CH_2Cl_2/Et_2O to afford 14 as orange crystals (0.81 g, 77%; mp 176 °C). For IR and ^1H NMR data, see Table I. Anal. C, H, N.

Reaction of 1 with Me_3N. In a similar reaction, 1 (0.50 g, 0.95 mmol) and Me_3N (25 mL) were stirred at −116 °C ($EtOH/N_2$ (liquid) slush bath) for 2 h. Workup as described above yielded $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{\equiv}CH)]$, 15[2] (0.34 g, 82%), after recrystallization from toluene/hexane.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(Cl)Me\}]^+BF_4^-$ (16). A solution of 1 (1.15 g, 2.2 mmol) in CH_2Cl_2 (50 mL) was cooled to −78 °C and dry HCl gas was bubbled through the solution for 0.25 h. The mixture was stirred at −78 °C for 1 h, warmed to 25 °C, and stirred for 12 h. Removal of the solvent under vacuum and recrystallization of the residue from CH_2Cl_2/Et_2O afforded 16 as a brick-red solid (0.74 g, 60%; mp 85 °C dec). For IR data, see Table I. Satisfactory microanalysis results could not be obtained, and further recrystallizations led to further decomposition. Anal. Calcd for $C_{26}H_{23}BClF_4FeOP$: C, 55.71; H, 4.14; Cl, 6.32. Found: C, 55.17; H, 4.19; Cl, 5.22.

Alternatively, 16 was generated in a NMR tube by treating a solution of 1 (0.10 g, 0.19 mmol) in $CDCl_3$ (3 mL) with $[Ph_3P{=}N{=}PPh_3]Cl$ (0.11 g, 0.19 mmol) followed by CF_3SO_3H (0.17 mL, 0.19 mmol). ^1H and ^{13}C NMR spectra of the resultant mixture are reported in Table I.

$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(PPh_3)_2(\mu\text{-}C_4H_3)]^+BF_4^-$ (17) and (18). Compound 1 (0.50 g, 0.95 mmol) was dissolved in dry THF (50 mL), and the orange solution was stirred for 4.5 h. Removal of the solvent under vacuum and chromatography of the residue on a 150 × 2 cm deactivated silica gel column with CH_2Cl_2, eluted a bright orange band. Evaporation, followed by recrystallization from CH_2Cl_2/Et_2O afforded bright orange crystals (0.41 g, 89%; mp 165 °C dec), shown to consist of a 3:1 mixture of 17/18. For IR, ^1H NMR, ^{13}C NMR data, see Table II. Anal. C, H.

$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{P(C_6H_{11})_3\}_2(\mu\text{-}C_4H_3)]^+BF_4^-$ (19) was prepared similarly by stirring a solution of $[Fe(\eta\text{-}C_5H_5)(CO)\{P(C_6H_{11})_3\}(C{=}CH_2)]^+BF_4^-$ (0.86 g, 1.59 mmol) in THF (50 mL) for 12 h. Workup as above yielded 19 as red-orange crystals (0.65 g, 82%; mp 145 °C dec). For IR, ^1H NMR, ^{13}C NMR data, see Table II. Anal. C, H.

Reaction of 1 with $EtOCH{=}CH_2$. A suspension of 1 (1.15 g, 2.2 mmol) in Et_2O (20 mL) was treated with freshly distilled $EtOCH{=}CH_2$ (10 mL), and CH_2Cl_2 (15mL) was then added to help dissolve 1. The mixture was stirred for 8 h and then evaporated to dryness. Chromatography of the residue on a 150 × 2 cm deactivated silica gel column, eluting with a 1:1 acetone/CH_2Cl_2 mixture, afforded a single yellow band, which on evaporation yielded 6 (1.21 g; 96%), identified by its ^1H NMR spectrum.

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Registry No. 1, 80642-55-3; 5, 32610-60-9; 6, 32611-17-9; 7, 80662-36-8; 8, 80662-38-0; 9, 80662-40-4; 10, 80662-42-6; 11, 80662-44-8; 12, 80662-46-0; 13, 80662-48-2; 14, 80662-30-2; 15, 80642-59-7; 16, 80662-32-4; 17, 80735-08-6; 18, 80662-34-6; 19, 80679-12-5; $[Fe(\eta\text{-}C_5H_5)(CO)\{P(C_6H_{11})_3\}(C{=}CH_2)]^+BF_4^-$, 80642-58-6; $Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)Me\}$, 12101-02-9.

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Relationships between Structure and Ligand Dynamics in Organometal Clusters

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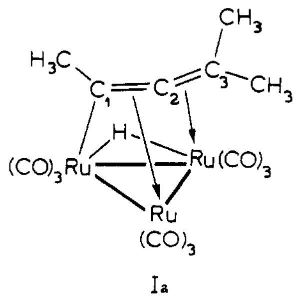
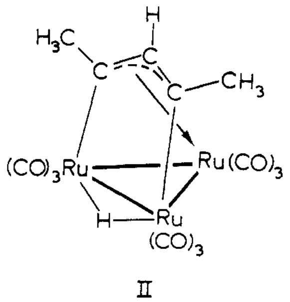
The variable-temperature ^1H and ^{13}C NMR spectra of the hydrido organometal clusters $HM_3(CO)_9[CH_3C{=}C{=}C(CH_3)_2]$ (M = Ru, Os) have been examined. When M ≈ Ru, a dynamic process is observed which averages the magnetically inequivalent methyl groups on the ligand and also results in a twofold symmetry plane at the metal cluster with respect to the carbonyl ligands. These observations are explained in terms of edge hopping of the hydride ligand and a simultaneous "wagging" motion of the organic ligand. For the osmium derivative the barrier to the motion of the organic ligand is higher, but it cannot be established whether it is directly coupled with the edge-hopping of the hydride. For comparison, the variable-temperature ^{13}C NMR spectrum of $HRu_3(CO)_9(CH_3CCHCCH_3)$ was investigated. Here, no motion of the organic ligand could be detected although opening of the hydride bridge appears to be occurring as evidenced by the different barriers to axial–radial CO site exchange at the different ruthenium atoms. The phosphine derivative $HRu_3(CO)_8P(C_6H_5)_3(CH_3CCHCCH_3)$, in which the phosphine is bound to the metal atom which is σ-bound to the organic ligand, shows a higher barrier to axial–radial site exchange at the hydride-bridged metal atoms.

Introduction

Although there have been numerous investigations of ligand mobility in metal clusters by NMR techniques, the relationships between the motions of different types of ligands on the same metal cluster have not been clearly delineated in many cases.[1] This is particularly true in the case of hydrido organometal clusters where a wide variety of bonding modes of the organic ligand to the metal cluster have been observed.[2] We have recently completed a detailed investigation of the ligand dynamics in $HRu_3(CO)_9[C_2C(CH_3)_3]$ where two carbon atoms are bound to a trimetallic cluster, and our evidence indicates that the organic ligand is static in this species.[3-5] Shapley and co-workers have shown that σ–π interconversion of the organic ligand in $HOs_3(CO)_{10}(CH{=}CHR)$ is independent of other ligand migrations in the molecule.[6] Additionally, it has been suggested that an oscillating motion of the organic ligand in $H_2Os_3(CO)_9$ ($R'C{\equiv}CR$) along with hydride migration around the metal triangle (which must be at least as fast but now slower than the oscillation of the organic ligand) and axial–radial exchange of the carbonyl ligands can fully explain the observed dynamic behavior in this class of compounds.[7-9] For the isomeric complexes $H_2Os_3(CO)_9(C{=}CH_2)$ edge migration of one hydride is thought to average the magnetically inequivalent protons on the organic ligand while at higher temperatures migration of both hydrides is observed.[10,11] The relationship of the CO migrations to these two hydride-exchange processes remains unclear, and the organic ligand appears to be static in these complexes as well. Thus for two carbon fragments bound to trimetallic sites, the nature of the ligand-exchange processes observed does vary with the structure of the organic ligand. We report here the initial results of our investigation of the relationships between ligand migrations in hydrido organometal clusters where three carbon fragments are bound to a trimetallic site by two different metal carbon frameworks, Ia and II.



Ia



II

Previously it has not been possible to compare the dynamic NMR spectra of these structural types since I isomerizes to II when one of the substitutents on the C(3)

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(1) "Transition Metal Clusters", B. F. G. Johnson, Ed., Wiley, New York, 1980.

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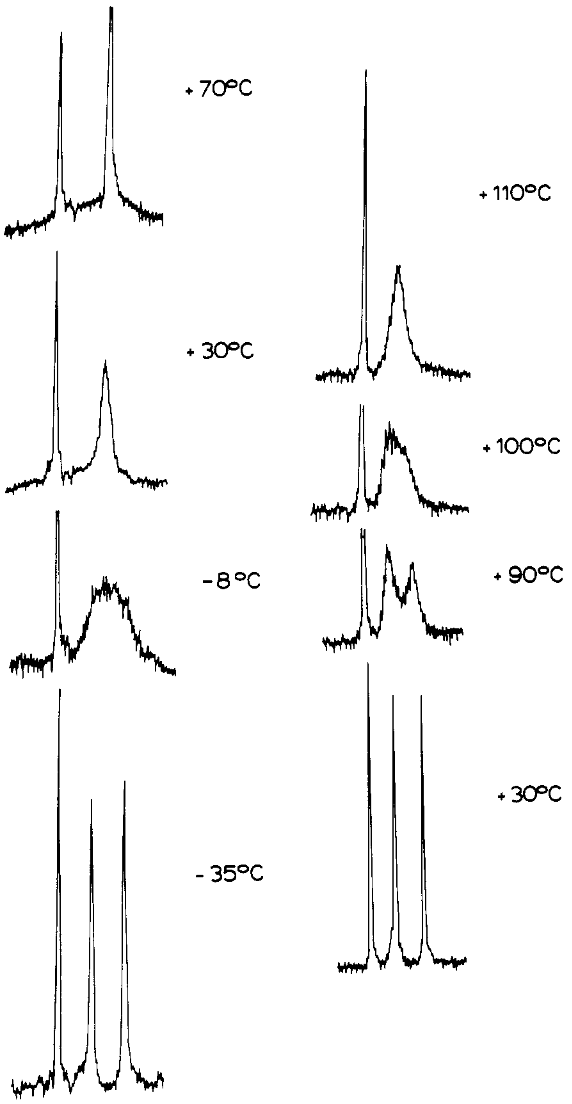

Figure 1. Variable-temperature ^{1}H NMR spectra of HM$_3$(CO)$_9$[CH$_3$C=C=C(CH$_3$)$_2$] (M = Ru (Ia, left) and Os (Ib, right)) in the aliphatic region.

carbon of the allene is hydrogen.[12] We recently found that the reaction of M$_3$(CO)$_{12}$ (M = Ru, Os) with 4-methyl-2-pentyne gives I which does not isomerize.[13]

Results and Discussion

(A) Allenic Derivatives. The reaction of Ru$_3$(CO)$_{12}$ with 4-methyl-2-pentyne gives Ia as one of several products.[13] The yield and purity of Ia can be optimized by modification of the reaction conditions previously reported for this compound (see Experimental Section).

The low-temperature limiting ^{1}H NMR spectrum of Ia is attained at −35 °C where three methyl resonances at δ 2.54, 2.23 and 1.9 are observed (relative intensity 1:1:1; Figure 1). Above this temperature, the two upfield resonances broaden, merge, and coalesce to a single resonance δ 2.04. The hydride resonance at δ −20.04 and the methyl resonance at δ 2.54 remain unchanged throughout the temperature range examined. With a coalescence temperature 265 K, the free energy of activation for this process is 56.0 ± 1 kJ/mol.[14] Due to the relatively low

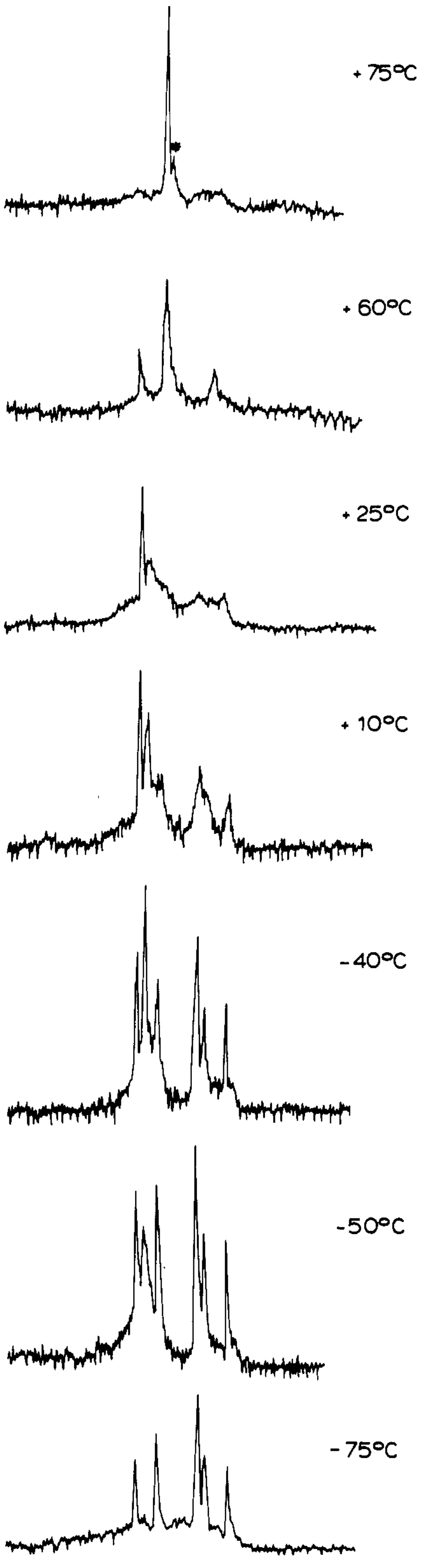

Figure 2. Variable-temperature ^{13}C NMR spectra of HRu$_3$(CO)$_9$[CH$_3$C=C=C(CH$_3$)$_2$] in the carbonyl region. The * denotes an impurity due to an incipient decomposition of the compound.

symmetry of this complex, it would appear that no single motion of the organic ligand nor any combination of just hydride and carbonyl migrations would average the methyl resonances. We then undertook an investigation of the variable-temperature ^{13}C NMR spectra of a ^{13}CO-enriched

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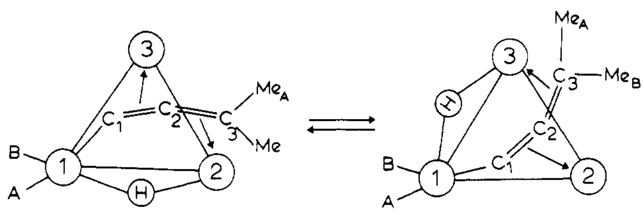
[13] S. Aime, L. Milone, E. Sappa, E. Rosenberg, A. M. Manotti Lanfredi, and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 2023 (1981).

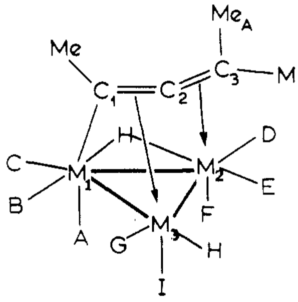
[14] Estimated from coalescence temperature (±1.0 K) using the equation $\Delta G_c^* = 4.57\,(T_c)\,(9.97 - \log T_c/\delta\nu)$: D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.* 656 (1971).

Scheme I



sample of Ia. At −75 °C five resonances are resolved in the carbonyl region at δ 197.9, 195.9, 192.0, 191.3, and 189.1 (relative intensity 1:1:2:1:1 (Figure 2). Nine resonances should be observed in the low-temperature limit according to the solid-state structure for a direct analogue of Ia,[15] but the limited solubility of Ia below −80 °C precluded going to lower temperature. As the temperature is increased to −50 °C, however, a new resonance appears at δ 197.2 (relative intensity 3). Thus, at −50 °C, we can account for nine carbonyl groups. This resonance continues to sharpen as the temperature is increased. At +10 °C all the resonances except the resonance at δ 197.9 (relative intensity 1) are beginning to broaden. The resonance at δ 197.9 remains sharp to +25 °C. At this temperature, a new broadened resonance at δ 190.2 appears which is the weighted average of the resonances at δ 191.3 and 189.1. As the temperature is raised to +60 °C, a single resonance of relative intensity 6 is observed at δ 195.3, which is the weighted average of all resonances except the ones at δ 197.9 and 190.2, which are only slightly broadened. Above this temperature, the resonance at δ 195.3 continues to sharpen while the resonances at δ 197.9 and 190.2 collapse into the base line. At −75 °C only the resonances at δ 192.0 and 189.1 show coupling to the hydride (8 and 10 Hz, respectively) indicating trans H–M–CO relationship.[2] One of the two resonances at δ 192.0 remains as a singlet in the ^1H-coupled spectrum showing that the decoupled resonance of relative intensity 2 at this frequency is actually the superposition of two magnetically inequivalent resonances, only one of which is coupled to the hydride.

We can interpret the changes in the ^{13}C NMR spectra of Ia with temperature and assign almost all the resonances unambiguously by considering the multistage exchange process using the labeling scheme for Ia. The first stage of the process involves axial–radial exchange at Ru(3), CO(G), CO(H), and CO(I) which gives rise to the resonance of relative intensity 3 at δ 197.2. We have recently shown that the barriers to axial–radial carbonyl site exchange in $HM_3(CO)_9L$ (L = 5-electron donor organic ligand) (M = Ru, Os) are considerably lower at the metal atoms not bridged by the hydride.[3,4,16,17] The second stage of the process results in the averaging of the carbonyl groups at Ru(3) with three other carbonyls and in the simultaneous averaging of the two carbonyl resonances at δ 191.3 and 189.1 with each other. It is in this temperature range that the two methyls are also averaged in the ^1H NMR spectra. An exchange process which averages the carbonyl groups on Ru(3) with those on Ru(2) CO(D), CO(E), and CO(F) while averaging the two radial carbonyls on Ru(1) (CO(B) and C)(C) and the two methyl groups on C(3) of the organic ligand is shown in Scheme I. This involves "edge hopping" of the hydride from the Ru(1)–Ru(2) to Ru(1)–Ru(3) edge which appears to be concerted with a wagging motion of the organic ligand pivoting on C(2). We, of course, cannot be certain that the hydride migration does not directly preceed or follow the required wagging motion but both processes are necessary to explain the observed changes in the ^{13}C and ^1H NMR spectra. This process averages the two radial carbonyls on Ru(1) with each other but not with the axial carbonyl on Ru(1) (CO(A)). On this basis, we can assign the resonance at δ 197.9 to the axial carbonyl and the resonances at δ 191.3 and 189.1 to the radial carbonyls on Ru(1). Opening of the hydride bridge at Ru(2) only in this stage of the exchange allows for averaging of the axial and radial carbonyls at the ruthenium atoms as is observed. We have recently shown, by kinetic deuterium isotope effect studies, that opening of the hydride bridge is directly linked to axial–radial exchange of carbonyl groups in this type of complex.[16b] At the upper end of the temperature range examined, the axial and radial carbonyl groups on Ru(1) also begin to average and this process requires opening of the hydride bridge at Ru(1) as well. In the lower energy exchange process which averages the radial carbonyl groups with each other but not with axial carbonyl, no motion of the carbonyl groups is required. We cannot discern whether hydride bridge opening is actually necessary for averaging the CO groups on Ru(1). If it is, however, it seems reasonable that hydride migration around the cluster if taking place since alternate opening of the bridge at Ru(2) and then at Ru(1) (or Ru(3) and then Ru(1)) is not compatible with the fact that the edge hopping of the hydride from the Ru(2)–Ru(1) edge to the Ru(3)–Ru(1) edge is much faster than the alternate opening of the bridge on a single edge of the cluster.



Ia, M = Ru
Ib, M = Os

We have also been able to synthesize the osmium analogue of Ia by reaction of $H_2Os_3(CO)_{10}$ with 4-methyl-2-pentyne (see Experimental Section). Unlike the ruthenium analogue, Ib shows three sharp methyl resonances in the room-temperature ^1H NMR spectrum at δ 2.37, 2.08 and 1.79 (Figure 1) and a hydride resonance at δ −19.95. As the temperature is increased to +90 °C, the two high-field methyl resonances broaden and then merge to a single peak; with a coalescence temperature 373 K, the free energy of activation for this process is 80.6 ± 1 kJ/mol. We then went on to record the VT ^{13}C NMR spectra of an enriched sample of Ib. In the low-temperature limiting spectrum at −90 °C all nine carbonyl resonances can be accounted for at δ 206.5, 204.9, 202.7, 201.5, 200.2, 197.5, and 196.3 (relative intensity 1:1:1:3:1:1:1; Figure 3). At −70 °C the resonances at δ 206.5 and 202.7 are noticeably broadened, and by −52 °C a new resonance has appeared at δ 203.1 (relative intensity 3) which is the weighted average of the resonances at δ 206.5 and 202.7 and one of the

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(15) G. Gervasio, D. Osella, and M. Valle, *Inorg. Chem.*, **15**, 1221 (1976).

(16) (a) S. Aime, O. Gambino, L. Milone, E. Sappa, and E. Rosenberg, *Inorg. Chim. Acta*, **15**, 53 (1975). (b) E. Rosenberg, C. B. Thorsen, S. Aime, L. Milone, *J. Organometal. Chem.* submitted for publication.

(17) S. Aime, L. Milone, D. Osella, M. Valle, and E. W. Randall, *Inorg. Chim. Acta*, **20**, 217 (1976).

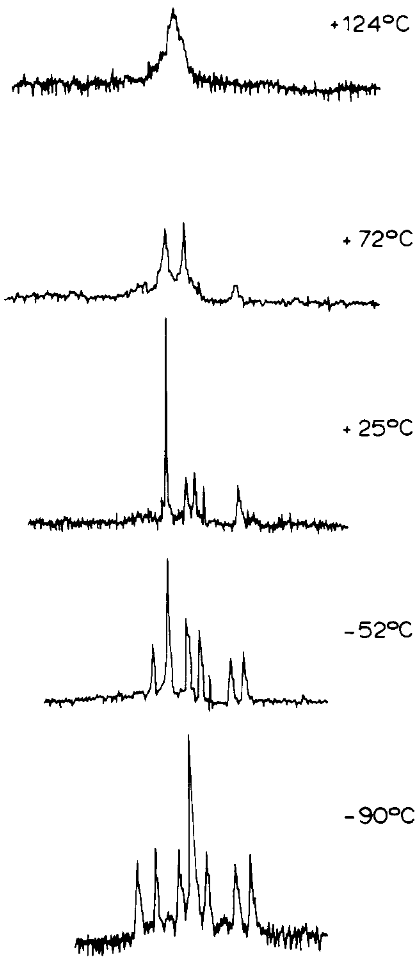


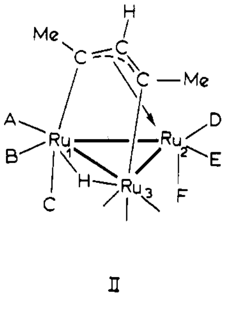
Figure 3. Variable-temperature ^{13}C NMR spectra of $HOs_3(CO)_9[CH_3C{=}C{=}C(CH_3)_2]$ in the carbonyl region.

apparently overlapping resonances of relative intensity 3 at δ 201.5. At +25 °C the resonances at δ 204.9 and 197.5 and one of the two overlapping resonances at δ 201.5 have broadened considerably, leaving three relatively sharp resonances of relative intensity 1 at δ 201.5, 200.2, and 196.3 and a sharp resonance of relative intensity 3 at δ 203.1. As the temperature is increased further the resonance at δ 203.1 remains sharp while a new peak emerges at δ 201.3 which masks the resonances at δ 201.5 and 200.2. The resonance at δ 196.3 is somewhat broadened above +72 °C. Above this temperature, this resonance continues to broaden and the two more intense resonances also begin to broaden and coalesce at approximately 124 °C. Only the resonances at δ 197.5 and 196.3 show coupling to the hydride (about 10 Hz), indicating a trans relationship to the hydride.

The changes in the variable-temperature ^{13}C NMR spectra can be understood in terms of a similar mechanism to that of the ruthenium analogue but where the barriers and the order of the various stages of the exchange process are somewhat different. These exchange processes are discussed in terms of the same labeling scheme used for Ia. The first stage of the exchange involves axial-radial exchange of carbonyl groups on Os(3) CO(G) and Co(H) CO(I) as in the ruthenium analogue. Here, however, the barrier is slightly higher, and the low-temperature limiting spectrum is observed before the compound becomes too insoluble. We have previously observed that the barrier to axial–radial carbonyl exchange is slightly higher at nonbridged osmium atoms than at nonbridged ruthenium atoms in other $HM_3(CO)_9(L)$ (L = $C{\equiv}CC(CH_3)_3$ compounds.[16] The second stage of the exchange process in Ib averages the carbonyl groups at (Os(2) CO(D), CO(E), and CO(F) without simultaneously averaging the radial carbonyls at Os(1) (CO(B) and CO(C)) as in the ruthenium analogue. This suggests that opening of the hydride bridge at Os(2) is occurring to allow averaging of the carbonyl groups on Os(2). We cannot discern whether the opening of the bridge at Os(2) is followed by edge hopping of the hydride. We do know, however, that the methyl groups on C(3) of the ligand are magnetically inequivalent in the same temperature range. At higher temperatures unfortunately, we only observe the progressive broadening of CO(C) and cannot tell if CO(A) remains sharp while CO(B) broadens, as in the ruthenium case, since both CO(A) and CO(B) are masked by the emerging resonance which is the average of the carbonyl groups of Os(2). The higher temperatures necessary to bring about the averaging of the carbonyl groups on Os(1) compared with Ru(1) apparently results in the overlap of this process with a higher energy process which results in the averaging of all the carbonyl groups. This could be brought about by intermetallic scrambling or by simultaneous rotation of the organic ligand and hydride migration around the metal triangle. We can conclude from these results that the barrier to the motion of the organic ligand is higher for osmium than for ruthenium. We cannot say at this time whether edge hopping of the hydride is directly coupled with wagging of the organic ligand in these systems. Our recent observations of deuterium isotope effects in hydride migrations[16b] holds out the possibility of observing such an effect on the averaging of the inequivalent methyl groups on C(3) of the ligand. The synthesis of the deuterated analogue and a study of their ^1H and ^{13}C NMR is under way.

(B) "Allylic" Derivatives. Our previous dynamic NMR work on the "allylic" derivatives of type II was confined to an examination of the low-temperature range (−90 to +25 °C).[17] We now report the high-temperature ^{13}C NMR of the symmetrical "allylic" complex $HRu_3(CO)_9(CH_3CCHCCH_3)$ (II) and of its monophosphine derivative $HRu_3(CO)_8(CH_3CCHCCH_3)P(C_6H_5)_3$ (III) in order to compare their high-temperature behavior with Ia.

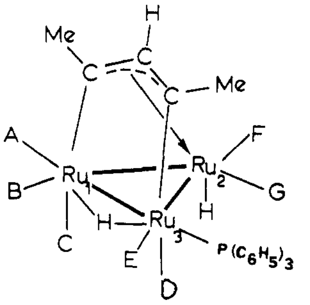
The ^{13}C NMR spectrum of II at +25 °C consists of one sharp resonance at δ 197.7 which is the average of the carbonyl groups on Ru(2) CO(D), CO(E), and CO(F) (relative intensity 3) and of these three broadened resonances at δ 195.9, 192.3, and 190.4 (relative intensity 2:2:2).



II

As the temperature is increased, these resonances average to a single resonance at δ 192.9 at +78 °C. This is the result of localized exchange of CO(A), CO(B), and CO(C) at Ru(1) and Ru(3). As the temperature is increased further, this resonance (relative intensity 6) continues to sharpen and then begins to broaden along with the resonance at δ 197.7. The averaging of the resonances of the carbonyl groups at Ru(1) and Ru(3) arises from either alternate opening or even stretching of the hydride bridge or by migration of the hydride around the metal triangle.[16b] For the "allenic" structure Ia it is clear that hydride edge hopping is a lower energy process than hydride migration around the ring. In the case of II, however, we can only say that within the temperature range examined the organic ligand is not moving and localized axial–radial exchange, which appears to require opening of the hydride bridge,[16b] is independent of any motion of the organic ligand. We cannot say whether the opening of the hydride bridge then results in actual hydride migration. The highest energy process of which only the initial stages are observed at +122 °C must involve either intermetallic CO scrambling or a combined rotation of the organic ligand and hydride migration around the triangle.

The phosphine derivative of II, III, has been previously reported[18] and its structure elucidated by ^1H NMR spectroscopy. The low-temperature limiting ^{13}C NMR spectrum of a sample of III at −87 °C shows seven resonances at 209.8, 201.9, 197.5, 195.2 (J(C,H) = 12.0 Hz), 194.5, 193.4, and 191.8 ppm (J(C,P) = 7.5 Hz, J(C,H) = 14.0 Hz, relative intensity 1:1:1:1:2:1:1). As the temperature is increased to −50 °C, the resonances at 209.8 and 194.5 ppm broaden, coalesce, and emerge as a single resonance of relative intensity 3. This corresponds to the axial–radial averaging process of the carbonyl groups on Ru(2) in II. As the temperature is increased to room temperature, no noticeable broadening of the remaining five resonances is observed. A further increase in the temperature to +50 °C did reveal some broadening of these resonances at 197.5, 193.4, and 191.8 ppm, but at this temperature the analogous carbonyl resonances due to the carbonyl groups on Ru(1) and Ru(3) in II were already coalesced. Above +65 °C III began to decompose. The dynamic behavior of the carbonyl groups in II and III are thus very similar except that phosphine substitution appears to raise the barrier for axial–radial exchange at the hydride-bridged Ru atoms. It is doubtful that this increased barrier is steric in origin since we have shown that phosphine substitution at a non-bridged Ru atom in $HRu_3(CO)_8(C{\equiv}CC(CH_3)_3)P(C_6H_5)_3$ does not effect the barrier to axial–radial exchange.[18] Since we do observe a noticeable effect here, it seems reasonable that the increased barrier to axial–radial exchange is due to an increased metal–hydrogen bond strength.[19]



III

Experimental Section

Synthesis of Compound Ia. A solution of $[Ru_3(CO)_{12}]$ (0.500 g) and $H_3CC{\equiv}CCH(CH_3)_2$ (0.3 mL) in cyclohexane (100 mL) was heated under reflux under N_2 for 1 h. After the solution was cooled, the unreacted $[Ru_3(CO)_{12}]$ was recovered by filtration of the reaction mixture. Chromatography of the filtrate (TLC, SiO_2; eluant, light petroleum) gave Ia with other products. Successive purification by TLC and crystallization were necessary in order to get Ia in sufficient purity (ca. 0.050 g, 10%). (See ref 13 for spectroscopic and analytical data).

Synthesis of Compound Ib. A solution of $H_2Os_3(CO)_{10}$ (0.450 g) and $H_3CC{\equiv}CCH(CH_3)_2$ in hexane (50 cm^3) was allowed to stand for 1 day at room temperature. Removal of solvent and TLC (SiO_2; eluant, toluene) gave $[Os_3(CO)_{10}(H_3C{\equiv}CCH(CH_3)_2]$ (0.300 g): mass spectrum, m/e (M^+) 938; IR (CO stretch (n-hexane)) 2099 (w), 2053 (vs), 2041 (w), 2027 (s), 2007 (m), 1998, 1846 (w, br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.55 (s, 3), 2.27 (sept 1, J_{HH} = 6.0 Hz), 0.97 (Cl, 6, J_{HH} = 6.0 Hz). When this compound was heated in n-heptane at reflux for 2 h, compound Ib is obtained in almost quantitative yield: mass spectrum, m/e (M^+) 910 followed by loss of nine CO; IR (CO stretch (n-hexane)) 2094 (m), 2066 (s), 2041 (vs), 2021 (vs), 2008 (s), 1997 (s), 1989 (m), 1984 (w), 1974 (w) cm^{-1}.

$[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ were enriched by stirring for 4 days in sealed ampules, at +50 and +110 °C, respectively, in the presence of <1 atm of 90% enriched ^{13}CO (Monsanto).

^1H NMR spectra were recorded on a JEOL 60 H1 spectrophotometer and ^{13}C NMR spectra on a JEOL PFT-100 spectrometer in the Fourier transform mode. The chemical shifts are downfield positive with respect to internal Me_4Si. The solvents ($CDCl_3$, CD_2Cl_2, and $C_6D_5CD_3$) were purchased from C.E.A. and used immediately after being dried over molecular sieves. $Cr(acac)_3$ (0.05 M) was used as a relaxation reagent for CO groups.

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Registry No. Ia, 80400-37-9; Ib, 80662-58-4; II, 56943-13-6; III, 72708-35-1; $Ru_3(CO)_{12}$, 15243-33-1; $H_2Os_3(CO)_{10}$, 41766-80-7.

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[18] C. Jangala, E. Rosenberg, D. Skinner, S. Aime, L. Milone, and E. Sappa, *Inorg. Chem.*, 19, 1571 (1980).

[19] Phosphine substitution on a hydride-bridged metal atom has been shown to quench the acidity of the metal hydrogen bond (see ref 2 for examples), and we have observed this for $HM_3(CO)_9L$ (L = $C{\equiv}CC(CH_3)_3$).

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Oxasilocins from Fluoride Ion Induced Ring Expansion

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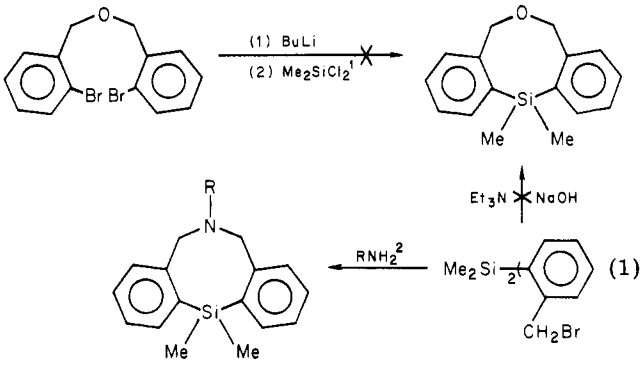
Reaction of fluoride ion sources with 11-(halomethyl)-11-methyl-5,11-dihydrodibenzo[*b*,*e*][1,4]oxasilepin generates isomers of 11-methyl-11-fluoro-11,12-dihydro-6*H*-dibenzo[*b*,*f*]oxasilocins. Maximum conversion of silepin to silocins occurs from the iodomethyl precursor and a slight stoichiometric excess of tetrabutylammonium fluoride. The oxasilocins are cleaved by excess fluoride ion to the ethers, benzyl *o*-tolyl ether and phenyl *o*-xylyl ether, and reduced with lithium aluminum hydride to the corresponding 11-methyldibenzo[*b*,*f*]oxasilocins. The spectroscopic properties of this new heterocyclic system are described.

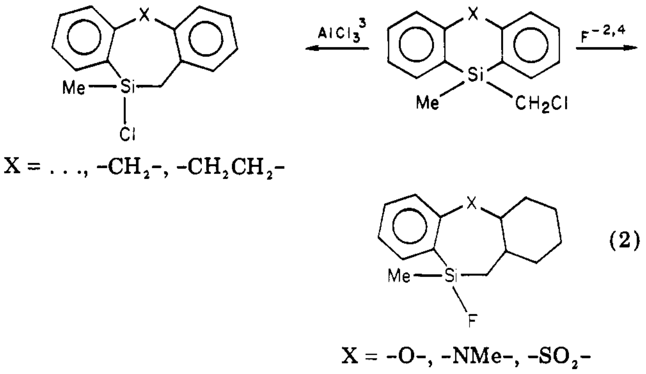
Introduction

The routes to medium-sized rings which contain silicon heteroatoms are few. The two tactics in general use include the reaction of a dilithio or diGrignard reagent with an organosilicon dihalide or by ring closure through reaction of an appropriate carbofunctional organosilane. The Grignard route is not useful when the size of the ring formed in the reaction process is larger than seven atoms. The failure of these two general approaches in attempts to form dibenzo[*c*,*f*][1,5]oxasilocins has been previously reported (eq 1),[1] although the related azasilocins may be formed from bis(*o*-(bromomethyl)phenyl)dimethylsilane and primary amines.[2]



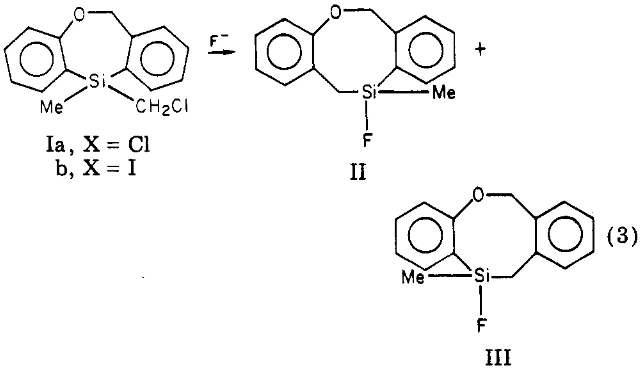
A third approach to medium-sized rings is through ring expansion. Dibenzo[*b*,*f*]silocins are formed in reasonable yields from the appropriate dibenzo[*b*,*f*]silepin precursor and aluminum chloride (eq 2), but acid catalysts are not effective for silacycles which contain heteroatoms with lone electron pairs. Dibenzoheterosilepins are generated from phenheterosilins on reaction with stoichiometric fluoride (eq 2).

The present study describes the results of the fluoride ion induced reactions of 11-(halomethyl)-11-methyl-5,11-dihydrodibenzo[*b*,*e*][1,4]oxasilepins which lead to the formation of isomers of the dibenzo[*b*,*f*]oxasilocin system.



Results and Discussion

The fluoride ion induced reaction of a dibenzo[*b*,*e*][1,4]oxasilepin could lead to two isomers of dibenzo[*b*,*f*]oxasilocin (eq 3). Initial efforts focused on the conditions which had previously proved successful for the conversion of six-membered rings to seven-membered rings (eq 2). No reaction was observed between Ia and KF·HF in refluxing acetonitrile after 20 h, and with addition of 18-crown-6 only minor reaction occurred after 22 h. With KF(tech), reaction also was slow but, when 18-crown-6 was added, no starting material was observed after 24 h (KF/Ia = 1.5). The product mixture that was obtained contained the silocin as a minor component. When the relative molar amount of KF(tech) and the reflux period were both decreased, the yield of silocin increased but starting material was still present. The preliminary studies also showed that the volatile reaction products contained only one silocin isomer as well as ethers that would be formed from cleavage of the ring-expanded products (eq 4 and 5). For verification of this assignment, authentic samples of IV and V were prepared from *o*-cresol/*α*-bromotoluene[5] and phenol/*o*-methylbenzyl bromide, respectively.



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[1] Chang, V. H. T.; Corey, J. Y. *J. Organomet. Chem.* **1980**, *190*, 217.

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[4] Corey, J. Y.; Chang, V. H. T. *J. Organomet. Chem.* **1979**, *174*, C15.

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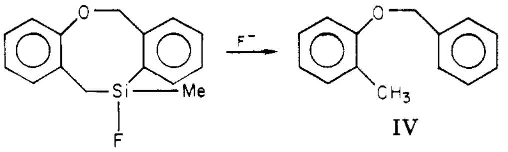

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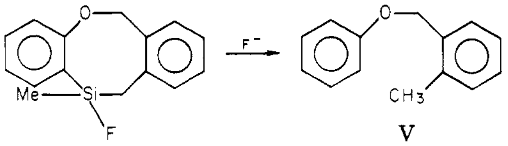
IV



(5)

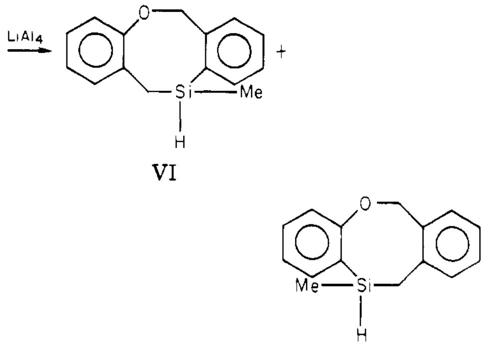
V

In an effort to improve conversion of Ia to the silocin other conditions were explored. The formation of IV and V suggests that both the starting silepin and the silocin product compete for the fluoride ion and thus an excess of fluoride should be avoided. When the ratio of F^-/Ia is decreased, the amount of silocin isolated is higher. If cleavage of silocins occurs more slowly than expansion of the silepin, then an approach designed to increase the rate of conversion of silepin when close to the stoichiometric quantity of F^- is present should improve the yields of silocins. The homogeneous conditions provided by $Bu_4N^+F^-$/THF result in a higher proportion of product isolated as silocin although the yields of II, III, IV, and V combined do not alter significantly. An alternative to homogeneous conditions was found in the combination of KF and KI (KF/KI = 10). The rate of conversion of Ia to Ib occurs faster than Ia to II or III, and in general, iodomethyl derivatives undergo ring expansion more rapidly than the chloromethyl derivatives.[3] Again, the percent of the combination of II through V is not significantly different from that achieved with KF/crown, but the silocin is the major product. With either $Bu_4N^+F^-$/THF or KF/KI only one silocin isomer appears to be formed in the time that Ia is consumed.

The reaction of the iodomethyl derivative, Ib, occurs with excess KF within 10 h in the absence of crown ether. When close to the stoichiometric amount of KF is employed, the product mixture contains both silocin isomers and minimal or no detectable cleavage-derived ethers. The two silocin isomers are formed in about a 2/1 ratio, with the major isomer identical with the silocin isolated from reactions of Ia. The use of $Bu^4N^+F^-$/THF also provides both silocins and no detectable cleavage-derived ethers although a minor component (~5%) of the product mixture contains what appears to be *o*-($MeSiH_2$)$C_6H_4OCH_2C_6H_4CH_3$-*o* or its isomer. The yield of silocin products exceeds 60% when Ib is used under homogeneous conditions.

The structure of the major isomer from the reaction of Ib and of the only isomer obtained from Ia was determined by reaction of isolated, purified samples of both silocin products with KF. The minor isomer reacts completely with KF(tech) in less than 18 h in refluxing CH_3CN to give *o*-$CH_3C_6H_4CH_2OC_6H_5$, V, as the major product as determined by ^1H NMR. These results are consistent with the silocin III as the minor isomer. The major silocin isomer shows no detectable reaction with KF(tech) after 24 h in refluxing acetonitrile. Addition of crown ether was required to convert the major isomer to *o*-$CH_3C_6H_4OCH_2C_6H_5$, IV, as the only identifiable product (91%). Authentic samples of IV and V are recovered unchanged (96%) after being heated with a 1.5 M excess of KF(tech) in refluxing acetonitrile for 22.5 h. The silocin mixtures are readily reduced with $LiAlH_4$ to the corresponding silanes VI and VII (eq 6).

II and III



VI

(6)

VII

The ^1H NMR spectra of II and III show the characteristic FSiMe doublet between 0.4 and 0.6 ppm (J(HCSiF) = 7.2 Hz) also reported for other heterocycles produced from ring expansion. The $SiCH_2Arom$ absorption appears as a broad singlet in II and as an apparent doublet in III both of which are easily observed in mixtures which contain II and III. In the case of the reduced silocins VI and VII, the $SiCH_2Arom$ absorption appears in the NMR spectra of both as an AB quartet split by SiH and in addition an SiH sextet is observed at about 4.5–4.8 ppm. Neither the ^1H nor ^{13}C NMR data could be used to uniquely define the structure of the major (or minor) silocin isomer generated in the ring expansion reaction. However, the distinction between these two isomers could be made from the mass spectral data, as illustrated in Scheme I. The mass spectrum of each silocin is characterized by elimination of O=SiMeH and hydrocarbon as well as hydrogen rearrangement followed by hydrocarbon loss. The ions generated in these processes clearly distinguish between VI and VII. For comparison, the data for the cleavage-derived ethers, IV and V, are also included.

These experiments demonstrate that eight-membered rings may be generated by anion-induced rearrangement of halomethyl-substituted silepins although not as smoothly nor in as high yields as has been demonstrated for six- to seven-membered ring conversions. Although both Ia and Ib may react completely with the fluoride ion, reactions other than silocin formation occur. The products of these alternate pathways were not analyzed but are probably oligomers since high-boiling, glassy residues are obtained after removal of the volatiles. Benzyl phenyl ether, which would be obtained from cleavage of Ia (or Ib), was not observed when starting materials were carefully purified. The highest yields of the eight-membered ring product are obtained from the iodomethyl precursor and when homogeneous conditions are employed for the rearrangement. The preparation of Ib requires an additional step. However, the combination of Ia/KF/KI actually generates both II and III, but III is consumed when additional KF is added at the end of the reflux period to complete the conversion of Ia. The conditions for maximum conversion of Ia to II and III with KF/KI were not determined.

Experimental Section

General Data. All reactions which involved organolithium reagents, chlorosilanes, and Grignard reagents were carried out under an atmosphere of dry nitrogen in flame-dried glassware.

The organic halide *o*-$BrC_6H_4OCH_2C_6H_4Br$-*o* was prepared according to the literature method from *o*-$BrC_6H_4CH_2Br$ and *o*-BrC_6H_4OH.[6] The commercial reagents *o*-BrC_6H_4OH, *o*-$CH_3C_6H_4OH$, C_6H_5OH, $C_6H_5CH_2Br$, $MeSi(CH_2Cl)Cl_2$, *n*-BuLi, KF(tech), $Bu_4N^+F^-$/THF, KI, and $LiAlH_4$ were used as supplied. The technical KF samples employed in this study contained 15% by weight of water (determined by heating to constant weight

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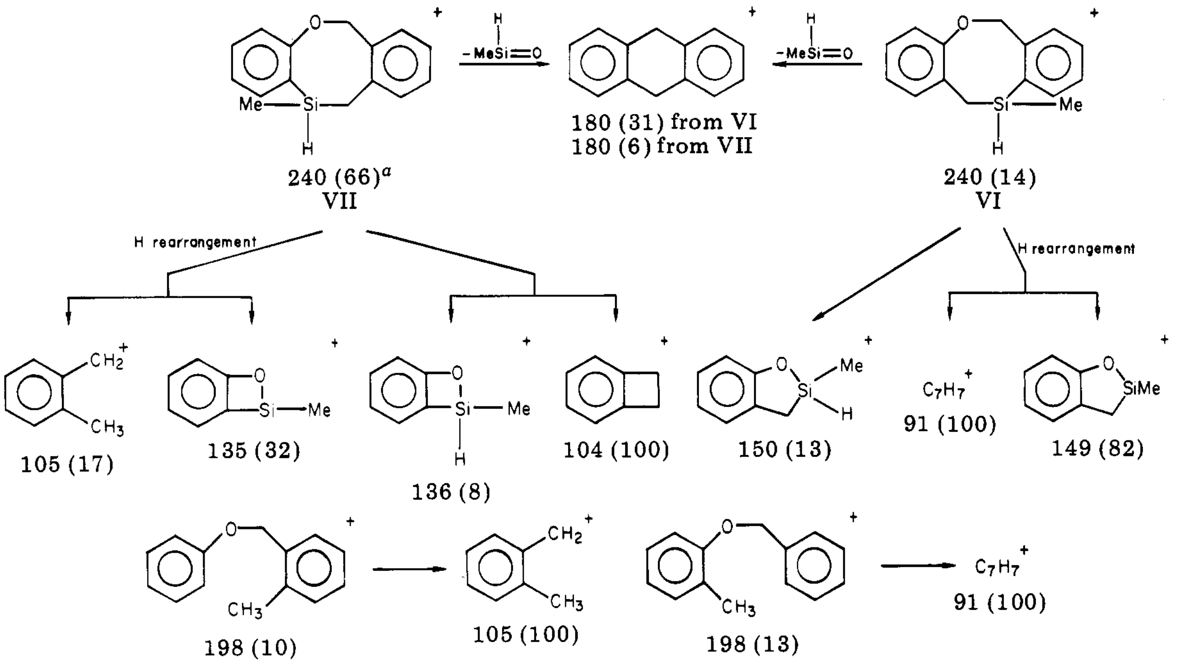
[6] Auwers, *Justus Liebigs Ann. Chem.* **1870**, *357*, 90.

Scheme I



[a] m/e (%).

at 110 °C). The o-$BrC_6H_4CH_2Br$ was prepared by bromination (Br_2) of o-$BrC_6H_4CH_3$.[7]

Tetrahydrofuran was dried by treatment with n-BuLi (o-phenanthroline indicator) followed by distillation,[8] and acetonitrile was dried over molecular sieves a minimum of 2 days prior to use.

Proton NMR spectra were recorded in $CDCl_3$ on a Varian T-60 spectrophotometer (internal Me_4Si as reference (ppm) unless otherwise specified). Mass spectral data were collected at 70 eV on an AEI MS-1201 B or an HP 5985A GC/MS mass spectrometer. The Kugelrohr distillation method was employed in all vacuum distillations.

Analyses were performed by Galbraith Laboratories, Inc., and by Miles Laboratories.

11-(Chloromethyl)-11-methyl-5,11-dihydrodibenzo[*b*,*e*]-[1,4]oxasilepin, Ia. The oxepin, Ia, was prepared by the published procedure[1] from o-bromobenzyl o-bromophenyl ether (21 g, 0.061 mol), n-BuLi (7.7 g, 0.12 mol), and methyl(chloromethyl)dichlorosilane (10 g, 0.061 mol). After aqueous workup and removal of the solvent from the organic layer, Kugelrohr distillation of the resultant oil provided two fractions, 6.8 g boiling at 140–155 °C (0.05mmHg) and 1.7 g boiling at 155–175 °C (0.05mmHg) both of which contained Ia. The lower boiling fraction contains a benzyl phenyl ether impurity which is partially removed by redistillation or chromatography over silica gel.

Chromatographic purification of 1.5–2.0 g portions of each fraction (40 g of silica gel, 2:3 and 1:1 benzene–hexanes mixtures as eluant) gave Ia (5.8 g, 35%): ^1H NMR ($CDCl_3$) δ 7.8–6.7 (m, Arom), 5.4–4.9 (q, OCH_2), 3.4 (s, CH_2Cl), 0.85 (s, $SiCH_3$); m/e mass spectrum, (relative intensity) 274 (1.1), 225 (100), 197 (10), 165 (33), 147 (12). Presence of an impurity (5–8%) is indicated by an OCH_2 singlet at 5.1 ppm and enhanced aromatic absorption.

An analytical sample of Ia, obtained as a colorless oil, was prepared by column chromatography of purified samples of Ia (silica gel, 1:4 chloroform–n-hexanes mixture as eluant). (Anal. Calcd for $C_{15}H_{15}OSiCl$: C, 65.57; H, 5.46. Found: C, 65.63; H, 5.52.)

11-(Iodomethyl)-11-methyl-5,11-dihydrodibenzo[*b*,*e*]-[1,4]oxasilepin, Ib. A 2.9-g sample of crude, distilled Ia (80% Ia, 2.3 g, 8.5 mmol) was heated at reflux with KI (2.73 g, 16 mmol) in CH_3CN (50 mL) for 7 h. After removal of the solvent, the residue was treated with ether–water and the oil obtained from the ether layer was purified by column chromatography (50 g of silica gel, 3:2 and 1:1 hexanes–benzene mixtures as eluant) to give Ib (2.71 g, 87%). The eluted fractions consistently contained about 10% by weight of an impurity which could be removed by heating samples up to 130 °C (0.05mmHg) to eliminate the volatiles: ^1H NMR ($CDCl_3$) δ 7.7–6.9 (m, 8.3, arom), 5.5–4.9 (q, 1.7, OCH_2), 2.6 (s, 2.0, CH_2I), 0.73 (s, 3.0, $SiCH_3$). A sample was further purified by column chromatography (silica gel, 1:4 chloroform–n-hexane mixture as eluant) but Ib, a colorless oil, still contained minor impurities. (Anal. Calcd for $C_{15}H_{15}OSiI$: C, 49.18; H, 4.10. Found: C, 50.02; H, 4.60.) No further effort was made to obtain an analytical sample.

Benzyl *o*-Tolyl Ether, IV. To a solution of sodium ethoxide prepared from sodium (2.3 g, 0.10 mol) and ethanol (50 mL) was added o-cresol (10.8 g, 0.100 mol). The mixture was stirred for 10 min and α-bromotoluene (17.1 g, 0.100 mol) added. After 20 min at room temperature, the solution was heated at reflux until the solution tested neutral. After extraction with ether and removal of the solvent, Kugelrohr distillation of the resultant oil gave 8.7 g (44%) of IV as a colorless oil: bp 110–115 °C (0.1mmHg) [lit. 110 °C (0.01mmHg)];[5] ^1H NMR ($CDCl_3$) δ 7.4–6.5 (m, 9.3, arom), 4.9 (s, 1.8, OCH_2), 2.2 (s, 2.9, CH_3); mass spectrum, m/e (relative intensity) 198 (14), 105 (13), 91 (100).

Phenyl *o*-Xylyl Ether, V. To a solution of sodium ethoxide prepared from sodium (3.2 g, 0.14 mol) and ethanol (100 mL) was added phenol (14 g, 0.15 mol). After the mixture had been stirred for 10 min, crude o-methylbenzyl bromide [prepared from o-xylene (16 g, 0.15 mol) and N-bromosuccinimide (2.7 g, 0.15 mol)] was added, whereupon NaBr begins to precipitate. The reaction mixture was heated at reflux for 1 h, the solvent removed, and the residue extracted with ether–water. The residue obtained from evaporation of the ether layer was distilled to give 18 g (61%) of V, bp 100–120 °C (0.05mmHg), which slowly solidified. Recrystallization of the solid from ethanol gave white crystals: mp 50–51 °C; ^1H NMR ($CDCl_3$) δ 7.5–6.7 (m, 9.3, arom), 4.9 (s, 1.8, OCH_2), 2.3 (s, 2.9, CH_3); mass spectrum, m/e (relative intensity) 198 (10), 105 (100), 91 (19), 77 (10). (Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.84; H, 7.13.)

Reaction of Ia and Ib with Fluoride Sources. A sample of (halomethyl)silepin and the metal salt were heated at reflux in acetonitrile until an aliquot showed that no or only minor amounts of I remained. The solvent was removed, hexanes were added to the residue, and insoluble material was removed by filtration. The oil obtained on concentration of the hexanes solution was distilled and all material with a boiling point up to 130–135 °C (0.05mmHg) was collected. Unreacted I was generally recovered from fractions with a boiling point of 135–150 °C

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[7] Letsinger, R. L.; Skoog, I. H. *J. Am. Chem. Soc.* **1955**, *77*, 5176.

[8] Purdum, W. R.; Bartling, G. J. *J. Chem. Educ.* **1975**, *52*, 120.

Table I. Reaction of 5-(Halomethyl)-5-methyl-5,11-dihydrodibenzo[*b,e*][1,4]oxasilepin, I, with Fluoride Sources

I, g	F^- sources	F^-/I	*T*, °C (*t*, h)	distilled product,[a] g	product,[b] g		recovered I,[c] g	sum II, III, IV, and IV,[a] %
					silocins	cleavage ethers		
Ia								
2.91[e]	KF/crown[f]	1.6	80 (24)	1.1	trace	0.72 (IV + V)[g,h]		30-35
3.0[e]	KF/crown	1.0	80 (9)	0.80	0.18 (II)	0.31 (IV + V)	0.36	26
2.89[i]	$Bu_4N^+F^-$	1.4[j]	20 (1)	0.88[k]	(II)			
2.93[i]	$Bu_4N^+F^-$	1.1	20 (0.8)	1.21	0.52 (II)[l,m]	0.11 (IV + V)[m]	0.30	29
1.38[i]	KF/KI[n]	1.0[o]	80 (20)	*p*	0.39 (II)	0.04 (V)		34
Ib								
0.93[e]	KF	1.0	80 (11)	0.37	0.49 (II + III)[q]	0.06 (IV + V)		29
2.00[e]	KF	2.0	80 (9)	0.67				
2.39[r]	KF	1.1	80 (10)	1.10	0.24 (III)[h] 0.54 (II)[h]		0.13	48
3.21[i]	$Bu_4N^+F^-$	1.07	20 (1)	1.32	0.38 (III)[l,h] 0.72 (II)[l,h]		0.40	67[s]
0.18[i]	AgF	2.0	20 (16)		(II) (43%)[t]		(16%)[t]	

[a] bp <135 °C (0.1 mm). [b] Distilled samples eluted over silica gel unless otherwise indicated. [c] Isolated from fractions with bp >135 °C (0.1 mm). [d] Corrected for any recovered starting material. [e] Distilled sample (estimated, 85% Ia). [f] No reaction in the absence of crown ether. [g] Contains unidentified benzyl phenyl ether (estimated 0.2 g). Ratio of V/IV = 2.5. [h] Isomer distribution estimated from ^1H NMR spectra. [i] Samples purified by distillation followed by chromatography. [j] Added in three increments until Ia disappeared. [k] Only silocin II is observed in addition to cleavage products. [l] Distilled product reduced with $LiAlH_4$ before elution over silica gel. [m] Product distribution estimated from ^1H NMR spectra of eluted fractions. [n] KF/KI = 10. [o] Ratio increased to 1.1 after 15 h of reflux to complete conversion of Ia. [p] Product eluted directly over silica gel. [q] Contains Ib. [r] Sample purified by elution over silica gel. [s] Includes partial silocin cleavage product *o*-$(CH_3SiH_2)C_6H_4OCH_2C_6H_4CH_3$-*o* or isomer. [t] Estimated from NMR data.

(0.05mmHg). The lower boiling fraction was chromatographed over silica gel.

Reactions with *n*-$Bu_4N^+F^-$ were carried out in THF for 30–60 min. A precipitate of *n*-$Bu_4N^+I^-$ formed in reactions of Ib. After the reaction period, the solvent was removed and the residue treated with ether–water. The ether was removed from the organic layer, and the oil was distilled and then chromatographed as described for reactions with metal salts.

The results are summarized in Table I.

11-Methyl-11-fluoro-11,12-dihydro-6*H*-dibenzo[*b,f*][1,5]oxasilocin, II, and 12-Methyl-12-fluoro-11,12-dihydro-6*H*-dibenzo[*b,f*][1,4]oxasilocin, III. A 2.39-g sample of (iodomethyl)silepin, Ib (purified by column chromatography and was 90% Ib, 5.9 mmol), 0.49 g of KF(tech) (85% KF, 7.2 mmol), and acetonitrile (50 mL) were heated at reflux for 10 h. The solvent was removed, hexanes were added to the residue, and insoluble material (0.69 g of a mixture of KF and KI) was removed by filtration. Kugelrohr distillation of the oil recovered from the hexanes gave a mixture of the silocins (1.10 g), bp 105–130 °C (0.05mmHg), and starting material (0.13 g), bp 130–145 °C (0.05mmHg). Column chromatography of the distilled oil (40 g of silica gel, eluant as indicated) gave a total of 0.83 g (58%) of silocins II and III as colorless oils.

The fraction which eluted with 1:1 benzene–hexanes contained 0.42 g of II contaminated with traces of a benzyl phenyl ether impurity: ^1H NMR ($CDCl_3$) δ 8.1–6.7 (m, arom), 5.6–5.0 (q, OCH_2), 2.3–2.1 (br m, $SiCH_2$), 0.58–0.47 (d, $FSiCH_3$); mass spectrum, *m/e* 258 (M^+). An attempt to prepare an analytical sample of II by further column chromatography over silica gel was not successful.

The fraction which eluted with 3:2 benzene–hexanes contained 0.27 g of a mixture of II and III. The fraction which eluted with 7:3 benzene–hexanes contained 0.14 g of silocin III: ^1H NMR ($CDCl_3$) δ 7.8–6.5 (m, 8.2, arom), 5.3–4.8 (q, 2.1, CH_2), 2.6–2.5 (apparent d, 1.7, $SiCH_2$), 0.53–0.40 (d, 3.0, $FSiCH_3$); mass spectrum, *m/e* 258 (M^+). (Anal. Calcd for $C_{15}H_{15}FOSi$: C, 69.77; H, 5.81. Found: C, 69.28; H, 5.88.) An attempt to further purify III resulted in decomposition of the sample.

11-Methyl-11,12-dihydro-6*H*-dibenzo[*b,f*][1,5]oxasilocin, VI, and 12-Methyl-11,12-dihydro-6*H*-dibenzo[*b,f*][1,4]oxasilocin, VII. To a sample of Ib (3.21 g, which had been purifed by removing volatiles with a boiling point below 130 °C (0.05mmHg) followed by column chromatography of the residue over silica gel, 8.8 mmol) dissolved in tetrahydrofuran (50 mL) was added dropwise a solution of $Bu_4N^+F^-$ (9.4 mL, 1.0 M). The solution was stirred at room temperature for 1 h during which time a precipitate formed. The solvent was evaporated and the residue extracted with water–ether followed by filtration to remove *n*-$Bu_4N^+I^-$ (2.73 g, 85%). Kugelrohr distillation of the residue obtained from the ether layer gave a mixture of II and III [1.32 g, 72% based on recovered starting material, bp 108–128 °C (0.1mmHg)] and starting material [0.4 g, bp 135–150 °C (0.1mmHg)].

The mixture of silocins was treated with $LiAlH_4$ (0.95 g, 25 mmol) in refluxing ether for 1 h. An oil was obtained from the organic layer after hydrolytic workup. Column chromatography of the oil (50 g of silica gel, eluant as indicated) gave a total of 1.10 g (62%) of silocins IV and V as colorless oils.

The fraction which eluted with 2:3 benzene–hexanes contained 0.58 g of VI: ^1H NMR ($CDCl_3$) δ 7.6–6.7 (m, 8.3, arom), 5.3 (s, 1.8, OCH_2), 4.9–4.6 (m, 1.1, SiH), 2.6–1.9 (AB portion of an ABX multiplet centered at 2.25, 1.8, $SiCH_2$), 0.48–0.47 (d, 2.9, $HSiCH_3$); mass spectrum, *m/e* (relative intensity) 240 (14), 239 (11), 225 (53), 180 (31), 179 (70), 178 (41), 163 (35), 166 (13), 150 (13), 149 (83), 135 (11), 121 (13), 91 (100). The silocin VI was further purified by additional column chromatography over silica gel. (Anal. Calcd for $C_{15}H_{16}OSi$: C, 75.00; H, 6.67. Found: C, 75.05; H, 6.82.)

The next fraction which eluted with 1:1 benzene–hexanes contained 0.42 g of a mixture of both VI and VII as well as a trace of 5,5-dimethyl-10,11-dihydro-5*H*-dibenzo[*b,f*]silepin. The fraction which eluted with 3:2 benzene–hexanes contained 0.20 g of VII: ^1H NMR ($CDCl_3$) δ 7.4–6.6 (m, 8.1, arom), 5.1 (s, 2.0, OCH_2), 4.7–4.3 (sextet, 0.9, SiH), 2.8–2.2 (AB portion of an ABX multiplet centered at 2.5, 1.9, $SiCH_2$), 0.38–0.32 (d, 3.0, $SiCH_3$); mass spectrum, *m/e* (relative intensity) 240 (66), 180 (6), 166 (3), 165 (10), 136 (8), 135 (32), 121 (20), 105 (17), 104 (100). The silocin VII was further purified by additional column chromatography over silica gel. (Anal. Calcd for $C_{15}H_{16}OSi$: C, 75.00; H, 6.67. Found: C, 74.25; H, 6.78.) Further efforts to obtain an anlytical sample of VII resulted in decomposition.

The earliest fraction which eluted with 1:4 benzene–hexanes contained 0.09 g of an oil which was tentatively identified as *o*-$(CH_3SiH_2)C_6H_4OCH_2C_6H_4CH_3$-*o* or its isomer: ^1H NMR ($CDCl_3$) δ (in part) 4.5–4.3 (q, SiH), 0.30–0.16 (t, $SiCH_3$).

Reaction of II with KF/18-Crown-6. A solution of II (0.40 g, 1.5 mmol) and 18-crown-6 (0.05 g) in acetonitrile (25 mL) was heated at reflux with KF(tech) (85% KF, 0.15 g, 2.2 mmol) for 18 h. The solvent was removed and the residue extracted with ether–water. The ether layer was dried over Na_2SO_4, and upon removal of ether, IV (0.28 g, 91%) was obtained which was identical with an authentic sample.

Reaction of III with KF(tech). A solution of III (0.08 g, 0.3 mmol) in acetonitrile (5 mL) was heated at reflux with KF(tech) (85% KF, 0.03 g, 0.4 mmol) for 18 h. After removal of the solvent an NMR spectrum of the residue showed only the presence of V.

Reaction of IV with KF(tech). A solution of IV (1.41 g, 7.12 mmol) in acetonitrile was heated at reflux with KF(tech) (85% KF, 0.64 g, 9.4 mmol) for 22.5 h. After removal of the solvent, the residue was extracted with ether–water and the ether layer dried over Na_2SO_4. Removal of the ether resulted in the recovery of IV (1.36 g, 96%).

Reaction of V with KF(tech). A solution of V (1.82 g, 9.2 mmol) in acetonitrile (50 mL) was heated with KF(tech) (85% KF, 0.83 g, 12 mmol) at reflux for 22.5 h. After workup, V (1.79 g, 98%) was recovered.

Acknowledgment. V.H.T.C. wishes to thank Miles Laboratories for the use of their facilities for a portion of the investigation.

Registry No. Ia, 71445-87-9; Ib, 80532-94-1; II, 80532-95-2; III, 80532-96-3; IV, 19578-70-2; V, 57076-47-8; VI, 80532-97-4; VII, 80532-98-5; o-bromobenzyl o-bromophenyl ether, 5310-54-3; o-cresol, 95-48-7; α-bromotoluene, 100-39-0; phenol, 108-95-2; o-methylbenzyl bromide, 89-92-9.

Reaction of Secondary and Tertiary Alkyllithium Reagents with Vinyl Di- and Trisiloxanes. Synthesis of α-Silyl Silanols

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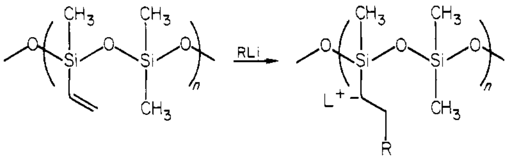
Department of Chemistry, University of Southern California, Los Angeles, California 90007

Received November 24, 1981

Secondary and tertiary alkyllithiuim reagents add to the carbon–carbon double bond of vinyl di- and trisiloxanes at low temperature (−78 °C) to yield α-lithioalkyl di- and trisiloxanes. If these are quenched with moist THF at low temperature alkyl di- and trisiloxanes are formed. However, if such α-lithioalkyl di- and trisiloxanes are warmed to 0 °C prior to quenching, α-silyl silanols are found. These products result from a 1,3 rearrangement of a silyl group from oxygen to the carbanion center. This converts the carbanion into an alkoxide anion. The scope and generality of these reactions have been explored.

We have been interested recently in developing methods to modify siloxane polymers. Despite previous reports that organolithium reagents easily cleave hexaorganodisiloxanes to yield tetraorganosilanes and lithium triorganosilanoates,[1] the possible addition of alkyllithium reagents to the carbon–carbon double bond of vinyl methyl siloxanes seemed worthy of examination.

$$Ph_3SiOSiPh_3 + PhLi \rightarrow Ph_4Si + Ph_3SiO^-Li^+ \quad (1)$$



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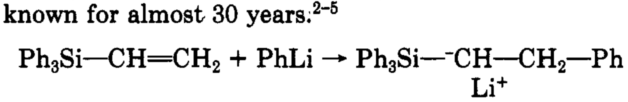
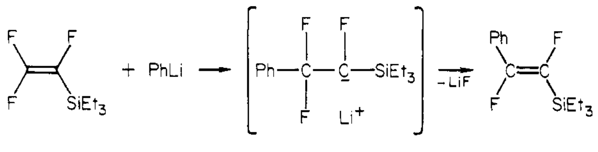
The addition of Grignard and organolithium reagents to vinylsilanes to yield α-silyl organometallics has been known for almost 30 years.[2-5]



$$Ph_3Si{-}CH{=}CH_2 + PhLi \rightarrow Ph_3Si{-}\underset{Li^+}{^-CH}{-}CH_2{-}Ph \quad (3)$$

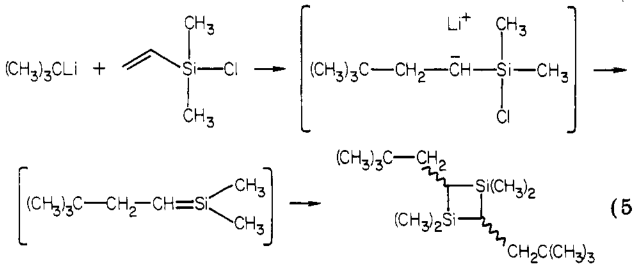
Such α-silyl organometallics have proved useful for the preparation of substituted alkenes via the Peterson olefination reaction.[6,7]

However, addition of organolithium reagents to (β-halovinyl)silanes or to vinylchlorosilanes yield α-silyl organometallics which may undergo elimination of the elements of lithium halide. This may result in the formation of a carbon–carbon double bond or reactive silicon–carbon doubly bonded intermediate. For example, addition of organolithium reagents to perfluorovinyltriethylsilane results in an α-silyl organolithium intermediate which undergoes loss of lithium fluoride to yield (β-organo-α,β-difluorovinyl)triethylsilanes (eq 4),[8,9] while addition of



(4)

tert-butyllithium to vinyldimethylchlorosilane gives substituted 1,3-disilacyclobutanes.[10-12] The formation of these compounds have been interpreted in terms of addition of the organolithium reagent to the vinylchlorosilane to yield an α-silyl organolithium reagents which undergoes loss of lithium chloride to yield a reactive intermediate possessing a silicon–carbon double bond. These dimerize in a head-to-tail manner to yield the products observed (eq 5).



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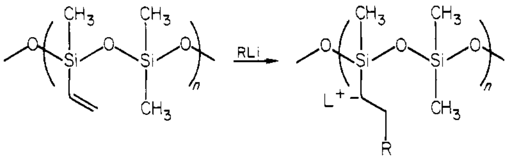

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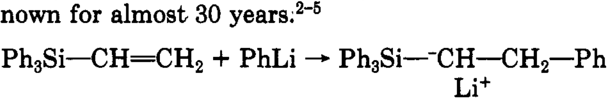
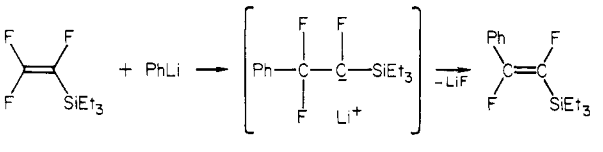
The addition of Grignard and organolithium reagents to vinylsilanes to yield α-silyl organometallics has been known for almost 30 years.[2–5]



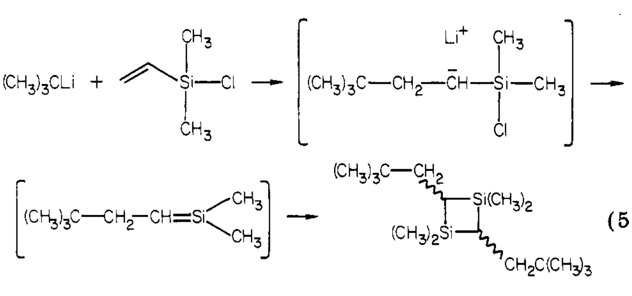
$$\mathrm{Ph_3Si{-}CH{=}CH_2 + PhLi \rightarrow Ph_3Si{-}\underset{Li^+}{^-CH}{-}CH_2{-}Ph} \quad (3)$$

Such α-silyl organometallics have proved useful for the preparation of substituted alkenes via the Peterson olefination reaction.[6,7]

However, addition of organolithium reagents to (β-halovinyl)silanes or to vinylchlorosilanes yield α-silyl organometallics which may undergo elimination of the elements of lithium halide. This may result in the formation of a carbon–carbon double bond or reactive silicon–carbon doubly bonded intermediate. For example, addition of organolithium reagents to perfluorovinyltriethylsilane results in an α-silyl organolithium intermediate which undergoes loss of lithium fluoride to yield (β-organo-α,β-difluorovinyl)triethylsilanes (eq 4),[8,9] while addition of *tert*-butyllithium to vinyldimethylchlorosilane gives substituted 1,3-disilacyclobutanes.[10–12] The formation of these compounds have been interpreted in terms of addition of the organolithium reagent to the vinylchlorosilane to yield an α-silyl organolithium reagents which undergoes loss of lithium chloride to yield a reactive intermediate possessing a silicon–carbon double bond. These dimerize in a head-to-tail manner to yield the products observed (eq 5).



(4)



(5)

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(1) H. Gilman, H. N. Bendict, and H. Hartzfeld, *J. Org. Chem.* **19**, 419 (1954).

(2) L. F. Cason and H. G. Brooks, *J. Am. Chem. Soc.*, **74**, 4582 (1952).

(3) L. F. Cason and H. G. Brooks, *J. Org. Chem.*, **19**, 1278 (1954).

(4) J. F. Mulvaney and Z. G. Gardlund, *J. Org. Chem.*, **30**, 917 (1965).

(5) A. G. Brook, J. M. Duff, and D. G. Anderson, *Can. J. Chem.*, **48**, 561 (1970).

(6) D. J. Peterson, *J. Org. Chem.*, **33**, 780 (1968).

(7) For a review see: D. J. Peterson, *J. Organomet. Chem. Libr.*, **7**, 295 (1972).

(8) D. Seyferth, T. Wada, and G. Raab, *Tetrahedron Lett.*, 20 (1960).

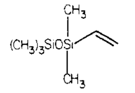
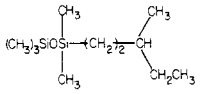
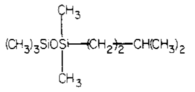
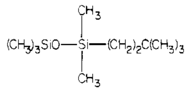
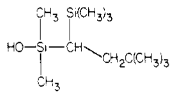
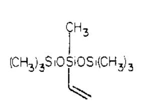
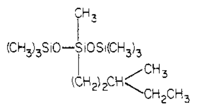
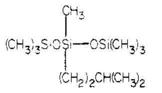
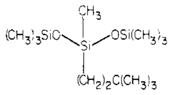
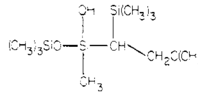
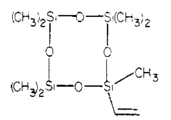
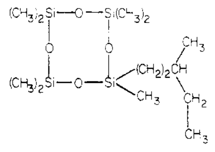
(9) D. Seyferth and T. Wada, *Inorg. Chem.* 1, 78 (1962).

(10) P. R. Jones and T. F. O. Lin, *J. Am. Chem. Soc.*, **99**, 2013 (1977).

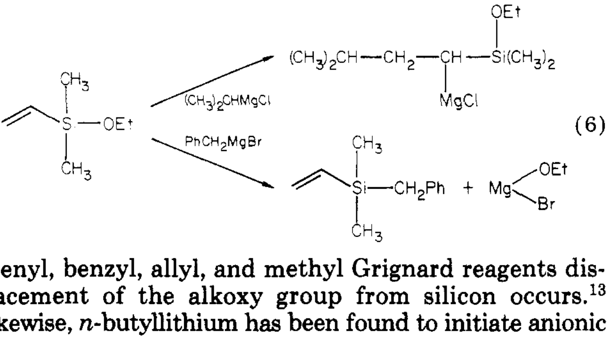
(11) P. R. Jones and T. F. O. Lin, *J. Am. Chem. Soc.*, **99**, 8447 (1977).

(12) P. R. Jones, T. F. O. Lin, and R. A. Pierce, *J. Am. Chem. Soc.*, **102**, 4970 (1980).

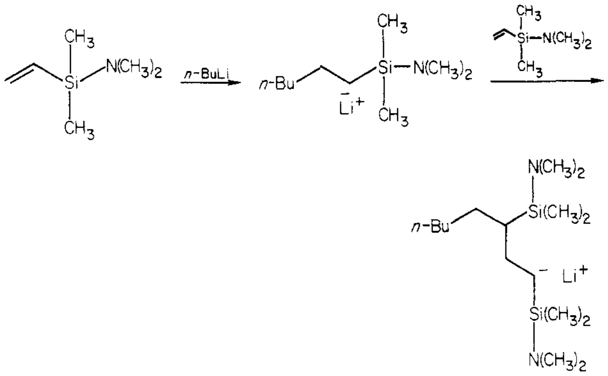
Table I. Reaction of Secondary and Tertiary Alkyllithium Reagents with Vinyl Siloxanes at Low Temperature

siloxane	alkyllithium	products	yield, %
 I	*s*-BuLi	 IV	90
I	*i*-PrLi	 VI	91
I	*t*-BuLi	 VIII	77
		 IX	23
 II	*s*-BuLi	 XI	95
II	*i*-PrLi	 XIII	91
II	*t*-BuLi	 XV	75
		 XVI	25
	*s*-BuLi	 XIX	90

On the other hand, addition of secondary and tertiary alkyl Grignard reagents to vinyl alkoxysilanes to yield α-silyl Grignard reagents has been observed (eq 6). With phenyl, benzyl, allyl, and methyl Grignard reagents displacement of the alkoxy group from silicon occurs.[13] Likewise, *n*-butyllithium has been found to initiate anionic polymerization of vinyldimethyl(dimethylamino)silane.[14] This polymerization involves an α-silyl organolithium species (eq 7).

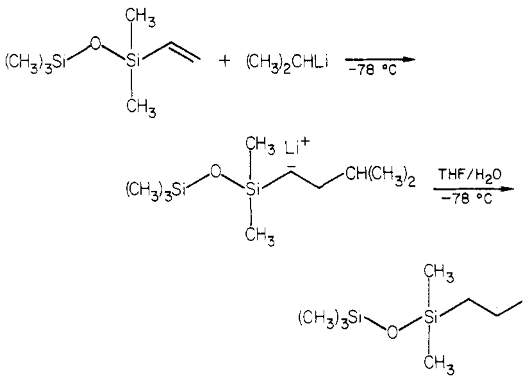


(6)



(7)

We have studied the reaction of vinyl di- and trisiloxanes with alkyllithium reagents. We have found that secondary and tertiary alkyllithium reagents rapidly add in essentially quantitative yield to the carbon–carbon double bond of vinyl siloxanes at −78 °C to yield (α-lithioalkyl)disiloxanes or (α-lithioalkyl)trisiloxanes. The addition does not occur with primary alkyl- or aryllithium reagents under these low-temperature conditions. Secondary and tertiary alkyllithium reagents are frequently found to be more reactive than primary alkyl- or aryllithium reagents.[15] If these anions are quenched at low temperature (−78° C) by addition of moist THF, alkyl siloxanes are obtained. These reactions have been studied with *tert*-butyllithium, isopropyllithium, and *sec*-butyllithium in combination with vinylpentamethyldisiloxane (I), 3-vinylheptamethyltrisiloxane (II) and vinylheptamethylcyclotetrasiloxane (III)(eq 8). See Table I for data.



(8)

On the other hand, if such (α-lithioalkyl)disiloxanes or (α-lithioalkyl)trisiloxanes are permitted to warm to 0 °C prior to quenching a rearrangement occurs in which a silyl group migrates from oxygen to the carbanion center to yield an α-silyl silanoate. In this process, a carbanion is converted to an alkoxide anion. In the case of *tert*-butyllithium this rearrangement can not be completely suppressed (~20–25%) even at −95° C. After quenching, such reactions yield hindered dimethyl(α-trimethylsilyl)alkyl)silanols (eq 9). See Table II for data. Possibly due to steric hindrance these are quite stable to dehydration and do not readily form siloxanes.

There is only one previous report in the literature of this type of rearrangement. West observed that metalation of hexamethyldisiloxane with *tert*-butyllithium gave dimethyl(trimethylsilylmethyl)silanol after quenching with

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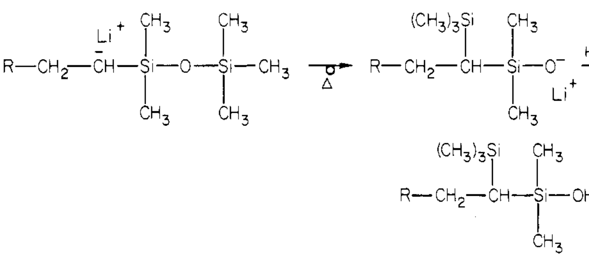
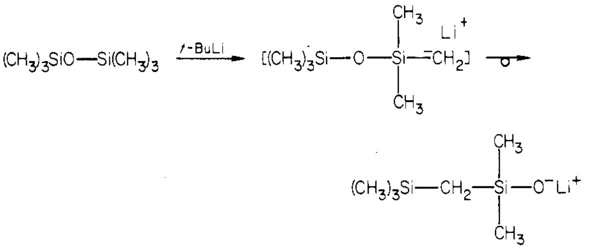
[13] G. R. Buell, R. Corriu, C. Guerin, and L. Spialter, *J. Am. Chem. Soc.*, **92**, 7424 (1970).

[14] M. R. Stober, K. W. Michaels, and J. L. Speier, *J. Org. Chem.*, **32**, 2740 (1967).

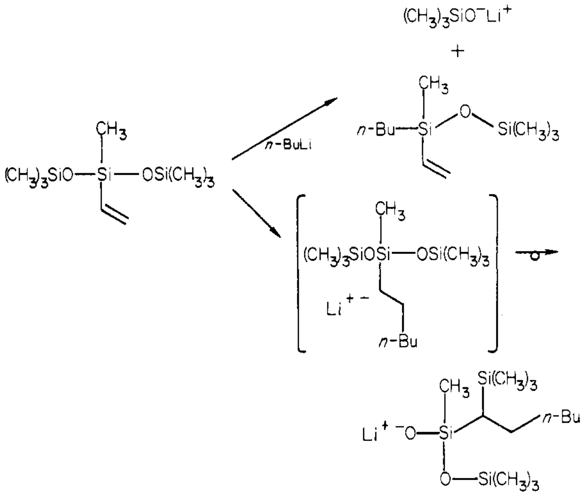
[15] P. D. Bartlett, S. J. Tauber, and W. P. Weber, *J. Am. Chem. Soc.*, **91**, 6362 (1969).


(9)

water[16] (eq 10). The rearrangement we have observed may also be related to the anionic rearrangements of cyclotrisilazanes to cyclodisilazanes[17] and of *N*-lithiocyclosiloxanes.[18]


(10)

Addition of primary alkyllithium reagents such as *n*-butyllithium to I does not occur at −78 °C but requires high temperature (0 °C). Under these conditions addition and rearrangement occur consecutively so that only rearranged dimethyl((α-trimethylsilyl)hexyl)silanol is obtained after workup. Reaction of *n*-butyllithium and II results in competitive addition rearrangement and substitution at silicon (eq 11). Reaction of I with methyllithium did not ooccur in ether. In THF at reflux only substitution occurs.


(11)

Finally, phenyllithium undergoes substitution at the silyl center in preference to addition to the carbon–carbon double bond of vinylsilanes. Thus I reacts with phenyllithium at 35 °C to yield phenyltrimethylsilane and phenylvinyldimethylsilane as well as siloxane products (eq 12).

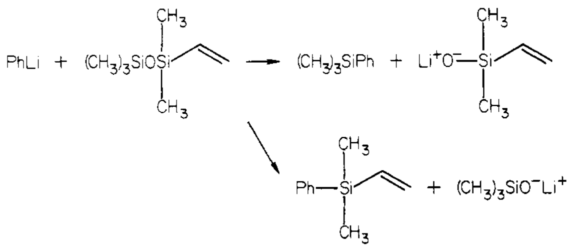
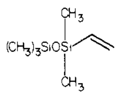
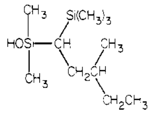
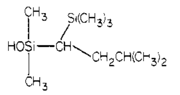
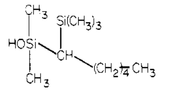
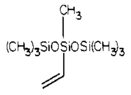
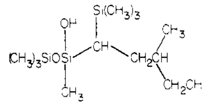
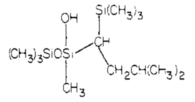
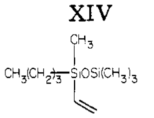
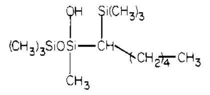

(12)

Table II. Reaction of Alkyllithium Reagents with Vinyl Siloxanes at Room Temperature. Synthesis of α-Silyl Silanols

siloxane	alkyllithium	products	yield, %
 I	*s*-BuLi	 V	100
I	*i*-PrLi	 VII	95
I	*n*-BuLi	 X	86
 II	*s*-BuLi	 XII	95
II	*i*-PrLi	 XIV	100
II	*n*-BuLi	 XVII	52
		 XVIII	40

The extension of this study to polymeric vinyl methyl siloxanes is under active investigation. Clearly, a major problem to be overcome is the solubility of such polymers at the low temperatures required to prevent rearrangement and thus scission of the siloxane polymer backbone.

Experimental Section

All reactions were carried out under an atmosphere of prepurified nitrogen. ^{1}H NMR spectra were obtained on a Varian XL-100 spectrometer operating in the FT mode using 5% solutions in deuteriochloroform. Chloroform was used as an internal standard. The integration of the NMR spectra sometimes gave too small intensities for the Si–CH_3 signals because of saturation problems. However, in all cases the integration was within 10% of the calculated value.[19] IR spectra were obtained on a Perkin-Elmer 281. IR bands were calibrated against known bands of a polystyrene film. The silanols and siloxanes show considerable differences in their IR spectra. The silanols show sharp absorptions at about 3760 cm^{-1} and hydrogen-bonded OH vibrations around 3540 cm^{-1} and no Si–O–Si absorptions between 1100 and 1000 cm^{-1}. Siloxane products, on the other hand, show no absorptions over 3000 cm^{-1} and have very strong Si–O–Si absorptions at 1050 cm^{-1}.[20] Mass spectra were obtained on a Hewlett-Packard 5985 GC/MS. A 6 ft × $^1/_4$ in. 5% OV-101 column was used in the gas chromatograph. GLPC analysis was performed on a

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(16) G. A. Gornowicz and R. West, *J. Am. Chem. Soc.*, **90**, 4478 (1968).

(17) L. W. Breed, *Inorg. Chem.*, **9**, 1940 (1968).

(18) R. P. Bush, N. C. Lloyd, and C. A. Pearce, *J. Chem. Soc., Chem. Commun.*, 1191 (1968).

(19) D. E. Leyden and R. H. Cox, "Analytical Applications of NMR", Wiley, New York, 1977, pp 17–18, 260–265.

(20) D. R. Anderson, "Infrared, Raman and Ultraviolet Spectroscopy in Analysis of Silicones", A. L. Smith, Ed.% Wiley, New York, 1979, pp 254, 275.

Hewlett-Packard F&M 700 using a 28 ft × $^1/_4$ in. 20% SE-30 on 60/80 mesh Chromosorb W column. Yields were calculated by using *n*-decane or *n*-hexadecane as internal standards. Elemental analysis were obtained from Galbraith Laboratories, Knoxville, TN. Starting materials are known compounds and had spectra in complete agreement with literature values.

Vinylpentamethyldisiloxane (I) was prepared by the method of Seyferth.[21]

3-Vinylheptamethyltrisiloxane (II) was prepared by cohydrolysis of excess trimethlchlorosilane and methylvinyldichlorosilane.[22]

Vinylheptamethylcyclotetrasiloxane (III) was prepared by cohydrolysis of dimethyldichlorosilane and methylvinyldichlorosilane.[23]

Isopropyllithium[24] was prepared by reaction of isopropyl chloride[25] and lithium shot in olefin-free petroleum ether.

Methyllithium, *n*-butyllithium and *sec*-butyllithium were obtained from Aldrich.

Phenyllithium and *tert*-butyllithium were purchased from Alfa.

Reaction of I with *sec*-Butyllithium. The two general procedures (a) at low temperature and (b) at 0 °C or room temperature described below were used for all of the reactions.

(a) In a 50-mL 2-necked flask equipped with a reflux condenser and a rubber septum were placed 25 mL of ether, I (1.23 g, 7.1 mmol), and a Teflon covered magnetic stirring bar. The solution was cooled to −198 °C. *sec*-Butyllithium (1.4 M in hexane) (5.6 mL, 7.8 mmol) was added slowly by syringe through the rubber septum. After waiting till the *sec*-butyllithium solution was frozen, we put the flask into a dry ice/acetone cooling bath, which caused the mixture to melt. This procedure of initially cooling all reagents to −198 °C prevents premature reaction when *sec*-butyllithium solution (temperature ~20 °C) is added. It was then stirred at −78 °C for 1 h and hydrolyzed by slow addition of a solution of 5 mL of THF and 100 μL of H_2O at −78 °C. The mixture was kept at −78 °C for another 30 min and then allowed to warm to room temperature. More water was added; the organic layer was separated, washed till neutral, and dried over Na_2SO_4. The ether was removed by distillation. GLPC analysis of the residue indicated the formation of 1-(3-methylpentyl)-1,1,3,3,3-pentamethyldisiloxane (IV) in 90% yield. It had the following spectral properties: NMR δ 1.55–1.16 (br m, 5 H), 0.98–0.77 (m, 6 H), 0.65–0.41 (m, 2 H), 0.13 (s, 9 H), 0.09 (s, 6 H); IR $\bar{\nu}$ 1055 cm^{-1} (SiOSi); mass spectrum, *m/e* (relative intensity) 217 (11.6% M$^+$ − 15), 147 (100.0%), 133 (46.3%), 73 (22.1%). Anal. Calcd for $C_{11}H_{28}O_1Si_2$: C, 56.82; H, 12.14. Found: C, 56.62; H, 12.07.

(b) A mixture of I (1.9 g, 11 mmol), *sec*-butyllithium (8.5 mL, 12 mmol), and 25 mL of ether was prepared as above. The reaction mixture was allowed to come to room temperature and stirred for 12 h. After the reaction mixture was poured into water/ice, the organic layer was separated. It was washed till neutral and dried over Na_2SO_4. The ether was removed by distillation. GLPC analysis of the residue indicated the formation of dimethyl(1-(trimethylsilyl)-3-methylpentyl)silanol (V) in 100% yield. It had the following spectral properties: NMR δ 1.58–1.12 (br m, 6 H), 1.43 (s, 1 H, overlapping the δ 1.58–1.12 (m)), 1.04–0.75 (m, 6 H), 0.20 (s, 6 H), 0.10 (s, 9 H) [the Si–CH–Si signal is obscured by the CH_3Si signals[26]]; mass spectrum, *m/e* (relative intensity) 217 (67.7%, M$^+$ − 15), 175 (16.8%), 159 (8.3%), 147 (100.0%); IR $\bar{\nu}$ 3760 cm^{-1} (O–H). Anal. Calcd for $C_{11}H_{28}O_1Si_2$: C, 56.82; H, 12.14. Found: C, 56.95; H, 12.34.

Reaction of I with Isopropyllithium. (a) Isopropyllithium (0.65 M in petroleum ether) (14.6 mL, 9.5 mmol) and I (1.5 g, 8.6 mmol) in 25 mL of ether were reacted at −78 °C for 2 h. 1-(3-methylbutyl)-1,1,3,3,3-pentamethyldisiloxane (VI) was formed in 91% yield. It had the following spectral properties: NMR δ 1.65–1.05 (m, 3 H), 0.93 (d, 6 H, *J* = 7 Hz), 0.53 (m, 2 H, $(J_{AX} + J_{AX'})/2$ = 8 Hz), 0.12 (s, 9 H), 0.09 (s, 6 H); IR $\bar{\nu}$ 1060 cm^{-1} (Si–O–Si); mass spectrum, *m/e* (relative intensity) 218 (3.7%, M$^{+\cdot}$), 203 (7.4%, M$^+$ − 15), 147 (100.0%), 133 (53.7%), 73 (24.1%). Anal. Calcd for $C_{10}H_{26}O_1Si_2$: C, 54.97; H, 11.99. Found: C, 55.01; H, 11.82.

(b) Isopropyllithium (0.61 M in petroleum ether) (19.7 mL, 12 mmol) and I (1.9 g, 11 mmol) in 25 mL of ether was warmed to room temperature and stirred for 6 h. Dimethyl(1-(trimethylsilyl)-3-(methylbutyl))silanol (VII) was formed in 95% yield. It had the following spectral properties: NMR δ 1.72 (s, 1 H), 1.66–1.22 (m, 3 H), 0.91 (d, 6 H, *J* = 6 Hz), 0.20 (s, 6 H), 0.11 (s, 9 H) [the Si–CH–Si signal is obscured by the $SiCH_3$ signals[26]]; mass spectrum, *m/e* (relative intensity) 203 (100.0%, M$^+$ − 15), 175 (21.7%), 147 (87.8%), 133 (61.1%). Anal. Calcd for $C_{10}H_{26}O_1Si_2$: C, 54.97; H, 11.99. Found: C, 54.78; H, 12.06.

Reaction of I with *tert*-Butyllithium. (a) *tert*-Butyllithium (2 M in pentane) (4.1 mL, 8.2 mmol) and I (1.3 g, 7.5 mmol) in 25 mL of ether were reacted at −95 °C (acetone/liquid nitrogen slurry) for 40 min. The clear yellow solution was hydrolyzed very carefully to make sure the reaction temperature did not rise. GLPC analysis indicated the formation of 1-(3,3-dimethylbutyl)-1,1,3,3,3-pentamethyldisiloxane (VIII) and dimethyl(1-(trimethylsilyl)-3,3-(dimethylbutyl))silanol (IX) in 77% and 23% yields, respectively. VIII had the following spectral properties: NMR δ 1.17 (m, 2 H, $(J_{AX} + J_{AX'})/2$ = 8.5 Hz), 0.86 (s, 9 H), 0.43 (m, 2 H, $(J_{AX} + J_{AX'})/2$ = 8.5 Hz), 0.07 (s, 9 H), 0.03 (s, 6 H); mass spectrum, *m/e* (relative intensity) 232 (0.2%, M$^{+\cdot}$), 217 (6.7%, M$^+$ − 15), 175 (1.6%), 147 (100.0%), 133 (28.5%); IR $\bar{\nu}$ 1060 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{11}H_{28}O_1Si_2$: C, 56.82; H, 12.14. Found: C, 56.89; H, 12.29. IX had the following spectral properties: NMR δ 1.52–1.37 (m, 2 H), 1.48 (s, 1 H, overlapping the δ 1.52–1.37 (m)), 0.87 (s, 9 H), 0.15 (s, 6 H), 0.05 (s, 9 H), −0.09 (t, 1 H, *J* = 4 Hz); mass spectrum, *m/e* (relative intensity) 217 (47.8%, M$^+$ − 15), 175 (32.8%), 159 (10.8%), 147 (100.0%), 133 (36.9%); IR $\bar{\nu}$ 3750 cm^{-1} (O–H). Anal. Calcd for $C_{11}H_{28}O_1Si_2$: C, 56.82; H, 12.14. Found: C, 56.67; H, 12.11.

(b) Similar reactions carried out at higher temperatures caused precipitation of a white solid. The formation of a number of products was indicated by GLPC. These have not been identified.

Reaction of I with *n*-Butyllithium. (a) At −78 °C no reaction occurred between I and *n*-butyllithium within 3 h as determined by GLPC analysis. (b) *n*-Butyllithium (1.59 M in hexane) (4.8 mL, 7.6 mmol) and I (1.3 g, 7.5 mmol) in 25 mL of ether were reacted at 0 °C for 2.5 h. Dimethyl(1-(trimethylsilyl)hexyl)silanol (X) was formed in 86% yield. It had the following spectral properties: NMR δ 1.67–1.11 (br m), 1.43 (s, overlapping the δ 1.67–1.11 (m), together 9 H), 1.00–0.72 (m, 3 H), 0.15 (s, 6 H), 0.05 (s, 9 H), −0.4 (t, 1 H, *J*= 5 Hz); mass spectrum, *m/e* (relative intensity) 217 (100.0%, M$^+$ − 15), 175 (4.1%), 159 (6.2%), 147 (82.9%), 133 (92.3%); IR $\bar{\nu}$ 3755 cm^{-1} (O–H). Anal. Calcd for $C_{11}H_{28}O_1Si_2$: C, 56.82; H, 12.14. Found: C, 56.95; H, 12.34.

Attempted Reaction of I with Methyllithium. Under reaction conditions either a or b no reaction occurs between I and methyllithium. When THF was used as the solvent, no reaction took place at room temperature. After the reaction mixture was refluxed for 24 h in THF, only unreacted I, vinyltrimethylsilane, and hexamethyldisiloxane could be observed by GC/MS analysis.

Attempted Reaction of I and Phenyllithium. Under reaction conditions either a or b no reaction occurs. When the reaction mixture is refluxed for 4 h, I, phenyltrimethylsilane, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, vinylphenyldimethylsilane, and hexamethyldisiloxane were observed by GC/MS.

Reaction of II and *sec*-Butyllithium. (a) *sec*-Butyllithium (1.4 M in hexane) (5 mL, 7.0 mmol) and II (1.45 g, 5.9 mmol) in 25 mL of ether were reacted at −78 °C for 1.5 h. 3-(3-Methylpentyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (XI) was produced in 95% yield. It had the following spectral properties: NMR δ 1.52–1.10 (br m, 5 H), 1.04–0.67 (m, 6 H), 0.60–0.32 (m, 2 H), 0.14 (s, 18 H), 0.05 (s, 3 H); mass spectrum, *m/e* (relative intensity) 291 (6%, M$^+$ − 15), 221 (44.0%), 207 (20.0%), 73 (100.0%); IR $\bar{\nu}$ 1060 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{13}H_{34}O_2Si_3$: C, 50.92; H, 11.18. Found: C, 50.96; H, 11.15.

(b) *sec*-Butyllithium (1.4 M in hexane) (6 mL, 8.4 mmol) and II (1.9 g, 7.7 mmol) in 25 mL of ether were reacted at room

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temperature for 2.5 h. 1-Hydroxy-1-(1-(trimethylsilyl)-3-methylpentyl)-1,3,3,3-tetramethyldisiloxane (XII) was formed in 95% yield. It had the following spectral properties: NMR δ 1.91 (s, 1 H), 1.59–1.15 (br m, 5 H), 1.00–0.73 (m, 6 H), 0.15 (s, 12 H), 0.07 ((s, 9 H) [the Si–Ch–Si signal is obscured by the Si–CH_3 signals[26]]; mass spectrum, *m/e* (relative intensity) 291 (39%, M – 15), 233 (21.3%), 221 (30.3%), 207 (16.8%), 133 (100.0%); IR $\bar{\nu}$ 3760 (O–H), 1050 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{13}H_{34}O_2Si_3$: C, 50.915; H, 11.175. Found: C, 50.90; H, 11.30.

Reaction of II and Isopropyllithium. (a) Isopropyllithium (0.65 M in petroleum ether) (10.9 mL, 7.1 mmol) and II (1.6 g, 6.5 mmol) in 25 mL of ether were reacted at –78 °C for 2 h. 3-(3-Methylbutyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (XIII) was formed in 91% yield. It had the following spectral properties: NMR δ 1.61–1.09 (m, 3 H), 0.91 (d, 6 H, J = 7 Hz), 0.47 (m, 2 H, $(J_{AX} + J_{AX'})/2$ = 8.5 Hz), 0.15 (s, 18 H), 0.05 (s, 3 H); mass spectrum, *m/e* (relative intensity) 277 (4.1%), 221 (30.6%), 207 (19.4%), 133 (39.8%), 73 (100.0%); IR $\bar{\nu}$ 1065 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{12}H_{32}O_2Si_3$: C, 49.25; H, 11.02. Found: C, 49.36; H, 11.19.

(b) Isopropyllithium (0.23 M in petroleum ether) (22 mL, 4.9 mmol) and II (1.1 g, 4.4 mmol) in 30 mL of ether were reacted at 0 °C for 3 h. 1-Hydroxy-1-(1-(trimethylsilyl)-3-methylbutyl)-1,3,3,3-tetramethyldisiloxane (XIV) was formed in 100% yield. It had the following spectral properties: NMR δ 1.91 (s, 1 H), 1.75–1.05 (m, 3 H), 0.87 (d of d, 6 H, J = 6 and 2.5 Hz), 0.13 (s, 12 H), 0.06 (s, 9 H), –0.05 (t, 1 H, J = 4 Hz); mass spectrum, *m/e* (relative intensity) 277 (77.9%, M$^+$ – 15), 261 (12.3%), 233 (40.2%), 221 (54.6%), 207 (41.6%), 205 (95.8%), 133 (100.0%); IR $\bar{\nu}$ 3760 (O–H), 1050 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{12}H_{32}O_2Si_3$: C, 49.25; H, 11.02. Found: C, 49.25; H, 11.20.

Reaction of II and *tert*-Butyllithium. (a) *tert*-Butyllithium (2 M in pentane) (2.9 mL, 5.8 mmol) and II (1.3 g, 5.2 mmol) in 25 mL of ether were reacted at –95 °C for 5 h. The mixture was hydrolyzed very carefully at this temperature. 3-(3,3-Dimetylbutyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (XV) and 1-hydroxy-1-(1-(trimethylsilyl)-3,3-dimethylbutyl)-1,3,3,3-tetramethyldisiloxane (XVI) were formed in 75% and 25% yields, respectively. XV had the following spectral properties: NMR δ 1.17 (m, 2 H, $(J_{AX} + J_{AX'})/2$ = 8.5 Hz), 0.84 (s, 9 H), 0.37 (m, 2 H, $(J_{AX} + J_{AX'})/2$ = 9 Hz), 0.10 (s, 18 H), 0.01 (s, 3 H); mass spectrum, *m/e* (relative intensity) 291 (9.6%, M$^+$ – 15), 221 (100.0%), 207 (22.4%), 205 (5.7%). IR $\bar{\nu}$ = 1060 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{13}H_{34}O_2Si_3$: C, 50.92; H, 11.18. Found: C, 50.78; H, 11.33. XVI had the following properties: NMR δ 1.58 (s, 1 H), 1.53–1.35 (m, 2 H), 0.87 (s, 9 H), 0.17 (s, 3 H), 0.15 (s, 9 H), 0.09 (s, 9 H), –0.04 to –0.23 (m, 1 H); mass spectrum, *m/e* (relative intensity) 291 (58.7%, M$^+$ – 15), 249 (11.9%), 233 (95.8%), 221 (70.9%), 207 (72.1%), 205 (47.7%), 133 (100.0%); IR $\bar{\nu}$ 3755 (O–H), 1050 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{13}H_{34}O_2Si_3$: C, 50.92; H, 11.18. Found: C, 51.02; H, 11.10.

(b) Similar reactions carried out at temperatures higher than –95 °C caused precipitation of a white solid and the formation of a large number of unidentified products.

Reaction of II and *n*-Butyllithium. (a) A mixture of II and *n*-butyllithium in ether was reacted for 7 h at –78 °C. This resulted in negligible reaction.

(b) *n*-Butyllithium (1.59 M in hexane) (4.5 mL, 7.1 mmol) and II (1.6 g, 6.5 mmol) in 25 mL of ether were reacted at 0 °C for 2 h. 1-Butyl-1,3,3,3-tetramethyl-1-vinyldisiloxane (XVII) (52% yield) and 1-hydroxy-1-(1-(trimethylsilyl)hexyl)-1,3,3,3-tetramethyldisiloxane (XVIII) (40% yield) were formed as the main products. XVII had the following properties: NMR δ 6.32–5.44 (m, 3 H), 1.50–1.12 (m, 4 H), 1.06–0.76 (m, 3 H), 0.70–0.39 (m, 2 H, $(J_{AX} + J_{AX'})/2$ = 7 Hz), 0.11 (s, 3 H), 0.09 (s, 9 H); mass spectrum, *m/e*, (relative intensity) 201 (4.7%, M$^+$ – 15), 159 (100%, M$^+$ – 57); IR $\bar{\nu}$ 3098 cm^{-1} (HC=C), 1615 cm^{-1} (C=C), 1065 cm^{-1}Si–O–Si). Anal. Calcd for $C_{10}H_{24}O_1Si_2$: C, 55.49; H, 11.18. Found: C, 55.70; H, 11.10. XVIII had the following properties: NMR δ 1.84 (s, 1 H), 1.61–1.11 (m, 8 H), 1.02–0.76 (m, 3 H), 0.14 (s, 12 H), 0.07 (s, 9 H), 0.00 to –0.23 (m, 1 H); mass spectrum, *m/e* (relative intensity) 291 (31.5% M$^+$ – 15), 221 (28.6%), 207 (22.2%), 205 (38.1%), 75 (100.0%); IR $\bar{\nu}$ 3760 cm^{-1} (O–H), 1060 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{13}H_{34}O_2Si_3$: C, 50.92; H, 11.18. Found: C, 51.03; H, 11.10.

Reaction of III and *sec*-Butyllithium. (a) *sec*-Butyllithium (1.4 M in hexane) (3.3 mL, 4.6 mmol) and III (1.3 g, 4.2 mmol) in 25 mL of ether were reacted at –78 °C for 2 h. 1-(3-Methylpentyl)-1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane (XIX) was formed in 90% yield. It had the following spectral properties: NMR δ 1.51–1.07 (m, 5 H), 1.02–0.74 (m, 6 H), 0.64–0.39 (m, 2 H), 0.14 (s, 18 H) , 0.11 (s, 3 H); mass spectrum, *m/e* (relative intensity) 351 (13.0% M$^+$ – 15), 276 (100.0%); IR $\bar{\nu}$ 1082 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{13}H_{34}O_4Si_4$: C, 42.57; H, 9.34. Found: C, 42.69; H, 9.10.

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Registry No. I, 1438-79-5; II, 5356-85-4; III, 3763-39-1; IV, 80485-61-6; V, 80485-62-7; VI, 80485-63-8; VII, 80485-64-9; VIII, 80485-65-0; IX, 80485-66-1; X, 80485-67-2; XI, 80485-68-3; XII, 80485-69-4; XIII, 80485-70-7; XIV, 80485-71-8; XV, 80485-72-9; XVI, 80485-73-0; XVII, 80485-74-1; XVIII, 80485-75-2; XIX, 80485-76-3; isopropyllithium, 1888-75-1; methyllithium, 917-54-4; *n*-butyllithium, 109-72-8; *sec*-butyllithium, 920-36-5; phenyllithium, 591-51-5; *tert*-butyllithium, 594-19-4.

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Some Novel Reactions of Tri-*tert*-butylphosphine with Iridium(III), Rhodium(III), Platinum(II), and Palladium(II) Chlorides

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Treatment of excess of tri-*tert*-butylphosphine with hydrated iridium(III) or rhodium(III) chloride, in DMF, at room temperature, affords intractable products which seem to contain iridium(III) or rhodium(III) hydrido complexes and protonated phosphine. Reaction in refluxing DMF gave *trans*-MCl(CO)[P-*t*-Bu)$_2$H]$_2$, 1 (M = Ir) and 2 (M = Rh), in quantitative yields. Treatment of P(*t*-Bu)$_3$ with PtCl$_2$ or K$_2$PtCl$_4$ gave *trans*-PtCl[PCH$_2$CMe$_2$(*t*-Bu)$_2$]P(*t*-Bu)$_3$, **3**, and [P(*t*-Bu)$_3$H]$_2$PtCl$_4$, **4**, at room temperature and the novel complex *trans*-PtCl[PCH$_2$CMe$_2$(*t*-Bu)$_2$]P(*t*-Bu)$_2$H, **5**, upon refluxing. Complex **5** was converted into *trans*-PtCl$_2$[P(*t*-Bu)$_2$H]$_2$, **6**, upon further heating. Reaction of P(*t*-Bu)$_3$ with PdCl$_2$ or Na$_2$PdCl$_4$, at room temperature, gave *trans*-Pd$_2$Cl$_2$(μ-Cl)$_2$[P(*t*-Bu)$_3$]$_2$, **4**; the dinuclear metalated complex [PdCl{PCH$_2$CMe$_2$(*t*-Bu)$_2$}]$_2$, **5**, was obtained if the reaction mixture was kept at room temperature for 48 h. The hydride *trans*-PdHCl[P(*t*-Bu)$_3$]$_2$, **9**, was obtained when the freshly prepared reaction mixture was heated to ~115 °C for ~30 min.

Introduction

It is now well recognized that platinum metal complexes of bulky phosphines readily undergo intramolecular metalation[1-7] to give cyclometalated complexes usually containing five-membered rings. Another interesting feature of the reactions of bulky phosphines with platinum metal halides is the formation of metal hydrido[8-10] complexes when the reaction is carried out in a protic solvent. Recent work[11] in this laboratory showed that tri-*tert*-butylphosphine undergoes facile intramolecular metalation upon treatment with platinum(II) or palladium(II) chloride in benzene, at room temperature, to give cyclometalated complexes containing four-membered rings. Shaw and co-workers[8,10] obtained the hydrido complexes, MH$_2$Cl[P(*t*-Bu)$_3$]$_2$ (M = Ir or Rh), from the treatment of the phosphine with hydrated iridium(III) or rhodium(III) chloride in propan-2-ol, at room temperature. In an attempt to prepare the complexes[12] *trans*-MCl(CO)[P(*t*-Bu)$_3$]$_2$ (M = Ir or Rh), reactions of tri-*tert*-butylphosphine with hydrated iridium(III) and rhodium(III) chlorides, in refluxing DMF, were carried out. To our surprise, the reactions resulted in the formation of the complexes, *trans*-MCl(CO)[P(*t*-Bu)$_2$H]$_2$, 1 (M = Ir) and 2 (M = Rh), in quantitative yields. Apart from the expected reduction of the metal, both the reactions involved hitherto unknown elimination of an alkene from the trialkylphosphine ligand. Therefore, reactions of tri-*tert*-butylphosphine with platinum(II) and palladium(II) chlorides were also examined. While this work was in progress, it was reported[13] that the six-coordinate cyclometalated hydrido complex IrHCl[PCH$_2$CMe$_2$(*t*-Bu)$_2$](NC$_6$H$_7$)$_2$ is formed upon refluxing P(*t*-Bu)$_3$ with [IrCl(COT)$_2$]$_2$ (COT = cyclooctene) and γ-picoline in hexane. The cleavage of phosphorus–phenyl bonds in triphenylphosphine and alkylphenyl tertiary phosphine complexes has been observed by several workers.[14-18] After the completion of this work, a report has also appeared[19] on the formation of diphenylphosphine along with biphenyl, triphenylphosphine, and methyldiphenylphosphine from the decomposition of Co(CH$_3$)[PPh$_3$]$_3$. Preliminary results on our investigations on the reactions of tri-*tert*-butylphosphine with iridium(III) and rhodium(III) chlorides have also been reported.[20]

Results and Discussion

Reactions with Iridium(III) and Rhodium(III) Chlorides. The complexes *trans*-MCl(CO)[P(*t*-Bu)$_2$H]$_2$, 1 (M = Ir) and 2 (M = Rh), were obtained in quantitative yields upon refluxing reaction mixtures containing tri-*tert*-butylphosphine and hydrated iridium(III) and rhodium(III) chloride in DMF. The formation of these complexes was accompanied by the evolution of 2-methyl-

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propene which was converted into 1,2-dibromo-2-methylpropane by treatment with bromine; the ^{1}H NMR spectrum of the resulting brominated product was identical with that of an authentic sample of 1,2-dibromo-2-methylpropane. **1** and **2** were fully characterized by elemental analyses and molecular weight measurements (in benzene) and by ^{1}H and ^{31}P NMR and infrared spectral measurements. Both the complexes have been prepared previously[21] from the reaction of di-*tert*-butylphosphine with the appropriate iridium(I) and rhodium(I) precursors. The ^{1}H NMR spectra for **1** and **2** were identical with those reported[21] by previous workers. Their ^{31}P{^{1}H} NMR spectra in dichloromethane, at ambient temperature, showed single broad resonances at 76.6 and 80.1 ppm, respectively. At 183 K, a sharp singlet at 72.7 ppm was observed for **1** and a sharp doublet at 77.5 ppm ($^1J_{\mathrm{Rh-P}}$ = 115 Hz) was observed for **2**. The infrared spectra for **1** and **2** showed strong bands at 1940 and 1965 cm^{-1}, respectively, due to the CO stretching frequencies. Medium bands at ca. 2360 and 890 cm^{-1}, attributable to the P–H stretching and P–H bending frequencies,[23] respectively, were also present in the spectrum of each complex.

No 2-methylpropene was produced when a solution of tri-*tert*-butylphosphine in DMF was refluxed for 4 h; the ^{1}H NMR spectrum of the refluxed solution was found to be identical with that of a freshly prepared solution. Thus, the formation of **1** or **2** does not seem to involve prior conversion of $\mathrm{P}(t\text{-Bu})_3$ into $\mathrm{P}(t\text{-Bu})_2\mathrm{H}$ and $\mathrm{H_2C{=}C(CH_3)_2}$ as a consequence of its thermal decomposition.

Addition of tri-*tert*-butylphosphine to a suspension of hydrated iridium(III) or rhodium(III) chloride in DMF, at room temperature, gave very dark red solutions which yielded intractable sticky solids which proved very difficult to characterize. The ^{31}P{^{1}H} NMR spectra of the dark red solutions showed a strong peak at $\delta \sim 44.0$ and a few weak peaks downfield from $\mathrm{H_3PO_4}$. The 44.0-ppm resonance is assignable to the phosphonium[20] cation $[\mathrm{P}(t\text{-Bu})_3\mathrm{H}]^+$ but the assignments for other resonances are not clear at present. The internally metalated tri-*tert*-butylphosphine gives rise to ^{31}P NMR resonance upfield from 85% $\mathrm{H_3PO_4}$. Thus, the presence of cyclometalated complexes in these solutions can be ruled out.

The ^{31}P{^{1}H} NMR spectrum of a mixture of $\mathrm{RhCl_3(H_2O)_3}$ and 3 mol equiv of $\mathrm{P}(t\text{-Bu})_3$ in DMF/$\mathrm{C_6D_6}$, kept at room temperature for 48 h, showed a weak 1:1 doublet at δ 86.5 [^1J(Rh–P) = 112 Hz)], a medium intensity 1:1 doublet at δ 37.0 [^1J(Rh–P) = 115 Hz], and a strong singlet at δ 44.4. Upon heating the reaction mixture to 100 °C the spectrum showed two medium intensity 1:1 doublets, one at δ 156.9 [^1J(Rh–P) = 164 Hz] and the other at δ 100.8 [^1J(Rh–P) = 183 Hz], a medium singlet at δ 63.6, and a strong singlet at δ 47.7. When the mixture was heated to $\sim$140 °C, the spectrum consisted of two singlets at δ 63.0 and 64.1, showing that $\mathrm{P}(t\text{-Bu})_3$ does not undergo metalation under these conditions. This is in marked contrast to the reported[13] intramolecular metalation of $\mathrm{P}(t\text{-Bu})_3$ in the reaction with $[\mathrm{IrCl(COT)_2}]_2$ in the presence of γ-picoline.

The ^{1}H NMR spectra of the dark red solutions of $\mathrm{MCl_3(H_2O)_3}$ (M = Ir or Rh) and $\mathrm{P}(t\text{-Bu})_3$ in DMF showed complex resonances in the *tert*-butyl region as well as resonances in the region upfield from $\mathrm{Me_4Si}$. An upfield triplet at –23.86 ppm ($^2J_{\mathrm{P-H}}$ = 16 Hz) was observed for the solution from the reaction with iridium(III) chloride. The spectrum of the solution from the reaction with rhodium(III) chloride showed two highfield doublets at –24.52 [^1J(Rh–H) = 5 Hz] and –50.44 [^1J(Rh–H) = 28 Hz] ppm, respectively. By analogy with the reported ^{1}H NMR data for $\mathrm{IrH_2Cl}[\mathrm{P}(t\text{-Bu})_3]_2$,[10] the –23.86-ppm triplet can be assigned to a dihydrido species such as $\mathrm{IrH_2Cl}[\mathrm{P}(t\text{-Bu})_3]_2$(DMF). The –24.52-ppm resonance for the rhodium(III) solution is similar to that reported for $\mathrm{RhH_2Cl}[\mathrm{P}(t\text{-Bu})_3]_2$, but the observation of another highfield resonance (–50.44 ppm) indicates the presence of another rhodium(III) hydrido species in the solution. Thus, the initial reaction of the phosphine with iridium(III) or rhodium(III) chloride seems to result in the formation of iridium(III) or rhodium(III) hydrido complexes which are converted into **1** or **2** in refluxing DMF.

Reactions with Platinum(II) and Palladium(II) Chlorides. Treatment of the phosphine with platinum(II) chloride or potassium chloroplatinate(II), in DMF, at room temperature, gave the internally metalated complex *trans*-$\overline{\mathrm{PtCl[PC}}\mathrm{H_2CMe_2}(t\text{-Bu})_2]\mathrm{P}(t\text{-Bu})_3$, **3**, and $[\mathrm{P}(t\text{-Bu})_3\mathrm{H}]_2\mathrm{PtCl_4}$, **4**. The reaction is similar to that observed in benzene and can be represented by eq 1. When the

$$6\mathrm{P}(t\text{-Bu})_3 + 3\mathrm{PtCl_2} \rightarrow 2\,trans\text{-}\overline{\mathrm{PtCl[PC}}\mathrm{H_2CMe_2}(t\text{-Bu})_2]\mathrm{P}(t\text{-Bu})_3 + [\mathrm{P}(t\text{-Bu})_3\mathrm{H}]_2\mathrm{PtCl_4} \quad (1)$$

reaction was carried out in refluxing DMF, the novel metalated complex *trans*-$\overline{\mathrm{PtCl[PC}}\mathrm{H_2CMe_2}(t\text{-Bu})_2]\mathrm{P}(t\text{-Bu})_2\mathrm{H}$, **5**, was obtained as the sole platinum-containing species. In another experiment, the reaction mixture was heated to reflux in a closed system for 24 h. This afforded the complex *trans*-$\mathrm{PtCl_2}[\mathrm{P}(t\text{-Bu})_2\mathrm{H}]_2$, **6**, along with some metallic platinum.

Complex **6** had been prepared[21] previously from the reaction of di-*tert*-butylphosphine with sodium tetrachloroplatinate(II). The observed ^{1}H NMR spectrum for **6** was identical with the reported[21] spectrum. Its ^{31}P{^{1}H} NMR spectrum in $\mathrm{CH_2Cl_2}$ at ambient temperature, consisted of a broad central peak and two broad satellite peaks [δ 56.8, ^1J(Pt–P) = 2416 Hz]. At 183 K, each peak was resolved into two peaks clearly showing the presence of two conformers [δ 56.1, ^1J(Pt–P) = 2380 Hz; δ' 50.0, ^1J(Pt–P) = 2382 Hz]. The characteristic infrared bands for **6** include a medium band at 2375 cm^{-1} and strong bands at 860 and 329 cm^{-1} which are assignable to the P–H stretching P–H bending and Pt–Cl stretching frequencies,[23,24] respectively.

The ^{1}H NMR spectrum of **5** in $\mathrm{C_6D_6}$ exhibited a set of three doublets at δ 1.68 [^3J(P–H) = 12.5 Hz], 1.60 [^3J(P–H) = 12.5 Hz], and 1.55 [^3J(P–H) = 12.5 Hz] in the 3:1:3 intensity ratio, respectively. The two intense peaks are assignable to the *tert*-butyl protons and the less intense peak to the $\mathrm{C(Me)_2}$ protons. A few very low intensity peaks due to the $\mathrm{CH_2}$ protons were also evident in the spectrum. Its ^{31}P{^{1}H} NMR spectrum in the same solvent showed 12 resonances consisting of two main doublets at 0.75 and 60.2 ppm[^2J(P–P′) = 417 Hz} and eight satellites due to ^{195}Pt–^{31}P spin–spin coupling [^1J(Pt–P) = 2312 and 2836 Hz, respectively]. Thus, the ^{31}P NMR spectrum unequivocally establishes the presence of two nonequivalent phosphorus nuclei, each showing coupling with the ^{195}Pt nucleus as well as with each other. By comparison with the spectra of **3** and **6**, the upfield doublet can be assigned to the metalated phosphine and the downfield doublet to the di-*tert*-butylphosphine. The large value of ^2J(P–P′)

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indicates that the two phosphorus nuclei are trans to each other. The infrared spectrum of **5** showed bands due to P–H stretching,[2,3] P–H bending,[23] and Pt–Cl stretching[2,25,26] frequencies at 2370 (medium), 866 (strong), and 265 (very strong) cm^{-1}, respectively. The marked decrease in the Pt–Cl stretching frequency[2,25,26] is consistent with the presence of the Pt–C bond trans to the Pt–Cl bond.

From the aforementioned results it is evident that in refluxing DMF **3** as well as **4** are converted into **5** which, upon further heating, is converted into **6**. The conversion of **4** into **5** most likely involves initial formation of *trans*-$PtCl_2[P(t\text{-}Bu)_3]_2$ which is not isolable and is rapidly converted into **3**. Conversion of **3** into **5** requires elimination of 2-methylpropene from either the coordinated $P(t\text{-}Bu)_3$ or the cyclometalated phosphine. A plausible reaction pathway could be elimination of $CH_2{=}C(CH_3)_2$ from the cyclometalated phosphine and rapid conversion of the resulting phosphido complex $PtCl[P(t\text{-}Bu)_2]P(t\text{-}Bu)_3$ into 5 (eq 2). Unfortunately, the appropriate isotopically labeled precursors, required to verify the proposed reaction pathway, are not easily accessible. Furthermore, phosphido derivatives of the type implicated in reaction 2 are also not known. The $^{31}P\{^1H\}$ spectrum of a mixture of $PtCl_2$ and $P(t\text{-}Bu)_3$ (1:3 mole ratio) in DMF/C_6D_6, heated to 100 °C for 12 h, showed characteristic resonances due to **3** and a broad resonance at ca. δ 60.5 which can be attributed to excess $P(t\text{-}Bu)_3$. Further heating to 140 °C caused complete conversion of **3** into **5** as shown by the $^{31}P\{^1H\}$ NMR data.

$$\textit{trans-}PtCl[PCH_2CMe_2(t\text{-}Bu)_2]P(t\text{-}Bu)_3 \rightarrow PtCl[P(t\text{-}Bu)_2]P(t\text{-}Bu)_3 + CH_2{=}C(CH_3)_2 \quad (2a)$$

$$PtCl[P(t\text{-}Bu)_2]P(t\text{-}Bu)_3 \rightarrow \textit{trans-}PtCl[P(t\text{-}Bu)_2H][PCH_2CMe_2(t\text{-}Bu)_2] \quad (2b)$$

Conversion of **5** into **6** involves cleavage of the Pt–C bond as well as a P–C bond of the cyclometalated phosphine as represented by eq 3.

$$\textit{trans-}PtCl[PCH_2CMe_2(t\text{-}Bu)_2]P(t\text{-}Bu)_2H + HCl \xrightarrow{\Delta} \textit{trans-}PtCl_2[P(t\text{-}Bu)_2H]_2 + CH_2{=}C(CH_3)_2 \quad (3)$$

Although it has been reported that the Pt–C bond in $PtCl[CHMeC_6H_4PPh_2]P(o\text{-vinylphenyl})Ph_2$ can be cleaved by HCl, most of the cyclometalated platinum(II) complexes of the type PtCl(P–C)L, where (P–C) is a metalated phosphine and L is unmetalated phosphine, are reported to be remarkably stable. For example, it has been reported that the complex *trans*-$PtCl[C_6H_3MeP(t\text{-}Bu)_2]P(t\text{-}Bu)_2(p\text{-tolyl})$[2] is recovered unchanged after remaining molten at ca. 200 °C for 30 min and the complexes *trans*-$PtCl[CH_2C_6H_4PPh(o\text{-tolyl})]PPh(o\text{-tolyl})_2$,[2] *trans*-$PtCl[CH_2C_6H_4P(t\text{-}Bu)(o\text{-tolyl})]P(t\text{-}Bu)(o\text{-tolyl})_2$,[3] and *trans*-$PtCl[C_6H_4P(t\text{-}Bu)_2]P(t\text{-}Bu)_2Ph$[2] remain unchanged upon treatment with HCl. There seems to be no precedent for the reactions involved in the conversion of **3** into **5** as well as its subsequent conversion into **6**.

The dinuclear complex, $Pd_2Cl_2(\mu\text{-}Cl)_2\{P(t\text{-}Bu)_3\}_2$, **7**, the metalated dinuclear complex, $[PdCl\{PCH_2CMe_2(t\text{-}Bu)_2\}]_2$, **8**, or the hydrido complex, *trans*-$PdHCl[P(t\text{-}Bu)_3]_2$, **9**, were obtained from the reaction of tri-*tert*-butylphosphine with palladium(II) chloride or potassium or sodium chloropalladate, depending upon the reaction temperature and reaction time. Complex **7** was obtained as the sole palladium-containing species when the phosphine and palladium(II) chloride were stirred in DMF at room temperature for ~1 h. When the reaction mixture was stirred for ~48 h, the metalated dinuclear complex, **8**, was obtained in almost quantitative yield. When the reaction mixture was heated to ~115 °C for ~30 min, most of the palladium(II) was converted into the hydrido complex, **9**. Heating the reaction mixture to reflux resulted in the reduction of the palladium(II) to the metallic form.

The ^1H NMR spectrum of a freshly prepared solution of **7** in CH_2Cl_2 showed a doublet at 1.35 ppm [$^3J(P\text{–}H)$ = 14.8 Hz], and its $^{31}P\{^1H\}$ NMR spectrum in the same solvent showed a single resonance at 121.3 ppm. The infrared spectrum of the freshly prepared **7**, in the solid state, showed a strong band at 340 cm^{-1} due to the terminal Pd–Cl stretching frequency[24] and medium and strong bands at 315 and 248 cm^{-1} due to the bridging Pd–Cl stretching modes.[24] The ^1H and $^{31}P\{^1H\}$ NMR spectra as well as the infrared spectrum of **7** were identical with that observed for an authentic sample of *trans*-$Pd_2Cl_2(\mu\text{-}Cl)_2[P(t\text{-}Bu)_3]_2$ prepared[28] by the treatment of *trans*-$Pd_2Cl_2(\mu\text{-}Cl)_2[As(t\text{-}Bu)_3]_2$ with $P(t\text{-}Bu)_3$. The dimeric nature of **8** was confirmed by molecular weight determination in benzene. Its ^1H NMR spectrum in dichloromethane showed a set of three doublets at 1.60 [$^3J(P\text{–}H)$ = 13.5 Hz], 1.56 [$^3J(P\text{–}H)$ = 14 Hz), and 1.48 [$^3J(P\text{–}H)$ = 14 Hz] ppm in the intensity ratio of 1:9:3, respectively, and its ^{31}P NMR spectrum in the same solvent showed a single resonance at −11.9 ppm. The infrared spectrum of **8** showed strong bands at 237 and 225 cm^{-1} which can be attributed to the stretching of the bridging Pd–Cl bonds.[24] The ^1H and ^{31}P NMR and infrared spectra of **9** were identical with those of an authentic sample of *trans*-$PdHCl\{P(t\text{-}Bu)_3\}_2$ prepared by the previously reported method.[29]

Previous work[11] has shown that treatment of 2 mol equiv of $P(t\text{-}Bu)_3$ with $PdCl_2(COD)$ or $PdCl_2(C_6H_5CN)_2$ results in the formation of *trans*-$PdCl_2[P(t\text{-}Bu)_3]_2$, **10**, which, unlike the analogous platinum(II) derivative, has been isolated and found to behave as a molecular species in benzene. The isolation of **7** instead of **10** in the present work seems to indicate that the equilibrium represented by eq 4 lies to the right in DMF. An investigation[28] on the preparation and characterization of authentic samples of **7** showed that it readily undergoes intramolecular metalation in solution as well as in the solid state to give **8**. However, in the present work, complex **8** is not solely derived from the intramolecular metalation reaction of **7** (vide infra).

$$2\,\textit{trans-}PdCl_2[P(t\text{-}Bu)_3]_2 \rightarrow \textit{trans-}Pd_2Cl_2(\mu\text{-}Cl)_2[P(t\text{-}Bu)_3]_2 + 2P(t\text{-}Bu)_3 \quad (4)$$

The $^{31}P\{^1H\}$ NMR spectrum of a freshly prepared mixture of $PdCl_2$ and $P(t\text{-}Bu)_3$ (1:3 mole ratio), in DMF/C_6D_6, showed a strong resonance (δ 122.7) due to **7**, a weaker resonance (δ 81.9) due to **9**, and a broad resonance at δ 63.0 which can be attributed to excess phosphine. When the mixture was heated to 70–100 °C, the resonance due to **7** disappeared completely, the resonance due to **9** increased in intensity, and the resonance at δ 63.0 remained unchanged, but a relatively strong new resonance appeared at δ 43.2. There can be little doubt that the δ 43.2 resonance is due to the protonated phosphine. The spectral data suggest that the initial product of the reaction of $P(t\text{-}Bu)_3$ with $PdCl_2$ in DMF is **7** which is rapidly con-

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verted into **9** with concomitant protonation of approximately 50% of the phosphine present in the system. Further heating of the mixture to ~120 °C resulted in the disappearance of the resonance due to protonated phosphine with a concomitant increase in the intensity of the resonance due to **9** From these observations it appears that the conversion of **7** into **9** is accompanied by the formation of the phosphonium salt, $[P(t\text{-Bu})_3H]_2PdCl_4$, which is converted into **9** at ~120 °C.

The reaction of $P(t\text{-Bu})_3$ with commercially available $PdCl_2$, in hot DMF, discovered in the present work provides a very convenient method of preparation of *trans*-$PdHCl[P(t\text{-Bu})_3]_2$ which has hitherto been obtained[29,30] from the oxidative addition of HCl to $Pd[P(t\text{-Bu})_3]_2$[31] which is not easily accessible. The ^1H NMR spectrum of a solution of **9** in DMF, kept at room temperature for 48 h, showed no resonance upfield from Me_4Si; the 1:2:1 *tert*-butyl triplet observed for **9** was replaced by a complex multiplet. The spectral changes clearly indicate conversion of **9** into the internally metalated complex, *trans*-$PdCl[PCH_2CMe_2(t\text{-Bu})_2]P(t\text{-Bu})_3$, **11**, as represented by eq 5.

$$trans\text{-}PdHCl[P(t\text{-Bu})_3]_2 \rightarrow trans\text{-}PdCl[PCH_2CMe_2(t\text{-Bu})_2]P(t\text{-Bu})_3 + H_2 \quad (5)$$

It was also found that the complexes **11** and **8** are readily interconvertible through a solvent dependent equilibrium represented by eq 6. Thus, the formation of **8** as the sole

$$2\,trans\text{-}PdCl[PCH_2CMe(t\text{-Bu})_2]P(t\text{-Bu})_3 \rightarrow [PdCl\{PCH_2CMe_2(t\text{-Bu})_2\}]_2 + 2P(t\text{-Bu})_3 \quad (6)$$

palladium(II)-containing species in the reaction mixture, kept at room temperature for 48 h, seems to involve a sequence of reactions. The spectral evidence suggests that complex **8** is derived mainly from **9** which undergoes intramolecular metalation to give **11** which is subsequently converted into **8**.

In summary, the course of the reaction of $P[t\text{-Bu})_3$ with the four platinum metals included in this investigation is markedly dependent upon the nature of the metal, and, for the given metal, upon the conditions of the reaction. All of the reactions examined in the present work give unexpected products. The reactions involving elimination of $CH_2{=}C(CH_3)_2$ and quantitative formation of the complexes containing $P(t\text{-Bu})_2H$ are without precedent and represent an hitherto unrecognized pathway for relieving steric crowding in metal complexes of bulky phosphines.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of oxygen-free dry nitrogen by using either a drybox (Vacuum Atmosphere Corp. Dri-Lab equipped with a Model HE-493 Dri-Train) or Schlenk-tube and vacuum-line techniques. Tri-*tert*-butylphosphine was prepared as described previously,[11] and its purity was checked by ^1H and ^{31}P NMR spectral measurements. Platinum metal salts were used as received from Johnson Matthey and Mallory Ltd. Reagent grade dimethylformamide (DMF) was stored over molecular sieves prior to use. Other solvents were purified by standard methods. Reactions were monitored periodically be recording the NMR spectra of reaction mixtures sealed in NMR tubes.

Physical Measurements. Elemental analyses were performed by M.H.W. Laboratories, Phoenix, AZ, by Galbraith Laboratories, Knoxville, TN, or By Guelph Chemical Laboratory, Guelph, Ontario. Molecular weights were determined on benzene solutions with Hitachi Perkin-Elmer 115 osmometer. Infrared spectra were obtained with a Perkin-Elmer 180 spectrometer using samples prepared as mulls in Nujol or halocarbon oil and pressed between KRS or polyethylene windows. ^1H NMR spectra were recorded either on a Varian A-60 and a HA-100 spectrometer or on a Bruker WP-60 FT spectrometer using solvent chemical shifts as internal reference; the reported chemical shifts are relative to internal Me_4Si. $^{31}P\{^1H\}$ spectra were measured with a Bruker WP- 60FT spectrometer using 85% H_3PO_4 as external reference; positive chemical shifts are downfield from 85% H_3PO_4. Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected.

Reactions of Tri-*tert*-butylphosphine with Iridium(III) and Rhodium(III) Chlorides. (a) $P(t\text{-Bu})_3$ (2–3 mmol) was added to a suspension or $IrCl_3{\cdot}3H_2O$ or $RhCl_3{\cdot}3H_2O$ (1 mmol) in dimethylformamide (25 mL), and the dark red suspension was stirred at room temperature for 3 h to give a dark reddish solution. Removal of the solvent gave dark sticky solids which could not be characterized.

(b) $P(t\text{-Bu})_3$ (3 mmol) was added to a suspension of $RhCl_3{\cdot}3H_2O$ or $IrCl_3{\cdot}3H_2O$ (1 mmol) in a two-necked flask fitted with a condenser on one neck and a source of oxygen-free dry nitrogen on the other. The top of the condenser was connected in series to a distilled water scrubber, a U-tube containing anhydrous calcium chloride, a flask containing 0.2 M solution of bromine in carbon tetrachloride, and a mercury bubbler. The suspension was refluxed, under nitrogen, with stirring, for 5 h to give a clear yellow solution, and the system was then flushed thoroughly with nitrogen. The reaction mixture was cooled to room temperature, concentrated in vacuo to half its volume, and then cooled in an ice-bath. Addition of cold methanol (40 mL) to the cold reaction mixture gave a yellow crystalline solid which was recrystallized from hexane; yields ~95%. Anal. Calcd for $Ir(CO)Cl[P(t\text{-Bu})_2H]_2$: C, 38.00; H, 7.08; Cl, 6.64; P, 11.50; mol wt 458. Found: C, 37.94; H, 7.08; Cl, 7.00; P, 11.00; mol wt 433 (in benzene) [mp 270 °C]. Calcd for $Rh(CO)Cl[P(t\text{-Bu})_2H]_2$: C, 44.50; H, 8.30; Cl, 7.80; P, 13.50; mol wt 547. Found: C, 44.00; H, 8.60; Cl, 8.00; P, 13.50; mol wt 520 (in benzene) [mp 265 °C]. ^1H NMR (in $CDCl_3$ at −30 °C): *trans*-$IrClCO[P(t\text{-Bu})_2H]_2$, δ(P–C–C–H) 1.46 [q, ^3J(P–H) + ^5J(P–H) = 14.3 Hz], *trans*-$RhClCO[P(t\text{-Bu})_2H]_2$, δ-(P–C–C–H) 1.44 [q, ^3J(P–H) + ^5J(P–H) = 14.8 Hz]; δ(P–H) 4.11 ppm [^1J(P–H) = 347 Hz]. The bromine solution was found to be partially decolorized and its ^1H NMR spectrum was found to be identical with that of an authentic solution of 1,2-dibromo-2-methylpropane in carbon tetrachloride prepared according to the literature procedure.

Reaction of Tri-*tert*-butylphosphine with Potassium Tetrachloroplatinate(II). (a) $P(t\text{-Bu})_3$ (3 mmol) was added to 25 mL of DMF containing 1 mmol of K_2PtCl_4, and the mixture was stirred at room temperature for 24 h to give an orange solution containing an off-white suspension. After the solvent was removed in vacuo, the residue was extracted with hexane to give 0.61 mmol of hexane-soluble *trans*-$PtCl[PCH_2C(CH_3)_2(t\text{-Bu})_2]P(t\text{-Bu})_3$. Anal. Calcd for $PtCl[PC_4H_5(t\text{-Bu})_2]P(t\text{-Bu})_3$: C, 45.44; H, 8.43; Cl, 5.58. Found: C, 45.50; H, 8.52; Cl, 5.60. ^1H NMR (C_6D_6): $\delta[P(t\text{-Bu})_3]$ 1.56 [d, ^3J(P–H) = 11.5 Hz]; $\delta[P(t\text{-Bu})_2]$ 1.62 [d, ^3J(P–H) = 12.4 Hz]; $\delta(PCMe_2)$ 1.48 [d, ^3J(P–H) = 12.7 Hz]. $^{31}P\{^1H\}$ NMR (C_6D_6) $\delta[P(t\text{-Bu})_3]$ 66.8 ppm [J^{195}(Pt–P) = 2680 Hz], $\delta[P(t\text{-Bu})_2CMe_2CH_2]$ −12.8 ppm [^1J(Pt–P) = 2360 Hz, ^2J(P–P′) = 382 Hz]. The hexane-insoluble solid was extracted with dichloromethane to give 0.3 mmol $\{P(t\text{-Bu})_3H\}_2PtCl_4$. Anal. Calcd for $[P(t\text{-Bu})_3H]_2PtCl_4$: C, 38.75; H, 7.60; Cl, 19.06. Found: C, 38.70; H, 7.80; Cl, 18.49 [Λ_M = 132 Ω^{-1} cm^2 mol^{-1} (~10^{-3} M solution in nitromethane)]. ^1H NMR (CH_2Cl_2): δ(P–C–C–H) 1.80 [d, ^3J(P–H) = 15.0 Hz]; δ(P–H) 7.40 [d, ^1J(P–H) = 464 Hz]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 40.0 (s).

(b) A mixture of $P(t\text{-Bu})_3$ (3 mmol) and K_2PtCl_4 or $PtCl_2$ (1 mmol) in DMF (25 mL) was refluxed for 3 h. After the solvent was removed in vacuo, the resulting solid was extracted with hexane to give a white solid which was recrystallized from hexane; mp 180 °C. Anal. Calcd for $PtCl[P(t\text{-Bu})_2CMe_2CH_2]P(t\text{-Bu})_2H$: C, 41.45; H, 7.78; Cl, 6.14; mol wt 579. Found: C, 41.52; H, 7.83; Cl, 6.38; mol wt 582 (benzene) [yield 95%].

(c) A mixture of K_2PtCl_4 (2 mmol) and $P(t\text{-Bu})_3$ (6 mmol) in DMF (30 mL) was refluxed in a closed system for 48 h. The

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solvent was removed in vacuo, and the residue was extracted with hexane to give an off-white solid which was recrystallized from the same solvent to give a white solid; mp 280 °C dec. Anal. Calcd for $PtCl_2[P(t\text{-}Bu)_2H]_2$: C, 34.53; H, 6.83; Cl, 12.77; mol wt 558. Found: C, 34.94; H, 6.93; Cl, 11.90; mol wt 556 (benzene) [yield 60%]. ^1H NMR ($CDCl_3$): δ(P–C–C–H) 1.60 [q, ^3J(P–H) + ^5J(P–H) = 14.2 Hz].

Reactions of Tri-*tert*-butylphosphine with Palladium(II) Chloride or Sodium Tetrachloropalladate. (a) $P(t\text{-}Bu)_3$ (3 mmol) was added to DMF (25 mL) containing Na_2PdCl_4 (1 mmol), and the mixture was stirred for 48 h to give a yellowish solution. The solution was filtered, and the solvent was removed in vacuo to give a yellow solid which was washed with cold ethanol (20 mL) and recrystallized from a mixture of benzene and hexane to give a yellow crystalline solid; mp 210 °C dec. Anal. Calcd for $[PdCl\{P(t\text{-}Bu)_2CMe_2CH_2\}]_2$: C, 42.24; H, 7.59; Cl, 10.36; mol wt 685. Found: C, 42.17; H, 7.85; Cl, 9.98; mol wt 694 (benzene) [yield 75%].

(b) A mixture of $P(t\text{-}Bu)_3$ (3 mmol) and $PdCl_2$ or Na_2PdCl_4 (1 mmol) in DMF (25 mL) was heated, with stirring, in an oil bath. As the temperature approached 100 °C, the reddish colour of the solution began to change to green. At 115 °C the solution became dark green when it was cooled to room temperature to give some greenish white solid. More solid was obtained upon concentrating the solution. Filtration and recrystallization of the solid from a mixture of benzene and hexane gave pure *trans*-$PdHCl[P(t\text{-}Bu)_3]_2$ in 90% yield; mp 146 °C. Anal. Calcd for $PdHCl[P(t\text{-}Bu)_3]_2$: C, 52.70; H, 10.06; mol wt 547. Found: C, 52.37, H, 10.19; mol wt 550 (benzene). ^1H NMR (C_6D_6):(δ[P(C–C–H)] 1.5 [t, ^3J(P–H) + ^5J(P–H) = 12.3 Hz]; δ(Pd–H) −18.3 [t, ^2J(P–H) = 12.3 Hz]. $^{31}P\{^1H\}$NMR (C_6D_6): δ 81.7 (s). IR (Nujol mull): ν(Pd–H) 2215, ν(Pd–H) 766, ν(Pd–Cl) 255 cm^{-1}.

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Dobson and Robinson[1,2] and more recently Rybak and Ziolkowski[3] have described their extensive studies into (trifluoroacetato)ruthenium(II) alcohol dehydrogenation catalysts and their polystyrene supported analogues, respectively. The mechanism originally proposed by Robinson[1] (Scheme I) requires an isomerization whereby the mutually trans phosphine ligands of intermediate **i** must rearrange to a cis configuration (isomer **j**) in order to complete the catalytic cycle. We felt that initially locking the phosphines into a cis configuration by means of a chelating diphosphine (L–L) could affect the rate of the overall reaction if the **i** → **j** rearrangement was involved in the rate-determining step of the overall catalytic sequence. We therefore now wish to report on a series of ruthenium(II) trifluoroacetate diphosphine complexes that we have prepared and compare their catalytic activity to that previously found for $Ru(OAc_F)_2CO(PPh_3)_2$. Products have been characterized by analytical and spectroscopic methods, and where possible, their stereochemistry has been assigned.

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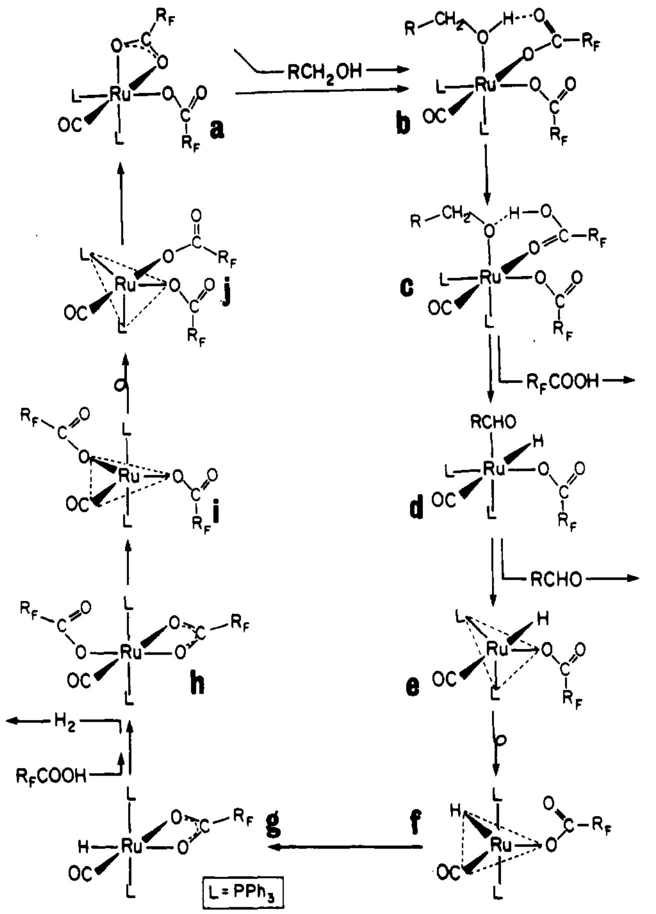
Scheme I



GLC analyses were performed on Hewlett-Packard 5730A gas chromatograph using 30-m SE30 capillary, or 3-m, 10% Carbowax 20M (Chromosorb W) columns. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Literature methods were used to prepare $RuH_2(CO)(PPh_3)_3$[5] and $Ru(OAc_F)_2(CO)(PPh_3)_2$.[6] The diphosphines and Arphos were obtained from Strem Chemical, Inc., and used without additional purification. Solvents and alcohols were reagent grade and dried with 3A molecular sieves and deoxygenated with bubbling argon or under vacuum before use. Trifluoroacetic acid was refluxed with the anhydride and fractionally distilled. All other chemicals were used as supplied.

Preparation of $RuH_2(CO)(PPh_3)[1,2\text{-}(Ph_2P)_2C_6H_4]$ (Id). A toluene (25 mL) solution of $RuH_2(CO)(PPh_3)_3$ (Ia, 0.52 g, 0.56 mmol) and $1,2\text{-}(Ph_2P)_2C_6H_4$ (0.25 g, 0.56 mmol) was refluxed for 6 h, yielding a deep brown solution after 1 h. Toluene was stripped under vacuum at room temperature to yield a viscous, brown oil. Methanol (25 mL) was added, and the mixture was stirred for 2 h. The resultant crude powder was filtered off in air and washed with methanol (ca. 75 mL) and hexane (ca. 25 mL). Recrystallization from THF/MeOH by slow concentration under vacuum afforded white crystals of $RuH_2(CO)(PPh_3)[1,2\text{-}(Ph_2P)_2C_6H_4]$ (Id, 0.38 g, 81%): IR (fluorolube mull) 1945 (s, ν(CO)), 1828 (m, ν(RuH)), 1806 (m, ν(RuH)) cm^{-1}. Anal. Calcd for $RuP_3C_{49}H_{41}O$: P, 11.06; C, 70.08; H, 4.92. Found: P, 10.60; C, 70.12; H, 5.10. Complex Id is attacked slowly by air in solution (several hours) and in the solid state (several months).

Analogous $RuH_2(CO)(PPh_3)(L_2)$ complexes were similarly prepared. **$RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$ (If)**: Ia (0.75 g, 0.82 mmol), $Ph_2PCH_2CH_2CH_2PPh_2$ (0.36 g, 0.87 mmol) in 25 mL of PhMe, 1-h reflux, 0.56 g (85%) yield; IR (Nujol mull) 1934 (vs, ν(CO)), 1900 (m, ν(RuH)), 1830 (w, ν(RuH)) cm^{-1}. Anal. Calcd for $RuP_3C_{46}H_{43}O$: Ru, 12.54; P, 11.53. Found: Ru, 12.14; P, 11.31. **$RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2AsPh_2)$ (Ie)**: Ia (0.50 g, 0.54 mmol), Arphos (0.31 g, 0.70 mmol) in 25 mL of PhMe, 1.5-h reflux, 0.29 g (64%) yield; IR (KBr) 1944 cm^{-1} (vs, ν(CO)). Anal. Calcd for $RuP_2AsC_{45}H_{41}O$: Ru, 12.09; P, 7.41; As, 8.96; C, 64.67; H, 4.94. Found: Ru, 12.28; P, 7.40; As, 9.41; C, 64.82; H, 4.92. **$RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2PPh_2)$ (Ic)**: Ia (0.52 g, 0.56 mmol), $Ph_2PCH_2CH_2PPh_2$ (0.23 g, 0.58 mmol) in 20 mL of PhMe, 1.5-h reflux, 0.20 g (45%) yield; IR (Nujol mull) 1945 cm^{-1} (s, ν(CO)). Anal. Calcd. for $RuC_{45}H_{41}P_3O$: C, 68.26; H, 5.22. Found: C, 68.70; H, 5.80.

Preparation of $RuH_2(CO)(PPh_3)[Ph_2P(CH_2)_4PPh_2]$ (Ig and Ih). $RuH_2(CO)(PPh_3)_3$ (Ia, 0.510 g, 0.556 mmol) and $Ph_2P(CH_2)_4PPh_2$ (0.287 g, 0.673 mmol) were refluxed for 3 h in toluene (10 mL). When the mixture was cooled to room temperature, petroleum ether (35 mL) was added. White crystals formed within 5 min. After 30 min, the product was filtered off under argon and washed with petroleum ether (60 mL). Recrystallization of the product from boiling toluene (35 mL) afforded 75 mg (16%) of complex Ih. Anal. Calcd for $RuP_3C_{47}H_{45}O$: Ru, 12.33; P, 11.33. Found: Ru, 12.25; P, 11.40. The combined filtrate was allowed to stand for 5 days at ca. −50 °C, yielding ca. 50 mg of off-white crystals. The $^{31}P\{^1H\}$ NMR spectrum of this product indicated that it was a mixture of Ih (24%) and Ig (76%). The filtrate was then concentrated under vacuum to 20 mL. Ethanol (50 mL) was added, and when the mixture was left standing overnight, white crystals of complex Ig were deposited. After the reaction mixture had been allowed to stand for 2 h at −50 °C, complex Ig was filtered off in air and washed with MeOH (50 mL) and petroleum ether (10 mL); yield 0.18 g (39%). Anal. Calcd for $RuP_3C_{47}H_{45}O$: Ru, 12.33; P, 11.33; C, 68.85; H, 5.53. Found: Ru, 12.25; P, 11.45; C, 68.88; H, 5.50.

Preparation of $Ru(OAc_F)_2(CO)(PPh_3)[1,2\text{-}(Ph_2P)_2C_6H_4]$ (IIId). Trifluoroacetic acid (0.31 mL, 4.2 mmol) was added slowly to a benzene (3.5 mL) solution of $RuH_2(CO)(PPh_3)[(Ph_2P)_2C_6H_4]$ (Id). A small amount of gas evolution occurred immediately, and the solution turned yellow within a few seconds. Heptane (20 mL) was added. Slow evaporation in air afforded light yellow crystals of IIId (0.14 g, 52%): IR (CH_2Cl_2) ν(CO) at 1980 (br, s), ν(OCO) at 1720 (w, sh), 1710 (m, sh), 1687 (vs), 1680 (vs), 1642 (w). Anal. Calcd for $RuP_3C_{53}H_{39}F_6O_5$: P, 8.73; C, 59.98; H, 3.70; F, 10.71. Found: P, 8.17; C, 59.85; H, 4.03; F, 11.11.

The analogous complexes $Ru(OAc_F)_2(CO)(PPh_3)_m(L_2)$ (m = 0, II; m = 1, III) were similarly prepared. **$Ru(OAc_F)_2(CO)(PPh_3)(Ph_2PCH_2CH_2AsPh_2)$ (IIIe).** Complex Ie (0.86 mmol) and $HOAc_F$ (1.2 g, 10.7 mmol) were reacted in toluene (10 mL). The large excess of $HOAc_F$ was used in an attempt to isolate only the cis-P_2 isomer of IIIe (see text). After the mixture was left standing for 50 h in air, $^{31}P\{^1H\}$ NMR analysis showed that only 47% of IIIe was in the *cis*-P_2 form. Yield of IIIe·$HOAc_F$: 0.69 g (59%); IR (CH_2Cl_2) 1975 (br, s, ν(CO)), 1780 (m, free $HOAc_F$, ν(CO)), 1682 (vs, ν(OCO)), 1647 (m, ν(OCO)) cm^{-1}. Anal. Calcd for $RuP_2AsC_{51}H_{40}F_9O_7$: Ru, 8.61; P, 5.28; As, 6.38; C, 52.19; H, 3.44; F, 14.57. Found: Ru, 8.52; P, 5.54; As, 5.92; C, 52.33; H, 3.53; F, 15.28. The reaction of Ie (0.178 g, 0.213 mmol) with $HOAc_F$ (0.31 mL, 19 equiv) in benzene (2 mL) afforded 0.14 g (69%) of IIIe consisting of 62% of the cis-P_2 isomer.

$Ru(OAc_F)_2(CO)(Ph_2PCH_2CH_2CH_2PPh_2)$ (IIf): complex If (0.221 g, 0.275 mmol), $HOAc_F$ (0.31 mL, 4.16 mmol) in benzene (3 mL), 0.050 g (24%) yield; IR (CH_2Cl_2) 1974 (s, ν(CO)), 1678 (vs, ν(OCO)), 1650 (m, ν(OCO)) cm^{-1}. Anal. Calcd for $RuP_2F_6C_{32}H_{26}O_5$: P, 8.07; F, 14.85; C, 50.07; H, 3.42. Found: P, 7.77; F, 15.14; C, 49.05; H, 3.64. **$Ru(OAc_F)_2(CO)(Ph_2PCH_2CH_2CH_2CH_2PPh_2)$ (IIg)**: complex Ig (0.060 g, 0.073 mmol), $HOAc_F$ (0.040 mL, 0.54 mmol) in benzene (5 mL), 0.025 g (44%) yield. Anal. Calcd for $RuP_2F_6C_{33}H_{28}O_5$: Ru, 12.93; F, 14.58. Found: Ru, 12.38; F, 14.06. Complexes IIf and IIg tend to form viscous, yellow oils and crystallize only with difficulty from PhH/heptane or CH_2Cl_2/heptane. Usually, large yellow needles of these complexes grow out of the oil which separates on slow solvent evaporation.

Alcohol Dehydrogenation. Kinetic runs were monitored either by GLC analyses of aliquots of the reaction mixture or by measuring the rate of hydrogen evolution using a mercury-filled

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(5) Ahmad, N.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1972**, 843. Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 45.

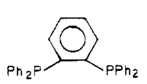
(6) Dobson, A.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc. Dalton Trans.* **1975**, 370; *Inorg. Synth.* **1977**, *17*, 124.

Table I.[a] ^1H NMR Spectra of $RuH_2(CO)(PPh_3)(L-L)$

compd	L–L	solvent	H_1	H_2	coupling const, Hz
Ic	$PPh_2PCH_2CH_2PPh_2$, dppe	C_6D_6	–7.1	–7.6	NA
Id	1,2-$(Ph_2P)_2C_6H_4$	C_6D_6	–6.62	–6.99	P-H_1 = 20, 26, 78; P-H_2 = 18.5, 25, 25; H_1-H_2 = 4.4
Ie	$Ph_2PCH_2CH_2AsPh_2$, Arphos	PhMe-d_8	–7.55	–8.12	P-H_1 = 21, 27.5; P-H_2 = 19, 23.6; H_1-H_2 = 4.6
If	$Ph_2PCH_2CH_2CH_2PPh_2$, dppp	C_6D_6	–6.98	–6.50	P-H_1 = 20, 26, 72; P-H_2 = 16, 21, 31; H_1H_2 = 5.6
Ig	$Ph_2P(CH_2)_4PPh_2$, dppb	C_6D_6	–7.90	–6.95[b]	NA
Ih	$Ph_2P(CH_2)_4PPh_2$, dppb	C_6D_6	–7.6	–8.0[c]	NA

[a] Chemical shifts in ppm from Me_4Si. Under Ar or N_2 atmosphere. NA = not available. See eq 2 for assignments. [b] Meridional P_3 isomer. [c] Facial P_3 isomer.

Table II. 36.2-MHz $^{31}P\{^1H\}$ NMR Spectra of $RuH_2(CO)(PPh_3)(L-L)$ Complexes[a]

compd	L–L	solvent	Ph_3P_1	L_2	L_3	J(P–Ru–P), Hz
Ib	$Ph_2PCH_2PPh_2$, dppm[b]	PhMe	(61.76)	–0.21	17.16	$J_{13} = 244$, $J_{12} = 24$, $J_{23} = 21$
Ic	$Ph_2PCH_2CH_2PPh_2$, dppe	THF-d_8	59.66	64.50	79.80	$J_{13} = 238$, $J_{12} = 18$, $J_{23} = 5$
Id		THF-d_8	59.28	65.25	80.28	$J_{13} = 238$, $J_{12} = 19$, $J_{23} = 8$
Ie	$Ph_2PCH_2CH_2AsPh_2$	PhMe-d_8	59.97		81.48	$J_{13} = 240$
If	$Ph_2P(CH_2)_3PPh_2$, dppp	THF-d_8	58.34	27.64	37.70	$J_{13} = 229$, $J_{12} = 26$, $J_{23} = 22$
Ig	$Ph_2P(CH_2)_4PPh_2$, dppb (*mer* isomer)	C_6D_6	58.46	35.06	52.73	$J_{13} = 232$, $J_{12} = 18$, $J_{23} = 17$
Ih	$Ph_2P(CH_2)_4PPh_2$, dppb (*fac* isomer)	PhMe-d_8	49.85[c]	48.77[c]	36.55[c]	$J_{AB} = 17.5$, $J_{AX} = 5.0$, $J_{BX} = 7.4$
Ia	$(PPh_3)_2$	THF-d_8	56.98	44.54		$J_{12} = 18$

[a] Chemical shifts in ppm with respect to external 85% H_3PO_4, downfield shifts are positive. See eq 2 for assignments. [b] Complex is $RuH_2(CO)(\eta^2\text{-DPM})(\eta^1\text{-DPM})$ (not isolated); uncoordinated phosphine of η^1-DPM at –4.84 ppm. [c] Assignments not applicable.

gas buret. An efficient, double-jacketed spiral condenser was used to minimize vaporization of $HOAc_F$, particularly when high boiling alcohols were studied.

In a typical kinetic run, monitored by hydrogen evolution, the substrate alcohol (4.50 g) was refluxed for ca. 15 min. A solution of the catalyst (2 × 10^{-2} mmol) and $HOAc_F$ (10 μL) in 0.50 g of the alcohol was then injected (usually this mixture had to be heated in a stream bath for 2–3 min to disolve the catalyst). The system was allowed to equilibrate for 1–2 min before volume measurements were recorded.

With inactive substrates, particularly low boiling alcohols or primary alcohols, hydrogen evolution was too slow or too limited to yield accurate rate data. Consequently, these reactions were monitored by GLC analyses only.

In our attempts to dehydrogenate methanol to formaldehyde, the reaction mixtures were analyzed by ^1H and ^{13}C FT NMR using the JEOL *Double Precision* data processing program to extend the dynamic ranges of the spectra. No HCHO was detected. Only complexes IIa or IIf remained upon evaporation of the methanol under vacuum (i.e., no paraformaldehyde was present).

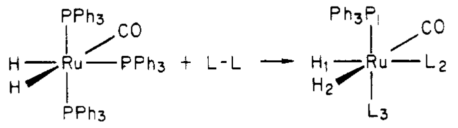
Hydrogenation of Heptanal and Cyclohexanone. Hydrogenations were conducted in a stirring autoclave (Autoclave engineers, Inc.). A typical run is illustrated in the following example: complex IIIe (20.4 mg, 1.74 × 10^{-2} mmol), cyclohexanone (1.71 g, 17.4 mmol), *n*-decane (0.52 g, internal GLC standard), and toluene (16.48 g, total solvent 17.00 g) were weighed into a glass liner and then charged into the autoclave. The system was purged with nitrogen (two times to 700 psig) and then pressurized with hydrogen to 265 psig. The autoclave was then heated to 87–90 °C for 89 min (system required 10 min to reach reaction temperature). At the end of the reaction, the heater assembly was removed and the autoclave cooled in an ice water bath to ca. 15 °C. The reaction mixture was then removed and analyzed by $^{31}P\{^1H\}$ NMR spectroscopy and GLC on an SE30 capillary column.

Results and Discussion

Synthesis and Characterization of $RuH_2(CO)(PPh_3)(L-L)$ Complexes. Reaction of $Ru(OAc_F)_2(CO)(PPh_3)_2$ with diphosphines (L–L) produced a mixture of products instead of the desired derivatives $Ru(OAc_F)_2(CO)(L-L)$. A cleaner reaction is the conversion of the corresponding dihydridoruthenium complexes to the bis(trifluoroacetato) complexes by treatment with excess trifluoroacetic acid ($HOAc_F$).[6,7]

$$RuH_2(CO)(L_n) + 2HOAc_F \rightarrow Ru(OAc_F)_2(CO)(L_n) + H_2 \quad (1)$$

Therefore, a series of $RuH_2(CO)(PPh_3)(L-L)$ (L–L = diphosphine or $Ph_2PCH_2CH_2AsPh_2$ (Arphos)) complexes were prepared by metathesis of $RuH_2(CO)(PPh_3)_3$, Ia, with L–L.



Ia I (2)

Spectral data for complexes I are summarized in Tables I and II. Except for complexes Ie and Ih, their $^{31}P\{^1H\}$ NMR spectra consisted of three ABX quartets (Figure 1). The ^1H NMR spectra of these complexes in the high-field region contained two 16-line multiplets (Figure 2), consistent with coupling of each hydride to four nonequivalent nuclei (i.e., an ABMPX spin system). The large values of $^2J_{PP}$ (ca. 240 Hz) and $^2J_{PH}$ (ca. 75 Hz) are characteristic of two trans phosphines and hydride trans to phosphorus.[8] These data are consistent with a meridional configuration of three phosphine ligands and cis-dihydrides as illustrated in eq 2. ^{31}P peak assignments could be made by knowledge of the Δ_R values expected for these (L–L) diphosphines which would form 4-, 5-, and 6-membered rings. All ^{31}P

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(7) Dobson, A.; Robinson, S. D. *Inorg. Chem.* **1977**, *16*, 1321.
(8) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231.

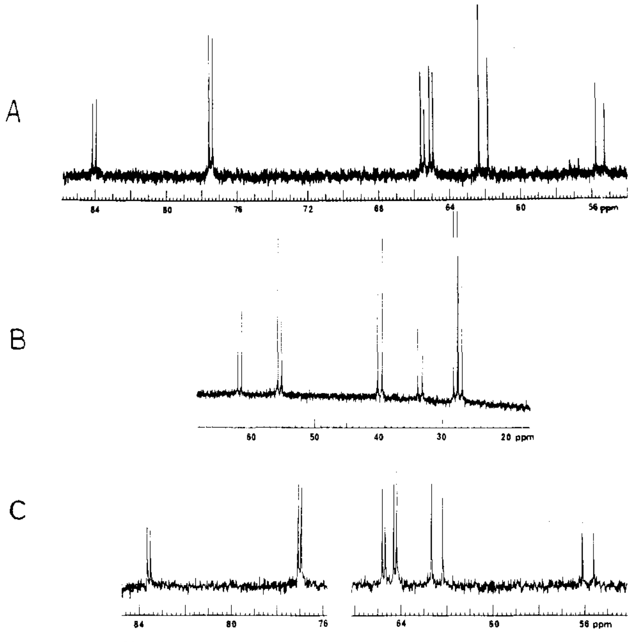

Figure 1. $^{31}P\{^1H\}$ NMR spectra of (A) $RuH_2(CO)(PPh_3)[1,2\text{-}(Ph_2P)_2C_6H_4]$ (Id) in THF-d_8, (B) $RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$ (If) (C) $RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2PPh_2)$ (Ic) in THF-d_8.

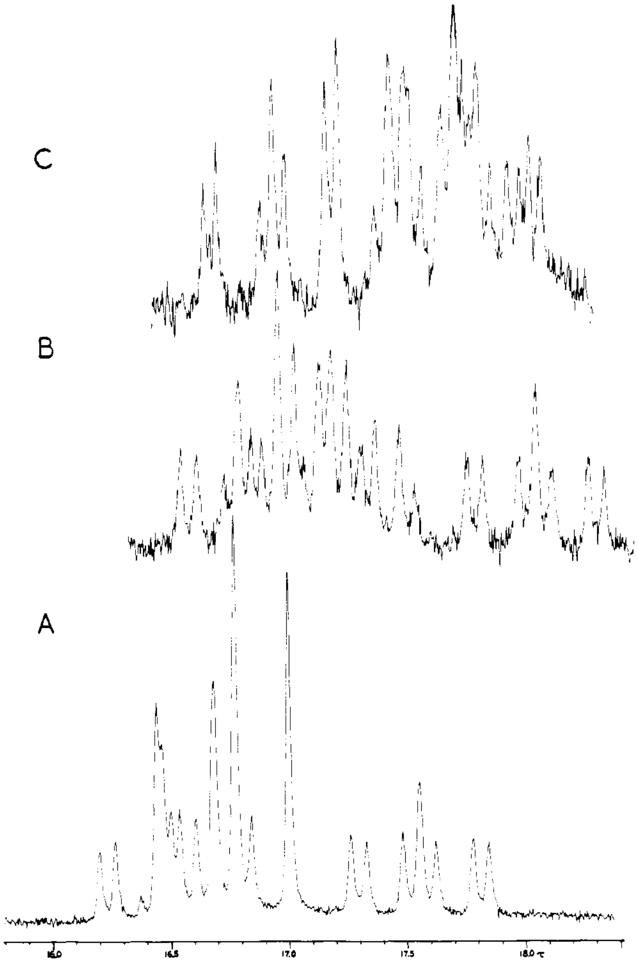

Figure 2. Partial 89.56-MHz ^1H NMR spectrum of (A) $RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$ (If) in toluene-d_8; (B) $RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$ (If) in THF-d_8; (C) $RuH_2(CO)(PPh_3)[1,2\text{-}(Ph_2P)_2C_6H_4]$ (Id) in THF-d_8.

spectra reported here show the expected downfield shift for phosphorus incorporated in 5-membered rings and upfield shift for phosphorus incorporated in 4-membered rings.[9]

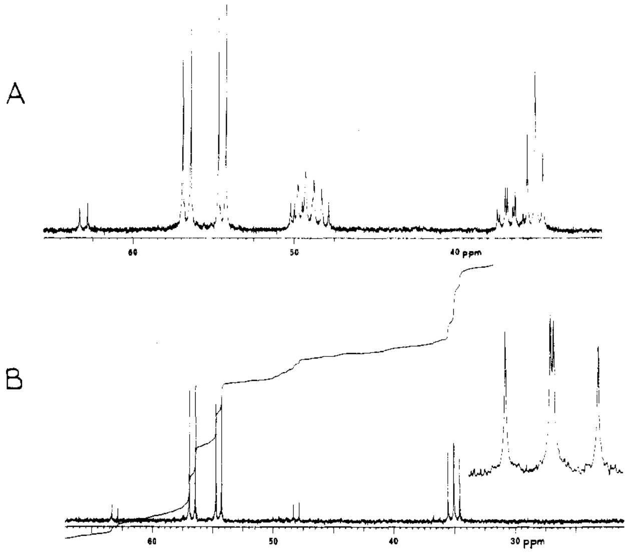

Figure 3. $^{31}P\{^1H\}$ NMR spectra of (A) *mer* and *fac* isomers of $RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2CH_2PPh_2)$ in C_6H_6 obtained from $RuH_2(CO)(PPh_3)_3$ and $Ph_2P(CH_2)_4PPh_2$ after 4 h at 130 °C (free PPh_3 resonance at −6.06 ppm is not shown) and (B) mer-$RuH_2(CO)(PPh_3)[Ph_2P(CH_2)_4PPh_2]$ (Ig).

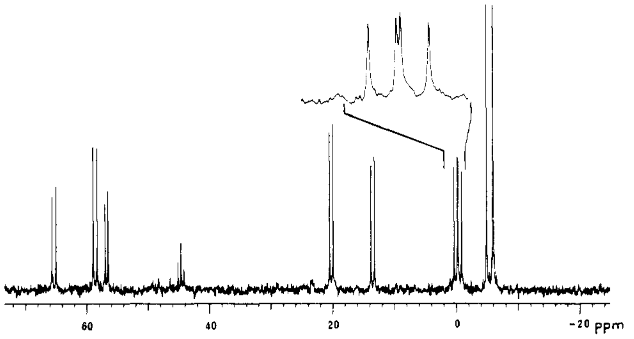

Figure 4. $^{31}P\{^1H\}$ NMR spectrum of toluene solution of $RuH_2(CO)(PPh_3)_3$ (Ia) and $(Ph_2P)_2CH_2$ after 1 h at 120 °C.

The $^{31}P\{^1H\}$ NMR spectrum of Ie (L–L = $Ph_2PCH_2CH_2AsPh_2$) consisted of an AB quartet with $^2J_{AB}$ = 240 Hz. Its ^1H NMR spectrum in the high-field region showed the presence of two nonequivalent hydride ligands which are cis to each other and to the two phosphines. Consequently, we believe complex Ie has the same geometry as the other tris(phosphine) complexes with the two phosphines trans to each other. No isomer with phosphine trans to arsine was observed.

The reaction of $RuH_2(CO)(PPh_3)_3$ (Ia) with $Ph_2P(CH_2)_4PPh_2$ (dppb) afforded two white crystalline products which were separable by fractional crystallization (Figure 3). The NMR spectra of the major isomer Ig are consistent with the meridional P_3 structure shown in eq 2. The minor, less-soluble isomer is assigned the geometry with a facial arrangement of the three phosphines based on $^{31}P\{^1H\}$ (no large $^2J_{PP}$ values) and ^1H NMR spectra (no large $J_{P\text{-}Ru\text{-}H}$ values).

Reaction of Ia and 1 equiv of $Ph_2PCH_2PPh_2$ (dppm) in refluxing toluene for 1 h afforded a mixture of Ia and Ib. No additional change was apparent when the reaction time was extended to 17 h. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture (Figure 4) contained resonances due to Ia and an ABX pattern assigned to complex Ib. In ad-

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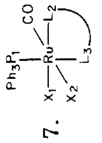
[9] Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

Table III. NMR Spectra of (Trifluoroacetato)ruthenium Complexes $H_nRu(OAc_F)_{2-n}CO)(PPh_3)_m(L\text{-}L)$[a]

compd	n	m	L-L	solv	$^{31}P\{^1H\}$ NMR			^{19}F NMR, δ_{CFCl_3}		^1H NMR		coupling const, Hz
					Ph_3P_1	P_2	P_3	X_1	X_2	H_1	H_2	
IId	0	0	$1,2\text{-}(Ph_2P)_2C_6H_4$[b]	CH_2Cl_2		69.84		(−75.33,	−75.73)			
IIId	0	1	$1,2\text{-}(Ph_2P)_2C_6H_4$[b]	CH_2Cl_2	25.0	58.0	52.5	(−73.87,	−75.03)			$P_1P_2 = 23, P_2P_3 = 15, P_1P_3 = 307$
IIIe	0	1	$Ph_2PCH_2CH_2AsPh_2$									
			(a) *trans*-P_2 isomer[b]	PhMe-d_8	26.13		50.12	(−72.49,	−73.81)			$P_1P_3 = 295$
			(b) *cis*-P_2 isomer[b]	PhMe-d_8	25.50	57.40		(−72.64 (d),	−74.14)			$P_1P_2 = 21, P_2\text{-}^{19}F = 1.2$
IVe	1	1	$Ph_2PCH_2CH_2AsPh_2$	PhMe-d_8	45.16		66.33		−73.61	−5.66		$P_1P_3 = 268, PH_1 = 16.6, 18.1$
IIf	0	0	$Ph_2PCH_2CH_2CH_2PPh_2$	CH_2Cl_2		37.84		(−75.58, br asym s)				
IIIf	0	1	$Ph_2PCH_2CH_2CH_2PPh_2$[b,c]	C_6H_6	14.0	~21.0	22.0	−73.8	−74.70			$P_1P_3 = 300$
IVf	1	1	$Ph_2PCH_2CH_2CH_2PPh_2$[b,c]									
			(a) isomer IVf′	C_6D_6	26.0	4.12	42.0			−4.66		$P_2H_1 = 110, PH_1 = 16, 23$
			(b) isomer IVf″	C_6D_6	~27.0	~47.0	~51.0	NA			−2.63	$PH_2 = 15, 21, 24$
IIg	0	0	$Ph_2P(CH_2)_4PPh_2$	C_6D_6		42.78		NA				
IIa	0	2	none[d]	$CDCl_3$	42.75			NA				
IVa	1	3	none[e]	$CDCl_3$	41.0	18.7		NA		−5.6		$PP = 15, P_1H_1 = 24.5, P_2H_1 = 110$

[a] Chemical shifts in δ referenced to (1) ^{31}P NMR (external reference 85% H_3PO_4), (2) ^{19}F NMR (internal reference C_6F_6, converted to $\delta_{CFCl_3} = -162.28 + \delta_{C_6H_6}$); and (3) ^1H NMR ($Me_4Si = 0$). [b] Equilibrium mixture. [c] Prepared in situ, not isolated. [d] Reference 6. [e] Reference 7.



X = H or OAc_F

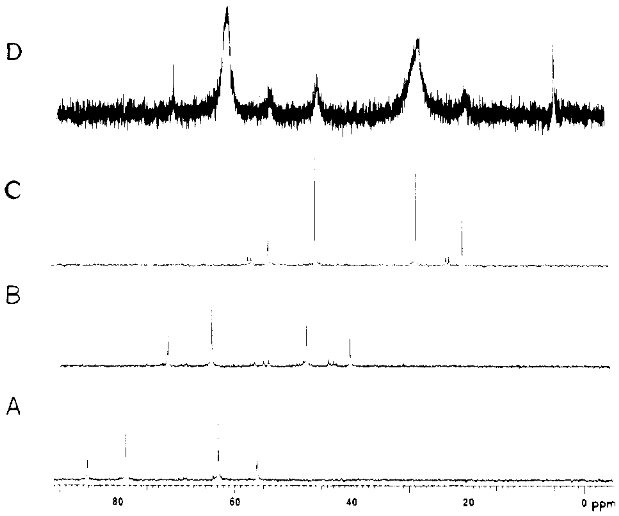
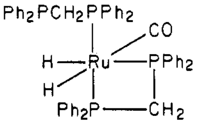


Figure 5. $^{31}P\{^1H\}$ NMR spectra (in C_6H_6): (A) $RuH_2(CO)(PPh_3)$(Arphos) (Ie); (B) +1.3 equiv of $HOAc_F$; (C) +3.8 equiv of $HOAc_F$; (D) +19.5 equiv of $HOAc_F$. $PHPh_3^+$ observed at 5.13 ppm.

dition, the spectrum contained the expected singlet due to free PPh_3 and a singlet at −4.84 ppm which we tentatively assign to the uncoordinated phosphine of a monodentate $Ph_2PCH_2PPh_2$ ligand. No unreacted $Ph_2PCH_2PPh_2$ was observed (singlet at −27 ppm). These data suggest that Ib has the structure

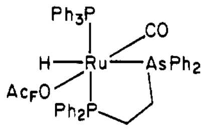


Ib

We had been unable to isolate pure Ib from these reaction mixtures. The introduction of a second equivalent of $Ph_2PCH_2PPh_2$ to the reaction mixture and additional refluxing (1 day) produced a complex mixture. No additional work was attempted with dppm.

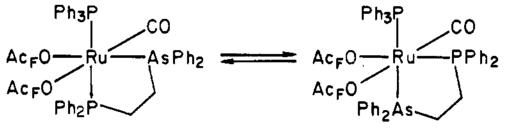
Synthesis of $Ru(OAc_F)_2(CO)(L\text{-}L)(PPh_3)_n$ (n = 0, 1). Robinson et al.[6] prepared $Ru(OAc_F)_2(CO)(PPh_3)_2$, IIa, by reacting complex Ia with $HOAc_F$ (>25× molar excess) in refluxing benzene solution. This procedure with complexes Ic–g yielded intractable yellow oils. To optimize the reaction conditions for these conversions, we monitored these reactions by ^{31}P and ^{19}F NMR spectroscopy. Our results indicate that only 3–10-fold molar excesses of $HOAc_F$ were required and that the reactions occurred smoothly at room temperature (ca. 25 °C). The resultant bis(trifluoroacetato) complexes exhibited three types of behavior in solution.

A. $Ru(OAc_F)_2(CO)(PPh_3)(Ph_2PCH_2CH_2AsPh_2)$, IIIe. upon addition of 1 molar equiv of $HOAc_F$, $RuH_2(CO)(PPh_3)$(Arphos), Ie, was converted virtually quantitatively to $RuH(OAc_F)(CO)(PPh_3)$(Arphos), IVe, within 5 min (Figure 5). The ^1H NMR spectrum of this complex contained a quartet at −5.66 ppm (C_6D_6, $^2J_{PH}$ = 16.6 and 18.1 Hz) due to hydride ligand cis to two nonequivalent phosphines. The ν(CO) band of this intermediate at 1936 (s) cm^{-1} suggests that the CO ligand is trans to the monodentate trifluoroacetate ligand instead of the hydride. The complex $RuH(CO)(OAc_F)(PPh_3)_3$ has a similar structure (determined by ^{31}P and ^1H NMR spectroscopy) with the CO trans to OAc_F.[7] The ν(CO) band of this complex is at 1927 cm^{-1}. Accordingly, complex IVe (which was not isolated in this work) is assigned the structure



IVe

Treatment of Ie with an excess (ca. 2×) of $HOAc_F$ afforded the expected bis(trifluoroacetato) complexes as an equilibrium mixture of two isomers with trans (IIIe′) or cis (IIIe″) phosphines. At 25 °C the major isomer is IIIe′ (ca. 90%). No dissociation of PPh_3 from these IIIe isomers to yield $Ru(OAc_F)_2(CO)(Arphos)$, IIe, was observed under these conditions. In the presence of ca. 9-fold excess of $HOAc_F$, a small amount of $PHPh_3^+$ (~1%) was observed in the $^{31}P\{^1H\}$ NMR spectrum as well as a singlet at 70.5 ppm which may be due to IIe. However, the major effect of such a large excess of $HOAc_F$ was the conversion of the trans-P_2 isomer (IIIe′) into the thermodynamically less stable isomer IIIe″ (ca. 70%). The broad resonances in the $^{31}P\{^1H\}$ NMR spectrum of these solutions are probably due to rapid exchange of free and coordinated trifluoroacetate. Addition of heptane to the reaction mixture afforded air-stable, light yellow crystals of $Ru(OAc_F)_2(CO)(PPh_3)(Arphos)\cdot HOAc_F$ consisting of 62% of the cis-P_2 isomer IIIe″ (from ^{19}F NMR, Figure 6). Upon dissolution of crystalline IIIe, isomer IIIe″ isomerizes back to the trans-P_2 isomer, IIIe′, with a half-life of approximately 1 day at 25 °C.

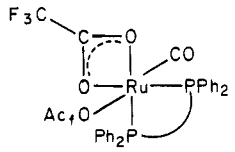


(3)

IIIe′ IIIe″

In the $^{31}P\{^1H\}$ NMR spectrum of the purified IIIe mixture, the Arphos resonance of the cis-P_2 isomer, IIIe″, appears as a doublet of quartets ($^2J_{PP}$ = 21 Hz, $^5J_{PF}$ = 1.2 Hz). The ^{19}F NMR spectrum of this mixture contain a doublet at −72.7 ppm (δ_{CFCl_3}, toluene-d_8 solution) assigned to a trifluoroacetate ligand of isomer IIIe″. No long-range ^{31}P–^{19}F coupling was observed for the PPh_3 resonance of IIIe″, nor for any of the resonances of the trans-P_2 isomer.

B. $Ru(OAc_F)_2(CO)(L–L)$, II. The complexes $Ru(OAc_F)_2(CO)(L_2)$ (IIa, L_2 = $(PPh_3)_2$; IIf, L_2 = $Ph_2P(CH_2)_3PPh_2$; IIg, L_2 = $Ph_2P(CH_2)_4PPh_2$) were formed by addition of ca 10-fold molar excess of $HOAc_F$ to benzene solutions of the corresponding dihydride complexes I. The resultant yellow solutions each contained two sharp singlets in their $^{31}P\{^1H\}$ NMR spectra assignable to free $HPPh_3^+$ and complexes II. Phosphorus-31 NMR spectra of the purified complexes II contain only a single broad resonance ($w_{1/2} \approx 15$ Hz). Infrared and ^{19}F NMR spectra of II show the presence of both mono- and bidentate trifluoroacetate ligands.[7] These data indicate that IIf and IIg has the same structure as the parent complex IIa. The reaction of $RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$ (If) with only 1 equiv of $HOAc_F$ afforded a complex mixture. At least three sets of ABX multiplets can be identified in the $^{31}P\{^1H\}$ NMR spectrum of this system (Figure 7). Proton NMR spectroscopy in the hydride region indicated that two of the intermediates are $RuH(OAc_F)(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$ (IVf) isomers with the hydride trans to phosphorus (doublet of quartets, $J_{PH_{(trans)}}$ = 110 Hz) or carbonyl (octet, J_{PH} < 25 Hz). The ratio of IVf′ to IVf″ is roughly 1.9 from integration of the hydride resonances. The third major complex present is $Ru(OAc_F)_2(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$ (IIIf, vide infra). The infrared spectrum of this mixture contained a ν(CO) band at 1934 cm^{-1} due to IVf′ and a more intense band at 1977 cm^{-1} assigned to IVf″ and IIIf. Contrast this behavior with that of Ie which formed only one isomer of IVe under the same conditions (vide supra). The infrared spectrum of IVe contained only one strong ν(CO) band at 1936 cm^{-1}.



IIf,g

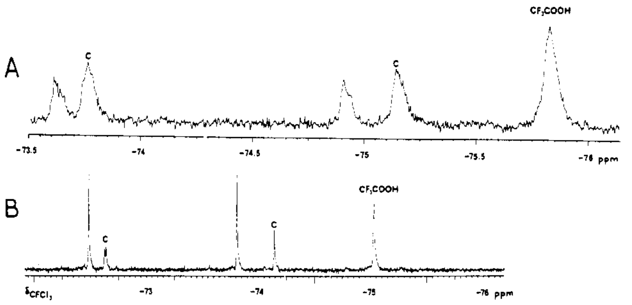


Figure 6. The 84.26-MHz ^{19}F NMR spectrum of $Ru(OAc_F)_2(CO)(PPh_3)(Arphos)\cdot HOAc_F$ (IIIe): (A) freshly prepared CH_2Cl_2 solution; (B) toluene-d_8 solution after 3 h at 100 °C in presence of 3.5 equiv of heptanal (no reaction under these conditions). "C" indicates resonances of the cis-P_2 isomer (IIIe″).

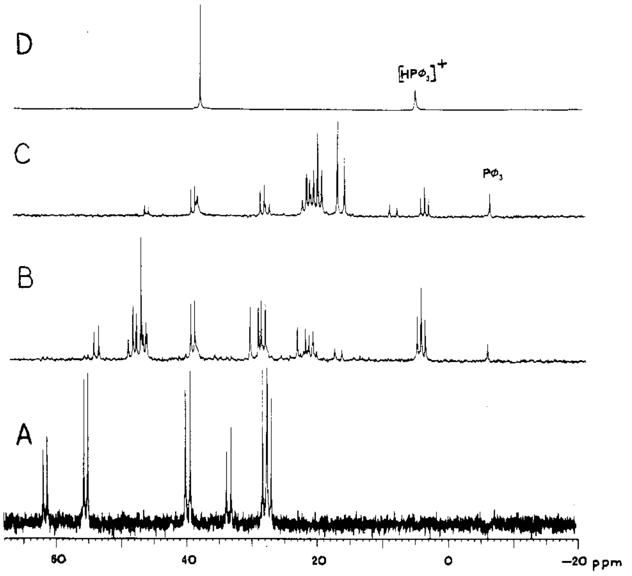
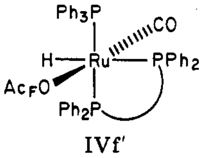
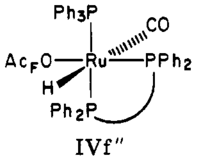


Figure 7. $^{31}P\{^1H\}$ NMR spectra (in C_6H_6): (A) $RuH_2(CO)(PPh_3)(DPPP)$ (If); (B) +1 equiv of $HOAc_F$; (C) +3 equiv of $HOAc_F$; (D) +15 equiv of $HOAc_F$.



IVf′



IVf″

The introduction of a second equivalent of $HOAc_F$ resulted in the disappearance of resonances due to isomer IVf″ (one set of ABX multiplets in the $^{31}P\{^1H\}$ NMR spectrum and the octet at ca. τ 12.6 in the proton spectrum). A small amount of complex IIf is also present under these conditions (broad singlet at ca. 38 ppm in the ^{31}P NMR spectrum). The strong 1977-cm^{-1} band observed

Table IV. Dehydrogenation of Cyclohexanol Using Ruthenium Catalysts

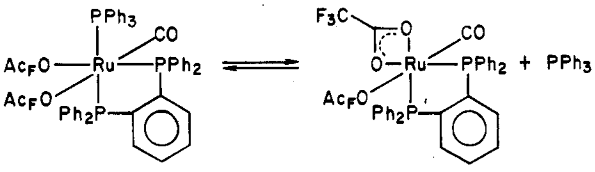
catalyst	substrate	10^5 mol of Ru	initial rate[a]	rel rate	max % reactn
$Ru(OAc_F)_2(CO)(PPh_3)_2$, IIa	cyclohexanol[b]	2.01	1.20	1.00	4.5
		4.54	(8.82)[c]		
$Ru(OAc_F)_2(CO)(PPh_3)[(Ph_2P)_2C_6H_4]$, IIId	cyclohexanol[b]	2.06	1.68	1.40	5.6[d]
$Ru(OAc_F)_2(CO)(PPh_3)(Ph_2PCH_2CH_2AsPh_2)\cdot HOAc_F$, IIIe	cyclohexanol[b]	1.75	2.76 ± 0.08	2.30	22.0
$Ru(OAc_F)_2(CO)(Ph_2PCH_2CH_2PPh_2)$, IIf	cyclohexanol[b]	2.06	4.20	3.50	17.0
IIa	ethanol[c]	4.54	0.45		
	ethanol[e]	2.62	0.074		
IIa	1-propanol[c]	4.54	1.36		
	1-propanol[e]	2.62	0.22		
IIa	2-propanol[c]	4.54	0.20		
	2-propanol[e]	2.62	0.032		
IIa	1-butanol[c]	4.54	4.1		
	1-butanol[e]	2.62	0.67		

[a] Mol of H_2 evolved/mol of Ru/min. [b] Reaction conditions: 175 °C, 5.0×10^{-2} mol of substrate, 1.3×10^{-4} mol of CF_3COOH. [c] References 1 and 2: reflux temperatures, 0.134 mol of substrate, 5.2×10^{-4} mol of CF_3COOH. [d] Kinetic run arbitrarily stopped at this maximum conversion. [e] Reference 3: reflux temperatures, 20 mL of substrate, 3×10^{-4} mol of CCl_3COOH.

previously is replaced by an asymmetric band at ca. 1970 cm^{-1} which is assigned to the $\nu(CO)$ modes of complexes IIf and IIIf. The 1934-cm^{-1} band of IV′ is still present but slowly diminishes in intensity. The reactions of complex If with trifluoroacetic acid is summarized in eq 4.

$$\mathrm{If} \rightarrow \mathrm{IIIf} + \mathrm{IVf'} + \mathrm{IVf''} \rightarrow \mathrm{IIf} + \mathrm{IIIf} + \mathrm{IVf'} \xrightarrow{\mathrm{HOAc_F}} \mathrm{IIf} \quad (4)$$

C. $Ru(OAc_F)_2(CO)[1,2\text{-}(Ph_2P)_2C_6H_4](PPh_3)_n$. The $^{31}P\{^1H\}$ NMR spectra of the benzene solution obtained by treating $RuH_2(CO)(PPh_3)[1,2\text{-}(Ph_2P)_2C_6H_4]$ with a ca. 8-fold excess of $HOAc_F$ contained sharp singlets due to $[HPPh_3^+]$, $Ru(OAc_F)_2(CO)[(Ph_2P)_2C_6H_4]$ (IId), and broad resonances assignable to $Ru(OAc_F)_2(CO)(PPh_3)[(Ph_2P)_2C_6H_4]$ (IIId). As in the case of complexes IIe and IIIe, the line-width differences of the resonances of IId and IIId may be caused by different exchange rates between free $HOAc_F$ and coordinated OAc_F^-. Only complex IIId was isolated from these solutions. In solution, purified complex IIId dissociated PPh_3 to yield a mixture of IIId, IId, and PPh_3.



(5)

IIId IId

Catalytic Activity. Alcohol Dehydrogenation. From the different solution behavior noted above, the relative activities of these complexes in catalyzing alcohol dehydrogenation can be predicted. Both complexes II and III are coordinatively saturated and cannot accommodate an additional ligand. For a vacant coordination site to be created for the activation of an alcohol molecule, the chelate trifluoroacetate ligand in complexes II must become monodentate. This bidentate–monodentate isomerization is much more facile than the required PPh_3 dissociation from complexes III.[10] Since the degree of PPh_3 dissociation is much larger with IIId, than with IIIe (at least at 25 °C), the activity order should be IIf > IIId > IIIe > IIa. Because of the unexpected, premature catalyst deactivation processes found in this study (vide infra), only a few representative bis(trifluoroacetato) complexes were screened for comparative catalytic activity.

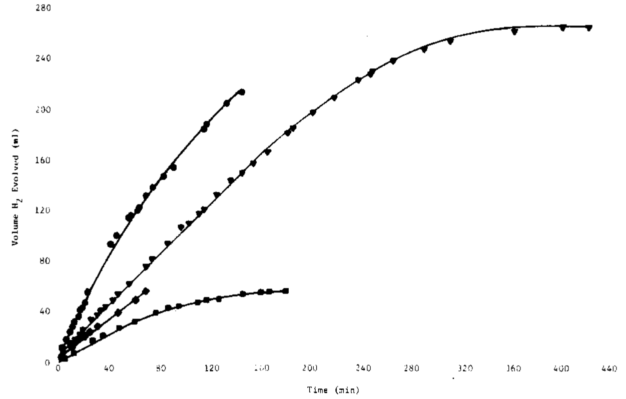


Figure 8. Dehydrogenation of cyclohexanol using catalyst: ■, $Ru(OAc_F)_2(CO)(PPh_3)_2$, ♦, $Ru(OAc_F)_2(CO)(PPh_3)[(PPh_2)_2C_6H_4]$, ▼, $Ru(OAc_F)_2(CO)(PPh_3)(Ph_2PCH_2CH_2AsPh_2)\cdot HOAc_F$, ●, $Ru(OAc_F)_2(CO)(Ph_2PCH_2CH_2CH_2PPh_2)$. Reaction conditions were 175 °C, 2.0×10^{-2} mmol of catalyst, 5.00 g of substrate, and 10.0 μL of CF_3COOH.

The rates of conversion of cyclohexanol to cyclohexanone at 175 °C using these catalysts are summarized in Table IV along with comparative data for other alcohols.[1-3] As expected, the chelate-modified catalysts are more active than $Ru(OAc_F)_2(CO)(PPh_3)_2$, IIa. The fact that IIIe is more active than IIId may indicate that the difference in the degree of PPh_3 dissociation between these two complexes at 25 °C is unimportant at higher temperatures. This point was not investigated further. The main unexpected result was that catalyst IIa deactivated rapidly, generally after roughly 100 turnovers (or ca 4% conversion). In contrast, the modified catalysts were still active to greater than 20% conversion (500 turnovers; Figure 8). The deactivation of the latter catalysts, we believe, is due in part to loss of $HOAc_F$ (bp 72 °C) at the 175 °C reaction temperature.

All of these ruthenium complexes seem to be specific for secondary alcohols. Little or no conversion of primary alcohols to aldehydes was observed. In attempts to dehydrogenate ethanol, 2-propanol, and 1-butanol at their reflux temperatures with these catalysts, very little hydrogen evolution was measured within 5 h. After the mixtures were refluxed for up to 20 h, some acetone and butanal were detected by GLC analyses, but the conversions amounted to less than two turnovers. With 1-heptanol, complexes IIa and IIe did form larger quantities of

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(10) Hoffman, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221.

Table V. Hydrogenation of Heptanal or Cyclohexanone with Ruthenium Catalysts[a]

catalyst	substrate	% conv	% select
$Ru(OAc_F)_2(CO)(PPh_3)_2$, IIa	heptanal	36	50
$Ru(OAc_F)_2(CO)(Ph_2PCH_2CH_2CH_2PPh_2)$, IIf	heptanal	80	68
$Ru(OAc_F)_2(CO)(PPh_3)(Arphos)\cdot HOAc_F$, IIIe	heptanal	84	62
$Ru(OAc_F)_2(CO)(PPh_3)_2$, IIa	cyclohexanone	3	99
$Ru(OAc_F)_2(CO)(Ph_2PCH_2CH_2CH_2PPh_2)$, IIf	cyclohexanone	99	99
$RuH_2(CO)(Ph_3)(Ph_2PCH_2CH_2CH_2PPh_2)$, If	cyclohexanone	59	99
$Ru(OAc_F)_2(CO)(PPh_3)(Arphos)\cdot HOAc_F$, IIIe	cyclohexanone	9	99

[a] Reaction conditions: 1.0 mmolal catalyst, 1.0 molal substrate in 4% *n*-decane/toluene (w/w); 84–89 °C; 20 atm of H_2; 90 min.

heptanal, with IIe approximately twice as efficient as IIa, but the reactions stopped after less than 12 catalytic cycles. No conversion of methanol to formaldehyde was observed at 150 °C with IIa or IIf in ca. 9 h (under 1400 psig argon). Because of these low catalytic activities, we felt that more detailed kinetic studies of the dehydrogenation of primary alcohols were unwarranted.

Dobson and Robinson[1] and, more recently, Rybak and Ziolkowski[3] reported that $Ru(OAc_F)_2(CO)(PPh_3)_2$, IIa, did dehydrogenate primary alcohols to aldehydes, but they disagreed on the specific activities (initial rates only) of IIa in catalyzing the conversions of ethanol, 1-propanol, and 1-butanol (Table IV). Under comparable reaction conditions, the former workers reported activities that were 6 times higher than those determined by the latter group and ca. 7 times higher than those obtained here. Both groups were vague in describing the stability of catalyst IIa. In any event, the activities of complexes II toward primary alcohols in our hands are too low to be of any practical value.

Catalyst Deactivation. The low activities and short catalyst lifetimes may in part be attributed to the loss of CF_3COOH required to regenerate complexes II from intermediates $RuH(OAc_F)(CO)L_n$ ($n = 2, 3$), but deactivation or decomposition of the catalyst is also a major factor.

After our unsuccessful attempt to convert cyclopentylmethanol to cyclopentylcarboxaldehyde using IIe, we analyzed the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy. The spectrum indicated that IIe had partially decomposed to a mixture of (phosphine)ruthenium complexes during the course of the reaction (170 °C, 18.5 h, ca. 6 equiv excess $HOAc_F$). The major species present was the intermediate $RuH(OAc_F)(CO)(PPh_3)(Arphos)$, IVe, indicating that the bis(trifluoroacetato) complex was not being regenerated, probably due to physical loss of $HOAc_F$ from the solution. Under these conditions, we believe most of the trifluoroacetic acid will be in vapor phase rather than in solution. The actual acid concentration in solution would be difficult to control as it depends on such variables as condenser efficiency and amount of dead space in the reactor. This problem can be resolved by continual addition of excess $HOAc_F$. The use of more than ca. 12 equiv of $HOAc_F$[1] or use of higher boiling carboxylic acids such as CCl_3COOH[1,3] results in even lower activities. However, the large differences in catalyst lifetimes between IIa and the modified chelate complexes IId–f cannot be attributed entirely to the loss of regenerating carboxylic acid.

The deactivation of catalysts II can be due to thermal decomposition or side reactions, yielding inactive products. In general, metal complexes with chelating phosphines are more thermally stable than the analogous complexes with monodentate phosphine.[11] The enhanced catalyst lifetimes of complexes IIf and IIId,e can be due in part to this chelate effect, especially at the higher temperatures required to obtain reasonable reaction rates.

Phosphorus-31 NMR analysis of a solution obtained by refluxing a mixture of IIa (0.107 mmol), $HOAc_F$ (0.72 mmol), 1-heptanol (1.00 g), and *n*-decane (10.0 g) for 4 h showed that no IIa was left at the end of the reaction. This spectrum consisted of a singlet at 28.0 ppm which we assign to $Ru(OAc_F)_2(CO)_2(PPh_3)_2$, V (lit. value:[6] 30.3 ppm in $CDCl_3$). Complex V is inert in catalyzing this conversion and could have been formed by stoichiometric decarbonylation[12] of the heptanal produced in this reaction (yield of heptanal was 4%).

$$CH_3(CH_2)_5CHO + Ru(OAc_F)_2(CO)(PPh_3)_2 \rightarrow n\text{-}C_6H_{14} + Ru(OAc_F)_2(CO)_2(PPh_3)_2 \quad (6)$$

This decarbonylation reaction was confirmed in a separate experiment in which complex IIa (0.082 mmol) was reacted with a 4.5-fold molar excess of heptanal in toluene-d_8 (2.8 mL) at 100 °C. Phosphorus-31 NMR analysis showed that ca. 10% of complex IIa had been converted to V (singlet at 29.4 ppm) within 30 min. Additional heating (2.5 h) afforded a complex mixture suggesting that other decomposition reactions had occurred. The conversion of complex IIa to V may be cleaner by using a larger excess of heptanal. A small amount of hexane was found by GLC analysis of the reaction mixture. Under the same conditions, $Ru(OAc_F)_2(CO)(PPh_3)(Arphos)$, IIIe, did not react with heptanal over 3.5 h. After 13 h at 175 °C in 10% heptanol/decane, complex IIIe had decomposed mainly to $Ru(OAc_F)_2(CO)_2(Arphos)$ (broad singlet at 28.2 ppm, $w_{1/2} = 14.5$ Hz).

Prior workers[1] claimed that complex IIa was not carbonylated by alcohols, aldehydes, or ketones under conditions of dehydrogenation catalysis but did not specify which substrates, products, or reaction conditions were employed in reaching this conclusion. We have found that the formation of complex V did not occur with low boiling alcohols (e.g., methanol, ethanol, 2-propanol). However, the ruthenium catalysts studied here were ineffective in converting these alcohols to carbonyl products which poison the catalysts. This catalyst poisoning could be minimized by continuous removal of the aldehyde by fractional distillation. However, this process would also eliminate the carboxylic acid needed to regenerate the catalyst. The volatile trifluoroacetic acid could be replaced with polymer-bound carboxylic acids, but the activities of these catalysts would be greatly reduced.[3]

Hydrogenation of Ketones and Aldehydes. Since similar Ru(II) complexes have been shown to be active for the hydrogenation of aldehydes and ketones to alcohols,[13–15] we set out to also study our diphosphine com-

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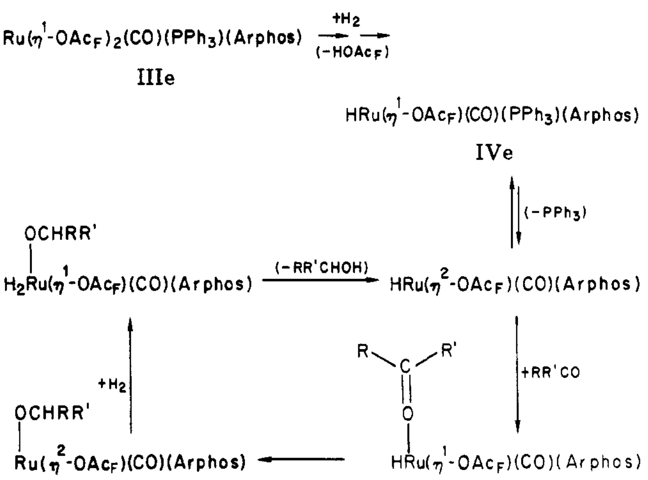
(11) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, 1972; pp 650–652.

(12) Baird, M. C.; Mague, J. T.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A.* **1967**, 1347.

(13) Sanchez-Delgado, R. A.; Andriollo, A.; deOchoa, O. L.; Suarez, T.; Valencia, N. *J. Organomet. Chem.* **1981**, *209*, 77.

(14) Strohmeier, W.; Wiegelt, L. *J. Organomet. Chem.* **1978**, *145*, 189.

Scheme II



plexes as hydrogenation catalysts, compare their activities to IIa, and compare the conditions necessary for hydrogenation vs. dehydrogenation. The reaction sequence shown in Scheme I can be reversed to envision the reduction of carbonyl compounds to alcohols. Strohmier and Weigelt[14] reported that $RuH_2(CO)(PPh_3)_3$ (Ia) and $Ru(OAc_F)_2(CO)(PPh_3)_2$ (IIa) catalyze ketone hydrogenation. We have found that the modified complexes If, IIf, and IIIe are much more efficient hydrogenation catalysts than IIa (Table V). Complex Ia was not screened in this work, but Strohmeier and Weigelt[14] reported that IIa is much more efficient than Ia in catalyzing cyclohexanone hydrogenation.

After GLC analyses, the reaction mixtures were analyzed by $^{31}P\{^1H\}$ NMR spectroscopy. In the hydrogenation of heptanal, catalysts IIa, IIIe, and IIf were not present at the end of the reaction. The first catalyst was almost entirely converted to $Ru(OAc_F)_2(CO)_2(PPh_3)_2$, V, by decarbonylation of heptanal. The lower heptanal conversion with this catalyst may be due to this premature catalyst poisoning. Complex IIf appears to have similarly reacted to form the analogous complex $Ru(OAc_F)_2(CO)_2(Ph_2PCH_2CH_2CH_2PPh_2)$ ($^{31}P\{^1H\}$ NMR: broad singlet at 32.90 ppm, $w_{1/2} \sim 7$ Hz). The ^{31}P NMR spectrum of a reaction mixture with catalyst IIIe contained a large, broad singlet at 28 ppm which is attributable to $Ru(OAc_F)_2(CO)_2(Arphos)$ and numerous resonances in the 55-to 75-ppm region. Apparently, complex IIIe decomposed under these reaction conditions to yield a mixture of catalytically active, (phosphine)ruthenium complexes (no free PPh_3 or $Ph_2PCH_2CH_2AsPh_2$ was observed).

In cyclohexanone hydrogenation, the catalysts can be divided into two categories. Phosphorus-31 NMR analyses indicated that the less active catalysts IIa and IIIe did not decompose during the reaction. Approximately 35% of IIa decarbonylated cyclohexanone to yield $Ru(OAc_F)_2(CO)_2(PPh_3)_2$, V. This deactivation process was not as extensive as that found in IIa-catalyzed heptanal hydrogenations. Transition-metal complexes stoichiometrically decarbonylate aldehydes more readily than ketones.[12]

Only $RuH(OAc_F)(CO)(PPh_3)(Arphos)$, IVe, was detected in solution when IIIe was used. Complex IVe is probably the actual catalyst precursor in this reaction (Scheme II). The catalytic cycle shown in Scheme II is essentially the reverse of that shown in Scheme I.

The fact that complex IIIe is roughly 3 times as active as IIa in cyclohexanone hydrogenation suggests that the isomer of intermediate $HRu(\eta^2\text{-}OAc_F)(CO)(PPh_3)_2$ with trans-PPh_3 ligands (*g* in Scheme I) which inhibits the IIa-catalyzed dehydrogenation of alcohols[1] also inhibits the reverse reaction (ketone hydrogenation). The Arphos analogue, $HRu(\eta^2\text{-}OAc_F)(CO)(Ph_2PCH_2CH_2AsPh_2)$, cannot form an analogous inactive intermediate due to the steric constraints imposed by the chelate ligand.

The most active cyclohexanone hydrogenation catalyst $Ru(OAc_F)_2(CO)(Ph_2PCH_2CH_2CH_2PPh_2)$, IIf, was converted to a mixture of ruthenium complexes with broad resonances in the 37–43-ppm region of the $^{31}P\{^1H\}$ NMR spectrum (the phosphorus NMR spectrum of complex IIf consists of a broad singlet ($w_{1/2}$ = 14 Hz) at 37.8 ppm in CH_2Cl_2 solution). Sanchez-Delgado and co-workers[13,15] studied the kinetics of aldehyde and ketone hydrogenation using a variety of (phosphine)ruthenium catalysts and found that the most efficient catalyst tested, $RuHCl(CO)(PPh_3)_3$, decomposed during the reaction to an intractable mixture of ruthenium species which actually catalyzed the reaction. Our most active chelate-modified catalysts appear to similarly decompose to yield mixtures with activities comparable to those generated by the decomposition of $RuHCl(CO)(PPh_3)_3$.

Acknowledgment. We are indebted to Dr. J. D. Fellmann, Dow Chemical-New England, for technical assistance.

Note Added in Proof. S. D. Robinson[16] has suggested that the discrepancy in the catalytic activities of complex IIa may be due to differences in the configuration of our reactor systems. The larger dead space, or less efficient condensor used in the work described in ref 1 and 2, may have resulted in lower concentrations of aldehyde or ketone in solution, thus retarding the rate of catalyst deactivation. However, this phenomenon would also decrease the catalytic activity due to decreased concentration of trifluoroacetic acid. Since we both agree that there is no hydrogen evolution from reaction of methanol, it is clear that there was no constant source of error leading them to systematic over estimation of their rates of gas evolution.

Registry No. Ia, 22337-78-6; Ib, 80515-23-7; Ic, 80515-24-8; Id, 80515-35-1; Ie, 80515-25-9; If, 80515-26-0; Ig, 80515-27-1; Ih, 80581-15-3; IIa, 80558-89-0; IId, 80515-28-2; IIf, 80515-29-3; IIg, 80515-30-6; IIId, 80515-31-7; IIIe′, 80515-32-8; IIIe″, 80558-90-3; IIIf, 80515-33-9; IVa, 61966-66-3; IVe, 80532-10-1; IVf′, 80515-34-0; IVf″, 80558-91-4.

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Organometallics **1982,** *1,* 667–674

Stability and Oxidative Coupling of Chiral Vinyl- and Cyclopropylcopper Reagents. Formation of a Novel Dissymmetric Diene

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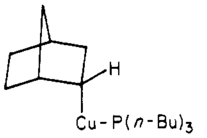
Chiral (*S*)-((4-methylcyclohexylidene)methyl)copper (**3**) and chiral (*S*)-(1-methyl-2,2-diphenylcyclopropyl)copper (**4**) have been prepared and shown to be optically stable. Oxidative coupling of (*R*)-**3** leads to the formation of an unusual chiral 1,3 diene having biaxial dissymmetry, (+)-(*aR*,*aR*)-bis(4-methylcyclohexylidene)ethane (**9**). The chiroptical properties of **9** are reported. The thermal and dioxygen reaction of (*S*)-(1-methyl-2,2-diphenylcyclopropyl)copper aggregate ((*S*)-**13**) leads to a variety of reaction products other than coupling to chiral and *meso*-bis(1-methyl-2,2-diphenylcyclopropane), (+)-(*R*,*R*)-**17** and (*R*,*S*)-**18**, respectively. The radical nature of the reaction is discussed.

Introduction

Organocopper reagents are versatile synthetic intermediates and their chemistry has been the subject of several reviews.[2] The most convenient method of preparation of these compounds is the reaction of an organolithium or Grignard reagent with a copper(I) salt such as in the reaction of an equimolar amount of an organolithium reagent with cuprous iodide. These compounds exist as aggregated clusters with structures which depend on the nature of the organic moiety and upon the presence of coordinating ligands.[3]

Reaction of 2 equiv of an organolithium reagent with 1 equiv of cuprous iodide results in the formation of a second type of organocopper reagent, the organocuprate or "ate complex".[4] Mixed cuprates can be prepared by the addition of 1 equiv of organolithium reagent to a preformed organocopper compound. The cuprates also appear to be aggregates in which the organic ligands are bound to a cluster of lithium and copper atoms. Moreover, there is no evidence for an equilibrium existing between organocuprates and their components, RLi and RCu.[5]

The stereochemical stability of organocopper reagents has received relatively little attention. Whitesides and co-workers[6] have shown that *endo*-2-norbornyl(tri-*n*-butylphosphine)copper(I) (**1**), phosphine-stabilized Cu–Csp^3 σ bond, is configurationally stable in ether at −30 °C. Recently, we have prepared an exceptionally stable chiral organocopper(I) compound, (1-isocyano-2,2-diphenylcyclopropyl)copper(I) (**2**), Cu–Csp$^{2.28}$ σ bond, which was shown to be stable at ambient temperature.[7] Vinylcopper(I) reagents,[8] Cu–Csp^2 σ bond, have also been shown to retain their configuration at −75 °C. Chiral vinylcopper reagent **3** has been prepared[9] and shown to be optically stable at −35 °C. In this article we report the results of our studies on the stability and oxidative coupling of chiral vinylcopper **3** and chiral cyclopropylcopper **4**.



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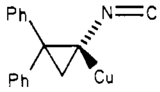
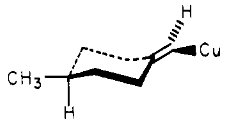
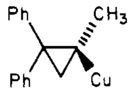


(*S*)-**2**



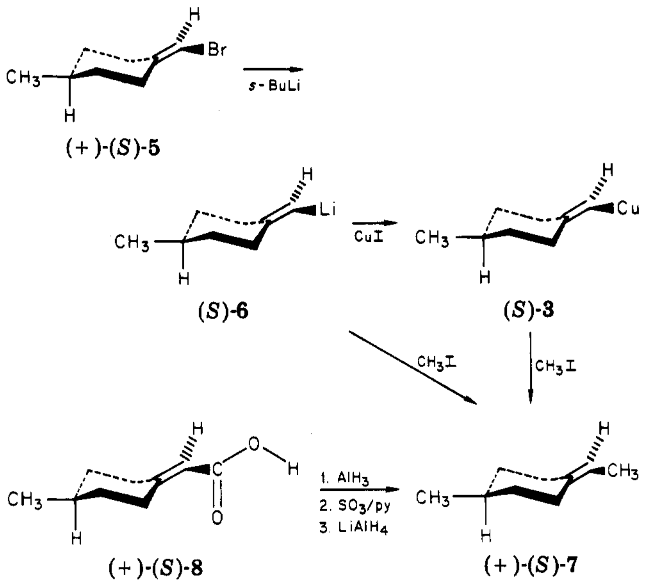
(*S*)-**3**



(*S*)-**4**

Results and Discussion

Chiral Vinylcopper. Optically active (*S*)-((4-methylcyclohexylidene)methyl)copper(I) (**3**) was prepared from (+)-(*S*)-(4-methylcyclohexylidene)methyl bromide (**5**)



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(1) This work was supported by a grant from the National Science Foundation.

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(9) A preliminary report of part of this work has appeared, see R. B. Banks and H. M. Walborsky, *J. Am. Chem. Soc.*, **98,** 3732 (1976) and references cited therein.

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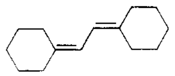
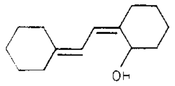
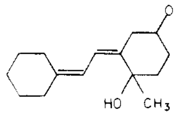
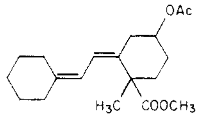
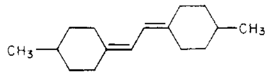
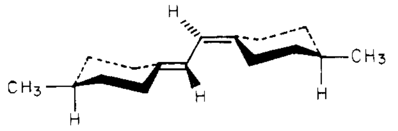
Table I. UV Spectra of Dicyclohexylideneethanes

compd	λ, nm	$10^{-3}\epsilon$	λ, nm	$10^{-3}\epsilon$	λ, nm 10	$10^{-3}\epsilon$
	241	31.6	250	38.1	259	26.5
	240	29.5	248	34.9	258	23.7
			245	16.4		
			246	18.8		
	242	31.8	250	38.8	259	27.5

whose absolute configuration has previously been established.[10] Halogen-metal exchange of **5** at −75 °C with *sec*-butyllithium, a reaction known to proceed with retention of configuration,[10,11] produced the corresponding (*S*)-((4-methylcyclohexylidene)methyl)lithium (**6**). The lithium reagent **6** was shown to be optically stable at temperatures below 0 °C.[10] Addition of 1 equiv of cuprous iodide to (*S*)-**6**, followed by stirring at −35 °C for 0.5 h, resulted in the formation of a dark suspension of (*S*)-**3**. With use of a modification of the Normant procedure,[8c] (*S*)-**3** was alkylated with methyl iodide to (+)-(*S*)-(4-methylcyclohexylidene)ethane (**7**). The lithium reagent (*S*)-**6** was also transformed to (+)-(*S*)-**7** by treatment with methyl iodide.

An authentic sample of (+)-(*S*)-**7** was prepared from (+)-(*S*)-4-methylcyclohexylideneacetic acid (**8**) using the Corey–Achiva procedure.[11] Since the absolute configuration and optical purity of **8** are known,[12] this enables one to establish the optical purity ($[\alpha]_{Hg}$ +17.7°) and absolute configuration of **7** as *S* with confidence, since the reactions used to effect this conversion would not be expected to lead to any racemization or inversion. With use of this datum, the conversion of **6** and **3** to **7** proceeds with 100% and 95% retention of optical activity or 100% and 98% retention of configuration.[13] Thus (S)-**3** represents the first example of a stable optically active vinylcopper compound.

Oxidative coupling of the optically active vinylcopper compound (*R*)-**3** resulted in the formation of a new optically active compound (+)-(*aR*,*aR*)-bis(4-methylcyclohexylidene)ethane. Passage of a stream of oxygen through a THF suspension of the vinylcopper reagent (prepared from (−)-(*R*)-bromide, 94% optically pure) at −35 °C, followed by workup and purification of the crude product by chromatography on silver nitrate–silicic acid, gave a 30% yield of (+)-(*aR*,*aR*)-**9**, $[\alpha]^{25}_{Hg}$ +37.9 ± 0.8° (*c* 0.83, absolute EtOH). Diene **9** was characterized by its UV, IR, NMR, ORD, CD, and mass spectra. The UV, ORD, and CD spectra are shown in Figure 1. The optical purity of **9** has not been determined. However, there is no reason to believe that **9** is formed with significant loss of optical purity, since the vinylcopper reagent is configurationally stable at −35 °C and since *cis*- and *trans*-vinylcopper reagents couple with complete retention of configuration.[8] The diene is optically stable in ethanol solution for long periods of time at 0 °C.



(+)-(*aR*,*aR*)-**9**

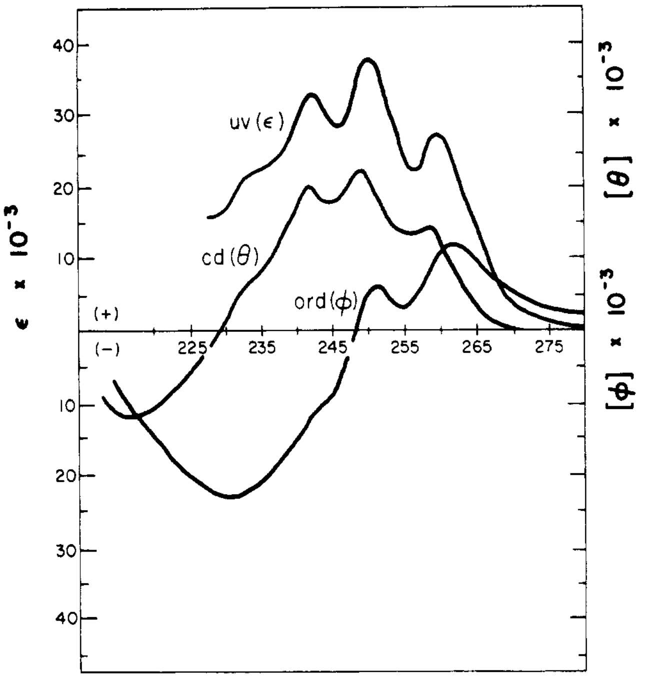


Figure 1. UV, CD, and ORD Spectra of (+)-(a*R*,a*R*)-bis(R-methylcyclohexylidene)ethane.

Optically active diene **9** arises from the stereospecific coupling of two dissymmetric axes of the same chirality and is assigned the absolute configuration (+)-(*aR*,*aR*). This assignment relates the configuration of **9** to that of (−)-(*R*)-**5** from which it is formed.

The ORD and CD spectra (Figure 1) of **9** show very intense Cotton effects associated with the conjugated diene chromophore. The structure of the CD maxima is analo-

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[10] H. M. Walborsky and R. B. Banks, *Bull. Soc. Chim. Belg.*, **89**, 849 (1980).

[11] E. J. Corey and K. Achiva, *J. Org. Chem.*, **34**, 3667 (1969).

[12] H. Gerlach, *Helv. Chim. Acta*, **49**, 1291 (1966).

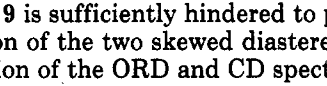
[13] That **3** is alkylated with retention of configuration is based on the reasonable assumption that the conversion of **6** to **3** proceeds with retention. This is certainly the case when **6** is treated with $MgBr_2$.[10]

gous to that of the corresponding UV absorption. The UV absorption maxima of **9** are very similar to those observed for achiral dicyclohexylideneethanes (Table I).[14]

A conjugated diene is chiral if the diene unit is structurally or sterically distorted from planarity (skewed) or if there are other elements of dissymmetry in the molecule (nonskewed). Previous research has focused primarily on skewed dienes.[15] The chiroptical properties of such nonplanar dienes are characteristic of inherently dissymmetric chromophores—large molecular rotations and intense CD maxima paralleling intense UV absorption.[16] The signs of the Cotton effects of a large number of homo- and heteroannular *cisoid* and heteroannular *transoid* dienes have been related to the sense of twist of the diene moities.[17] Recently, the barriers to enantiomerization of skewed conformers of several cyclic and acyclic conjugated dienes have been determined by dynamic NMR measurement.[15b,18]

Relatively few investigations have been made of planar diene chromophores in dissymmetric environments. The CD spectra of *cis*- and *trans*-(*S*)-(+)-5-methyl-1,3-heptadiene show weak maxima associated with asymmetric perturbation of the symmetrical butadiene moiety.[19]

The chromophore of **9** fits between the extremes of the inherently dissymmetric and symmetric (asymmetrically substituted) butadiene. The dissymmetry of **9** arises from the combination of two chiral olefinic axes rather than from skewed or asymmetrically substituted double bonds. Therefore, **9** is the first member of a new class of dissymmetric conjugated dienes—the dicyclohexylideneethane derivatives, **10**. This family includes **9** as a special case in which the axes, a_1 and a_2, are structurally identical ($R^1 = R^4$, $R^2 = R^3$). Similar optically active dicycloalkylidenealkanes may be envisioned for other even-numbered ring systems.

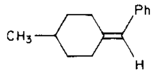
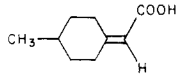
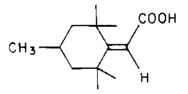
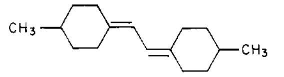


10

Suitable substituents, R^2 and R^3, of diene **10** should stabilize skewed rotamers with respect to the planar form. This would, therefore, introduce an additional element of chirality for this type of molecule. However, there is no evidence that **9** is sufficiently hindered to prevent rapid interconversion of the two skewed diastereomers.

Interpretation of the ORD and CD spectra of **9** is difficult since the diene chromophore of this molecule is novel.[20] The intense Cotton effects probably reflect the distortion of each double bond with respect to the attached cyclohexane rings rather than the twistedness of the diene chromophore itself.[21] In fact, the positve Cotton effects associated with the long wavelength absorption maxima of (*aR*,*aR*)-**9** correlate with the positive Cotton effects observed for similar cyclohexylidenealkane derivatives containing extended conjugation and having the same absolute configuration about the chiral olefinic axes (Table II).

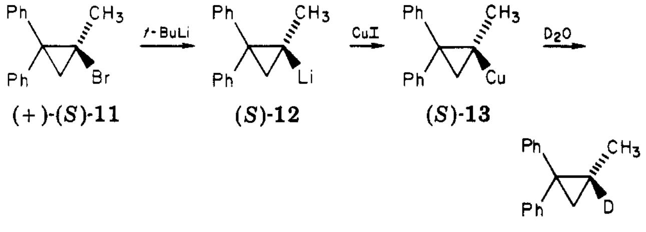
Table II. Observed Cotton Effects for Conjugated Cyclohexylidenealkanes

compd	configuration	cotton effect[a]	ref
	(−)-(*aR*)	+	21a, 22b
	(−)-(*aR*)	+	22a
	(−)-(*aR*)	+	22a
	(+)-(*aR*,*aR*)	+	this work

[a] For lowest energy absorption.

Chiral Cyclopropylcopper. We have recently reported the preparation of an unusually stable chiral copper(I) reagent, (1-isocyano-2,2-diphenylcyclopropyl)copper (**2**).[7] Since the isocyano substituent has been shown to have a stabilizing effect[23] on the cyclopropyl anion, it was not clear whether the stability of **2** was due to the isocyano group or to the cyclopropyl–copper σ bond. Therefore, a study of optically active cyclopropylcopper compounds without the isocyano substituent was undertaken for comparison with the vinylcopper and (isocyanocyclopropyl)copper reagents.

Chiral (+)-(*S*)-1-bromo-1-methyl-2,2-diphenylcyclopropane was converted to the corresponding lithium derivative (*S*)-**12** by metal–halogen exchange with *tert*-butyllithium in THF. Addition of 1 equiv of cuprous iodide to this cyclopropyllithium reagent resulted in the formation of a dark brown mixture. The reaction mixture was stirred at 0 °C for 1 h and then hydrolyzed with D_2O to give (−)-(*R*)-1-methyl-2,2-diphenylcyclopropane (83%). The



(+)-(*S*)-**11**
(*S*)-**12**
(*S*)-**13**
(−)-(*R*)-**14**

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(14) I. T. Harrison, B. Lythgoe, and S. Trippett, *J. Chem. Soc.*, 4016 (1955); O. Dimroth and H. Jonsson, *Chem. Ber.*, 71, 2658 (1938); H. Booker, L. K. Evans, and A. E. Gilliam, *J. Chem. Soc.*, 1453 (1940); R. Burckhardt, *J. Chem. Soc.*, 10 (1940).

(15) (a) U. Weiss, H. Ziffer, and E. Charney, *Tetrahedron*, 21, 3105 (1965); E. Charney, H. Ziffer, and U. Weiss, *ibid.*, 3121 (1965); E. Charney, *ibid.*, 3127 (1965); (b) L. W. Jelinski and E. F. Kiefer, *J. Am. Chem. Soc.*, **98**, 281 (1976); L. W. Jelinski and E. F. Kiefer *ibid.*, 282 (1976) and references cited therein.

(16) A. Moscowitz, Chapter 12 in "Optical Rotatory Dispersion: Applications to Organic Chemistry", C. Djerassi, Ed., McGraw-Hill, New York, 1960. A. Moscowitz, *Tetrahedron*, **13**, 48 (1961).

(17) A. W. Burgstahler, D. L. Boger, and N. E. Naik, *Tetrahedron*, **32**, 309 (1976); A. W. Burgstahler, L. O. Wiegel, and J. K. Gawronski, *J. Am. Chem. Soc.*, **98**, 3015 (1976); J. Gawronski and K. Gawronski, *J. Chem. Soc. Chem. Commun.*, 346 (1980); R. M. Moriarty, H. E. Paaren, U. Weiss, and W. B. Whalley, *J. Am. Chem. Soc.*, **101**, 6804 (1979).

(18) H. Bodecker, V. Jones, B. Kolb, A. Mannschrech, and G. Kobrich, *Chem. Ber.*, **108**, 3491 (1975) and references cited therein.

(19) A. DiCorato, *Gazz. Chim. Ital.*, **98**, 810 (1968).

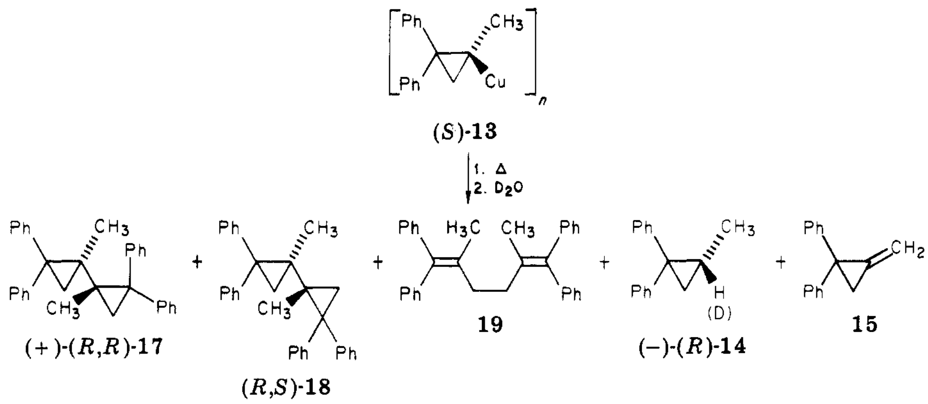
(20) Actually this chromophore is present in vitamin D_3 but has not been recognized as a chiral chromophore, and therefore their chiroptical properties have never been investigated. We have measured the CD spectra of a number of isomers of 10,19-dihydro vitamin D_3 kindly supplied to us by Professor W. H. Okamura. We will report on them in a future publication.

(21) (a) J. H. Brewster and J. V. Privett, *J. Amer. Chem. Soc.*, **88**, 1419 (1966); (b) D. N. Kirk and R. J. Mullins, *J. Chem. Soc., Perkin Trans. 1*, 14 (1974) and references cited therein.

(22) (a) J. F. Arnett and H. M. Walborsky, *J. Org. Chem.*, **37**, 3678 (1972); (b) H. J. Bestmann and J. Lienart, *Angew. Chem., Int. Ed. Engl.*, 8, 763 (1969).

(23) M. P. Periasamy and H. M. Walborsky, *J. Am. Chem. Soc.*, **99**, 2631 (1977).

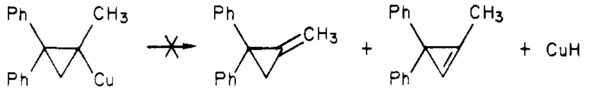
Scheme I



	(+)-(*R*,*R*)-17	(*R*,*S*)-18	19	(−)-(*R*)-14	15
$[\alpha]^{27}_{\mathrm{Hg}}$, deg	+34.3	0		−80.7	
yield, %	31*	19	5	28	1

*27% (+)-(*R*,*R*) and 4% (−)-(*S*,*S*)

hydrocarbon (−)-(*R*)-14 was formed with retention of configuration (100% optically pure) and with 88% deuterium incorporation. It should be noted that although 13 has a copper(I) attached to a tertiary carbon atom, one



13 **15** **16**

does not observe elimination of cuprous hydride under the conditions of the reaction since such an elimination would lead to highly strained products 15 and 16. The high retention of configuration (100%) observed and the stability toward elimination lead one to conclude that 13 is an extraordinarily stable Cu(I) species.

However, if after keeping 13 at 0 °C for 1 h one refluxes the THF solution for an additional 4 h, then 13 undergoes further reaction (Scheme I). The reaction mixture was hydrolyzed with D_2O before workup in order to detect any unreacted 13 or other organometallic intermediates.

As can be seen five products are formed in the thermal reaction of (*S*)-13 in the yields shown. The overall isolated material balance was 85%. Compounds 14, 15, 19, and the racemic modification of 17 have previously been characterized. They are products isolated from the reaction of 11 with magnesium metal, the Grignard formation reaction.[24] The *R*,*R* configuration has been assigned to 17 on the basis of the known propensity for copper reagents to couple with retention of configuration.[8] Compound 18 has been assigned the meso structure on the basis of the following data. It is optically inactive and gives a molecular ion of *m*/*e* 414 in the mass spectrum which is isomeric with 17. In the ^{1}H NMR spectrum it has two doublets for the H_A–H_B proton of the cyclopropane at 0.72 ppm (1 H) and at 1.33 ppm (1 H) each with a $J = 5$ Hz which is typical for this system. The methyl singlet is found at 1.13 ppm (3 H) and multiplets for the phenyl protons are observed between 6.8 and 7.3 ppm (10 H). The ^{13}C NMR shows six doublets and two singlets in the aromatic region (125–145 ppm) for the two different phenyl groups, a quartet for the methyl at 25.53 ppm, a triplet for the CH_2 of the cyclopropane at 24.77 ppm, a singlet at 32.61 ppm for the cyclopropyl carbon to which the methyl is attached, and a singlet for the cyclopropyl carbon which has two phenyl groups at 42.61 ppm. The simplicity of the NMR spectra, the molecular ion (EI) of *m*/*e* 414, and the observed 0 °C rotation are all consistent with the meso structure assigned to 18. The ^{1}H NMR and ^{13}C NMR spectra of 18 differ from 17 (see Experimental Section) so that 18 cannot be a racemic modification of 17.

Product analyses, including stereochemistry, lead one to the following mechanistic interpretation of the thermal reaction of $[(S)\text{-}\mathbf{13}]_n$. Existing evidence indicates that $[\mathrm{R{-}Cu^I}]_n$ exists in benzene as a tetramer ($n = 4$)[25-27] with tetrahedral configuration.[26,28] The copper triflate catalyzed thermal coupling of *p*-tolylcopper(I) in benzene leads exclusively to the formation of *p*,*p*′-bitolyl and no crossover coupling product with the solvent benzene.[27] This speaks strongly for an intramolecular coupling within the aggregate as does the stereospecific coupling observed in the thermal coupling of *cis*- and *trans*-propenylcopper(I).[8a] In the examples cited *free radicals* were excluded as intermediates in the thermal reaction although they have been postulated as intermediates in the thermolysis of neophyl(tri-*n*-butylphosphine)copper(I).[28]

Product analysis and stereochemical considerations lead one to postulate the mechanism depicted in Scheme II for the thermal decomposition of $[(S)\text{-}\mathbf{13}]_n$. The aggregate $[(S)\text{-}\mathbf{13}]_n$ is assumed to exist in solution where $n = 2$, 4, or 6. A mixture of aggregates probably exist in THF solution. The aggregates are stable at 0 °C for 1 h as judged by the deuteriolysis of $[(S)\text{-}\mathbf{13}]_n$ which resulted in 88% deuterium incorporation in 14 and 100% retention of configuration. We view the aggregates $[(S)\text{-}\mathbf{13}]_n$ as molecular species which exists in a solvent cage of THF. Upon thermolysis, a homolytic cleavage of two $R^{(S)}$–Cu bonds occurs with the formation of Cu^0 and the concomitant coupling, within the solvent cage (reaction *a*), of $R^{(S)}\cdot$ to (+)-(*R*,*R*)-17 with retention of configuration. If within the cage one of the $R^{(S)}\cdot$ rotates 180°, this would lead to formation of $R^{(R)}\cdot$ and coupling of the two radicals, $R^{(R)}\cdot$ and $R^{(S)}\cdot$, would produce *meso*-(*R*,*S*)-18 (reaction *c*). If two $R^{(S)}\cdot$ radicals rotate 180° and then couple, this would lead to the formation of (−)-(*S*,*S*)-17 (reaction *b*) which in combination with (+)-(*R*,*R*)-17 results in the production

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(24) H. M. Walborsky and M. S. Aronoff, *J. Organomet. Chem.*, **51**, 31 (1973) and references cited therein.

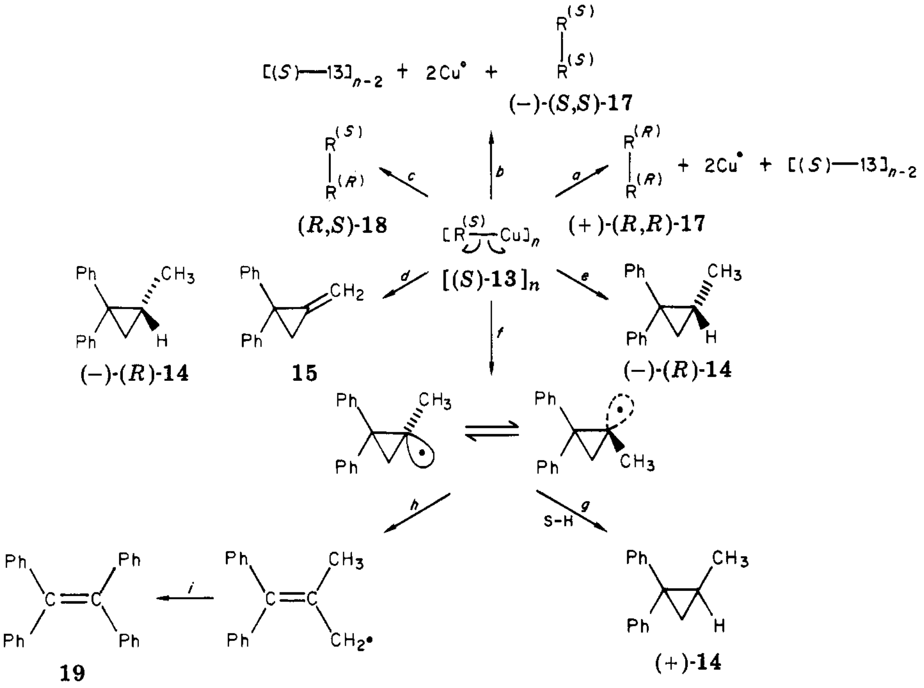
(25) J. A. Jarvis, B. T. Kilbourn, R. Pearce, and M. Lappert, *J. Chem. Soc., Chem. Commun.*, 475 (1973).

(26) A. Cairncross and W. A. Sheppard, *J. Am. Chem. Soc.*, **93**, 247 (1971).

(27) G. Van Koten, J. T. B. H. Jastrzerbski, and J. G. Noltes, *J. Org. Chem.*, **42**, 2047 (1977).

(28) G. M. Whitsides, E. J. Panek, and E. R. Stredronsky, *J. Am. chem. Soc.*, **94**, 232 (1972); However, in a later publication[8a] they claimed radicals were not involved.

Scheme II. Thermal Decomposition of (*S*)-(1-Methyl-2,2-diphenylcyclopropyl)copper (R = 1-Methyl-2,2-diphenylcyclopropyl)



of the racemic compound (±)-(*R*,*R*/*S*,*S*)-**17**. That (±)-**17** is a racemic compound can be seen from the fact that its melting point (184 °C)[24] is 19 °C higher than that of the pure enantiomer (165 °C). The racemic compound (±)-**17** could not be separated in a pure state from the enantiomer. However, the racemic compound, (±)-**17**, proved to be more soluble in methanol than the enantiomer (+)-**17** and the latter could be isolated by crystallization from methanol, mp 165 °C and $[\alpha]^{27}_{\text{Hg}}$ +46.4°. The mixture of (+)-**17** and (±)-**17** that remained in the mother liquors, mp 120–135 °C and $[\alpha]^{27}_{\text{Hg}}$ +8.2° had an NMR spectrum which was identical with that of pure (+)-**17**. Prior to recrystallization the mixture had a melting point of 152–154 °C and a $[\alpha]^{27}_{\text{Hg}}$ +34.3° which equates to 74% optical purity or that the mixture consists of 87% (*R*,*R*)-**17** and 13% (*S*,*S*)-**17** (74% (*R*,*R*)-**17** and 26% racemic **17**).

By itself, the formation of **17** takes on important significance. Its formation has never been observed in solution, only the products from reactions *g*, *h*, and *i* are observed. Also, the 1-methyl-2,2-diphenylcyclopropyl radical does not dimerize to **17** even in a cage reaction,[29a] but instead it follows the usual course expected for tertiary σ radicals, it disproportionates. The only other time that dimerization of this radical has been observed was when the radical was formed on a magnesium metal surface.[24] *Thus, the aggregates* [(*S*)-**13**]$_n$, *in their reactivity, resemble a surface reaction.*

The stereochemistry of reaction *e*, reaction with solvent cage wall, is not known but might be expected to proceed with overall retention of configuration. Reactions *a*–*e* are radical reactions which occur within the solvent cage, and the reaction of these radicals must occur, on a time scale, faster than diffusion of the radicals out of the cage,[30] $>10^{11}$ s^{-1}.

Reaction *f* is the diffusion of the radical from the solvent cage and into solution. The 1-methyl-2,2-diphenylcyclopropyl radical is a rapidly inverting (10^8 s^{-1}) σ radical.[31] In THF this free radical, generated from a precursor chiral diacyl peroxide, was shown to react with solvent to yield racemic (±)-**14** and the dimer **19**.[32] The latter, **19**, is formed by the rearrangement of the cyclopropyl radical to the corresponding allyl radical which undergoes subsequent dimerization.[32] This same sequence of reactions, *g*, *h*, and *i*, is observed in the thermal reaction of [(*S*)-**13**]$_n$.

The hydrocarbon **14** formed in the thermal reaction of [(*S*)-**13**]$_n$ contained 27% deuterium. This represents the amount of [(*S*)-**13**]$_n$ that remained unreacted (~8% of total reaction) at the end of the reaction when the reaction mixture was quenched with D_2O. The reaction of [(*S*)-**13**]$_n$ with D_2O proceeds with 100% retention of configuration. Subtracting the amount of deuterio hydrocarbon with its retained configuration and the amount (3%) of **15** in the hydrocarbon mixture leads to a specific rotation for (−)-(*R*)-**14**, formed in reactions *d*, *e*, and *g*, of $[\alpha]^{27}_{\text{Hg}}$ −54.6° (optically pure **14**, $[\alpha]^{27}_{\text{Hg}}$ −151°) or 36% optically pure. Perhaps fortuitously, this is comparable to the optical purity (~45%) observed for this radical forming hydrocarbon in a cage disproportion reaction.[29a] This would indicate that the solvent cage reactions *d* and *e* play a major role in the formation of **14**.

Reaction of [(*S*)-13]$_n$ with Dioxygen. The oxidative coupling of [(*S*)-**13**]$_n$, by passing a stream of dioxygen through the reaction mixture, also leads to coupling[8] of the organic ligands but the reaction has interesting differences from that of the thermal coupling.

As can be seen from Table III a 60% yield of coupled product, (*R*,*R*)-**17**, with an optical purity of 93.5% (97% retention of configuration) is obtained when dioxygen with

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[29] H. M. Walborsky and Jong-Chen Chen, *J. Am. Chem. Soc.*, **93**, 671 (1971). See also P. D. Bartlett and J. D. McBride, *Pure Appl. Chem.*, 15, 89 (1967); K. R. Kopecky and T. Gillam, *Can. J. Chem.*, **47**, 2371 (1969); F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Am. Chem. Soc.*, **92**, 867 (1970).

[30] S. W. Benson, "Foundation of Chemical Kinetics", McGraw-Hill, New York, 1960.

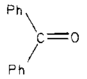
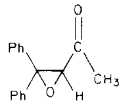
[31] For a detailed discussion of the cyclopropyl radical see H. M. Walborsky, *Tetrahedron*, **37**, 1625 (1981).

[32] H. M. Walborsky and Jong-Chen Chen, *J. Am. Chem. Soc.*, **92**, 7573 (1970).

[33] M. J. Jorgenson, *Tetrahedron Lett.*, 559 (1962).

[34] J. L. Webb, C. K. Mann, and H. M. Walborsky, *J. Am. Chem. Soc.*, **92**, 2042 (1970) report $[\alpha]^{25}_{\text{Hg}}$ 151° for optically pure **14**.

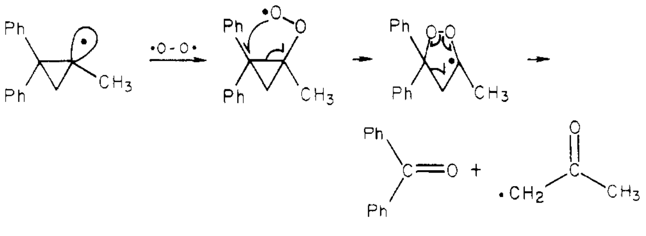
Table III. Products from the Reaction of $[(S)\text{-}\mathbf{13}]_n$ with Dioxygen

reaction		[(−)-(*R*)-**14** + **15**]	(*R*,*S*)-**18**	(*R*,*R*)-**17**		
A[a]	yield, %	15.6	trace	29.0	27.6	
	$[\alpha]^{25}_{\text{Hg}}$ (OP, %)[f]	−120.1 (79.5)[e]		+39.2 (84.5)		
B[b]	yield, %	9.0	trace	60.7	5.3	4.5
	$[\alpha]^{25}_{\text{Hg}}$ (OP)[f]	−102.1 (67.6)[e]		+42.5 (91.6)		
C[c]	yield, %	20.1	6.9	14.2	~2	
	$[\alpha]^{25}_{\text{Hg}}$ (OP)[f]	−106.0 (70.2)[e]		+34.3 (73.9)		
D[d]	yield, %	14.1	trace	60.1	12.2	
	$[\alpha]^{25}_{\text{Hg}}$ (OP)[f]	−125.6 (83.2)[e]		+43.4 (93.5)		

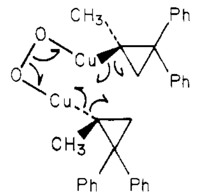
[a] *T*, 25 °C; O_2 flow rate, 50 mL/min. [b] *T*, −40 °C; O_2 flow rate, 180 mL/min. [c] *T*, −40 °C; O_2 flow rate, 50 mL/min. [d] *T*, −78 °C; O_2 flow rate, 100 mL/min. [e] Corrected for 0.2-3% **15** in mixture; $[\alpha]^{25}_{\text{Hg}}$ 151° for optically pure **14**. [f] Optical purity.

a flow rate of 100 mL/min is passed through the reaction mixture at −78° C (reaction *D*). Increasing the temperature to −40 °C but increasing the flow rate of dioxygen to 180 mL/min gives a similar yield and stereochemical result (reaction *B*). Both the yield and optical purity of the coupled product is markedly reduced at higher temperatures and slower flow rate of dioxygen (reactions *A* and *C*). These data show that the best conditions for the stereospecific coupling reaction is low temperatures and a high flow rate of dioxygen. Moreover, oxidative coupling with dioxygen gives a higher yield and stereochemically purer coupled product than does the thermal coupling. This is emphasized by the fact that a 19% yield of *meso*-(*R*,*S*)-**18** is obtained in the thermal reaction whereas only traces are observed in the dioxygen reaction (reactions *A*, *B*, and *D*). The highest yield of (*R*,*S*)-**18**, and that only 6.9%, was observed in reaction *C*.

The hydrocarbon (−)-(*R*)-**14** and a small amount of **15** are also formed in the dioxygen coupling reaction, although in lower yield but with higher optical purity than in the thermal reaction. Significantly, no open dimeric product **19** is observed, indicating that the 1-methyl-2,2-diphenylcyclopropyl radical which escapes into solution is being very efficiently trapped by dioxygen. This would account for the lower yield and higher optical purity of hydrocarbon **14** obtained in the dioxygen reaction as compared to the thermal reaction since it would eliminate much of the racemic hydrocarbon (±)-**14** which would have been formed by reaction *f* in Scheme II. It is the dioxygen trapped radical which is probably responsible for the formation of benzophenone in the reaction.[35]



We view the reaction with dioxygen as proceeding by way of intermediate **20** which is formed by the reaction of dioxygen with aggregate $[(S)\text{-}\mathbf{13}]_n$. The intermediate **20**, in solution, can then collapse by homolytic fission to form dimeric product (+)-(*R*,*R*)-**17**, disproportionate to hydrocarbons (−)-(*R*)-**14** and **15**, react with solvating portion of solvent to give (−)-(***R***)-**14** and (±)-**14**, or release radicals into solution to be trapped by dioxygen.



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It is also interesting to note that in one reaction ((*C*)) a small yield of an epoxy ketone was isolated. The origin of this product is currently under investigation.

Experimental Section

All melting points are uncorrected. Infrared spectra were measured with a Perkin-Elmer Model 257 grating infrared spectrophotometer. ^{1}H NMR spectra were obtained by using a Varian A-60 spectrometer. The spectra for measurement of deuterium content and ^{13}C were recorded with a Bruker 270-MHz spectrometer. Mass spectra were obtained with a A.E.I. Picker high-resolution mass spectrometer.

Optical rotations were measured at the 546.1-nm mercury line with a Bendix-Ericsson Model 987 automatic polarimeter with digital display attachment. Cell length was 0.4 dm. Error limits for rotations were calculated by multiplying the relative standard deviation by the specific rotation. The relative deviation was determined by dividing the standard deviation (0.002°) by the observed rotation.

The ORD and CD spectra were obtained with a Jasco Model recording spectrometer with 1.0-cm cells. UV spectra were obtained with a Cary 14 spectrophotometer with 1.0-cm cells.

GLPC analyses were conducted using an F&M Model 500 or Bendix Chroma-Lab Series 2100 gas chromatograph with thermal conductivity detectors. Analyses of 1-methyl-4-bromomethylenecyclohexane, 1-methyl-4-ethylidenecyclohexane, 1-methyl-4-methylenecyclohexane, and reaction mixtures containing these compounds were made with a 5 ft × $^1/_4$ in. copper column, packed with 20% Apiezon L on Chromasorb-P, on the Bendix chromatograph. Analyses of 1,2-bis(4-methylcyclohexylidene)ethane were carried out on the F&M Chromatograph using a 2 ft × $^1/_4$ in. copper column packed with silicone rubber. A 7 ft × $^1/_4$ in. copper column packed with 15% Lexan on Chromasorb P on the F&M chromatograph was used to analyze for methyl 4-methylcyclohexylideneacetate and 1-methyl-2,2-diphenylcyclopropane, HPLC was accomplished on a Waters Associates instrument equipped with a differential UV detector.

Optically Active ((4-Methylcyclohexylidene)methyl)copper ((*S*)-3) Reaction with Methyl Iodide. To a solution of (+)-(*S*)-(4-methylcyclohexylidene)methyl bromide (**5**), $[\alpha]^{25}_{\text{Hg}}$ +54.5° (*c* 1.0, absolute ethanol; 87% optically pure), 0.5 g in 10

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[35] We wish to acknowledge a helpful discussion of this point with Professor Peter J. Wagner.

mL of THF at −75 °C, was added a solution (6 mL, 3.0 mmol) of 0.5 M *sec*-butyllithium in hexane. The mixture was allowed to stir at −75 °C for 2 h after complete addition. Cuprous iodide (0.6 g, 3.1 mmol) was then added and the mixture allowed to reach −35 °C and to stir for 45 min. During this time a dark black suspension was formed. HMPA (2.5 mL, freshly distilled from 13X molecular sieves) and 1.4 g of triethyl phosphite were added, and the mixture was allowed to sitr at −35 °C for 5 min. Methyl iodide (0.4 g, 2.7 mmol) was then added. After being stirred at −35 °C for an additional 15 min, the mixture was allowed to warm to room temperature and to stir for 12 h. The reaction was quenched with water and the ether layer separated. The ether extracts were washed eight times with water. It was found that triethyl phosphite could be completely removed by washing the extracts several times with dilute silver nitrate solution. The extracts were then washed with saturated sodium chloride and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave 0.25 g (76%) of a liquid. This liquid was chromatographed on 25 g of 25% silver nitrate–silicic acid, eluting first with 400 mL of pentane and then with 100 mL of 5% ether–hexane. The alkene was obtained in the ether fraction and after removal of solvent was further purified by bulb-to-bulb distillation (25 °C (2 torr)) to give 50 mg (15%) of (+)-(*S*)-(4-methylcyclohexylidene)ethane (**7**), $[\alpha]^{25}_{\mathrm{Hg}}$ −14.7 ± 2.9° (*c* 0.16, $CHCl_3$; 83% optically pure; 95% optically pure based on starting bromide). The infrared and NMR spectra were identical with those of an authetic sample (vide infra).

Oxidative Coupling of (*S*)-((4-Methylcyclohexylidene)-methyl)copper (3). To a solution of 1 g (5.2 mmol) of (+)-(*S*)-**5**, $[\alpha]^{25}_{\mathrm{Hg}}$ −58.3° (*c* 2.3, absolute ethanol; 94% optically pure), in 10 mL of THF at −75 °C was added a solution (10 mL, 5.5 mmol) of 0.55 M *sec*-butyllithium in hexane. After complete addition the mixture was allowed to stir at −75 °C for 1.5 h. Cuprous iodide (1.1 g, 5.2 mmol) was then added and the mixture allowed to warm to −35 °C and to stir for 30 min. A stream of oxygen was passed through the solution for 15–20 min at −35 to −40 °C. The mixture was then allowed to warm to room temperature and to stir for 4 h. The reaction mixture was hydrolyzed with water and filtered. The ether layer was washed three times with saturated ammonium chloride and two times with saturated sodium chloride and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave 0.47 g (83%) of oil which was chromatographed on 25 g of 25% silver nitrate–silicic acid, eluting first with 200 mL of pentane and then with 200 mL of 10% ether–pentane. From the ether–pentane fraction was obtained 0.2 g (30%) of an oil, $[\alpha]^{25}_{\mathrm{Hg}}$ +37.9 ± 0.7° (*c* 0.63, absolute ethanol) which on the basis of its spectra was determined to be (*aR*,*aR*)-bis(4-methylcyclohexylidene)ethane (**9**): ^1H NMR (CCl_4) δ 5.81 (s, 1 H), 0.85–2.9 (complex, 12 H); IR (CCl_4) 3040, 2920, 1620, 1455, 1390, 950 cm^{-1}; mass spectrum, *m*/*e* (relative intensity) 218 (100), 161 (40.5), 122 (45.3), 108 (47.6), 107 (57.3), 93 (82.9), 91 (64.6); exact mass of $M^{+\cdot}$ *m*/*e* 218.2028 ($C_{16}H_{26}$) measured, *m*/*e* 218.2034 ($C_{16}H_{26}$) calculated; UV (*c* 1.93 × 10^{-5} M, 95% ethanol) λ 259 (ϵ 27 500), 250 (38 820), 242 (31 860), 233 (sh (23 000); CD (*c* 9.53 × 10^{-5} M, 95% ethanol) $[\theta]_{270}$ 0, $[\theta]_{258.5}$ +14 560, $[\theta]_{249}$ +22 360, $[\theta]_{241.5}$ +20 176, $[\theta]_{234}$ +7280 (sh), $[\theta]_{217.5}$ −12 376, $[\theta]_{206}$ −6136 (sh); ORD (*c* 9.53 × 10^{-5} M, 95% ethanol) $[\phi]_{310}$ +1049, $[\phi]_{262}$ +1539, $[\phi]_{255}$ +3147, $[\phi]_{251}$ +6294, $[\phi]_{229}$ −23 078, $[\phi]_{210}$ −2078.

(+)-(*S*)-(4-Methylcyclohexylidene)ethanol. A modification of the procedure of Jorgensen[33] was used. To a slurry of 8.5 g (0.225 mol) of lithium aluminum hydride in 150 mL of anhydrous ether at 0 °C was added dropwise, with vigorous stirring, a solution of 10.0 g (0.075 mol) of aluminum chloride in 100 mL of ether. After being stirred an additional 1 h, a solution of 6.0 g (0.039 mol) of (+)-(*S*)-4-methylcyclohexylideneacetic acid, $[\alpha]^{25}_{\mathrm{Hg}}$ +91.4° (*c* 0.64, absolute EtOH; 96.2% optically pure), in 50 mL of ether was added dropwise. After the mixture was stirred for 4 h, 16 mL of 5% sodium hydroxide was added slowly. The resulting lithium salts were filtered and washed with ether. The combined washings were dried ($MgSO_4$), and the solvent was removed in vacuo to give 4.8 g (88%) of (+)-(*S*)-2-(4-methylcyclohexylidene)ethanol: bp 78–79 °C (2 mm); $[\alpha]^{23}_{\mathrm{Hg}}$ +7.6 ± 0.1° (*c* 3.9, $CHCl_3$); IR ($CHCl_3$) 3590 (nonbonded OH), 3410 (bonded OH), 1660 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 0.90 (d, *J* = 5 Hz), 0.90–2.7 (m, aliphatic), 3.6 (s, 1, hydroxyl), 4.1 (d, 2, *J* = 7 Hz, C=CH*H*$_2$OH), 5.36 (t, 1, *J* = 7 Hz, C=C*H*CH$_2$OH); high-resolution mass spectrum *m*/*e* 140.1198 (calcd for $C_9H_{16}O$, *m*/*e* 140.1200).

(+)-(*S*)-(4-Methylcyclohexylidene)ethane (7). A modification of the procedure of Corey and Achiva was used.[11] A slurry of 2.2 g (0.015 mol) of (+)-(*S*)-2-(4-methylcyclohexylidene)ethanol (96.2% optically pure) and 3.18 g (0.02 mol) of sulfur trioxide–pyridine complex in 25 mL of THF was stirred at 0 °C for 20 h and at ambient temperature for 3 h. A solution of $LiAlH_4$ (0.09 mol) in THF was added at 0 °C, and then the mixture was stirred at 0 °C for 1 h. The mixture was cooled to 0 °C, 11 mL of 10% sodium hydroxide was added dropwise, and then 50 mL of ether was added. The salts were filtered and washed with additional ether. The combined filtrates were washed with dilute hydrochloric acid and dried ($CaSO_4$), and the solvent was removed in vacuo to yield 1.1 g of crude product. The product was chromatographed on a column of 40 g of alumina with elution by pentane and monitored by VPC on a 6 ft × $^1/_4$ in. 10% Apiezon L column to yield 0.3 g (15%) of (+)-(*S*)-(4-methylcyclohexylidene)ethane: bp 25–26 °C (2 mm); $[\alpha]^{24}_{\mathrm{Hg}}$ +17.7 ± 0.2° (*c* 2.02, $CHCl_3$); this corresponds to a corrected rotation of +18.7 ± 0.2°; IR ($CHCl_3$) 3000–2850 (aliphatic), 1660 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 0.85 (d, *J* = 6 Hz, CH_3), 1.2–2.9 (m, cyclohexyl), 1.55 (d, *J* = 6 Hz, =CHC*H*$_3$), 5.0 (q, *J* = 6 Hz, =C*H*CH$_3$).

Anal. Calcd for C_9H_{16}: C 87.01; H 12.98. Found: C 87.02; H 12.97.

(+)-(*S*)-(4-Methylcyclohexylidene)ethane (7). To a solution of 0.50 g (2.7 mmol) of (+)-(*S*)-1-methyl-4-(bromomethylene)-cyclohexane, $[\alpha]^{24}_{\mathrm{Hg}}$ +41.9 ± 0.2° (*c* 2.74, absolute EtOH; 67% optically pure), in dry THF at −76 °C was added 7.60 mL (5.32 mmol) of *tert*-butyllithium (1.21 M in pentane). The solution was stirred for 1.5 h, 2.14 g (15.0 mmol) of distilled methyl iodide was added, and the solution was allowed to warm to ambient temperature slowly. After 8 h, water was added, the aqueous layer extracted with ether, the combined ether layers were dried ($CaSO_4$), and the solvent was removed in vacuo to yield 0.3 g (91%) of (+)-(*S*)-(4-methylcyclohexylidene)ethane: bp 25–26 °C (2 mm); $[\alpha]^{24}_{\mathrm{Hg}}$ +12.1 ± 0.1° (*c* 4.71, $CHCl_3$); this corresponds to a corrected rotation of +18.0 ± 0.1° for the optically pure alkene. The infrared and NMR spectra were identical with those of the sample previously reported.

Optically Active (1-Methyl-2,2-diphenylcyclopropyl)-copper (4). To a mixture of 0.5 g (1.75 mmol) of 1-methyl-1-bromo-2,2-diphenylcyclopropane, $[\alpha]^{25}_{\mathrm{Hg}}$ +128.5° (*c* 0.72, $CHCl_3$; 98% optically pure)[34] in 25 mL of THF at −75 °C was added a solution (2.5 mL, 2.0 mmol) of 0.8 M *tert*-butyllithium in pentane. The mixture was stirred for 15 min, and then 0.35 g (1.75 mmol) of cuprous iodide was added. The mixture was then stirred at ice bath temperature for 1 h and hydrolyzed with D_2O. The ether extracts were washed with saturated sodium chloride and dried over anhydrous magnesium sulfate. Removal of solvent gave 0.3 g (83%) of a liquid which was shown by NMR and GLPC analysis to be 1-methyl-2,2-diphenylcyclopropane.[34] The hydrocarbon was purified by distillation (pot temperature 150–160 °C (2 torr): $[\alpha]^{25}_{\mathrm{Hg}}$ +148.0 ± 1.2° (*c* 0.4, $CHCl_3$; 98% optically pure);[34] ^1H NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.1 (m, 2 H), 2.2 (m, 0.22 H), 7.2 (m, 10 H). The corrected optical purity of the hydrocarbon was 100%, and the deuterium content determined by integration of the 270-MHz NMR spectrum was 88%.

Thermolysis of (*S*)-(1-Methyl-2,2-diphenylcyclopropyl)-copper (4). To a solution of 1.0 g (3.48 mmol) of (*S*)-(+)-1-methyl-2,2-diphenylcyclopropyl bromide ($[\alpha]^{27}_{\mathrm{Hg}}$ +127.25 ± 0.70° (*c* 0.7, $CHCl_3$)) in 50 mL of dry THF at −78 °C under argon atmosphere was added 4.65 mL of 1.50 M *tert*-butyllithium over a period of 5 min. The resulting yellow solution was stirred for 15 min, and then 0.67 g (3.5 mmol) of dry cuprous iodide was added. A dark green suspension was obtained, and it was stirred for 15 min. The cooling bath was replaced by an ice bath, and the stirring continued for 1 h at 0 °C. The mixture was then gently refluxed for 4 h. The mixture was hydrolyzed by adding D_2O. The copper powder was filtered off, the THF solution was poured into water and extracted twice with hexane. Evaporation of the hexane solution gave 0.72 g of the crude product.

The crude product was separated into five components by using HPLC (porasil B, 8 ft × $^3/_8$ in.; heptane).

Component 1. A few milligrams were obtained, and it was not identified.

Component 2. This fraction was a mixture of 1-methyl-2,2-diphenylcyclopropane (**14**) and 1-deuterio-1-methyl-2,2-diphenylcyclopropane in 73:27 ratio (0.225 g, 29%), $[\alpha]^{27.5}_{\mathrm{Hg}}$ −80.66 ± 0.63° (*c* 0.79, $CHCl_3$), corresponding to 53% optical purity of the hydrocarbons and 1-methylidene-2,2-diphenylcyclopropane (1%).

Component 3. A few milligrams were obtained and it was not identified.

Component 4. This component (0.100 g) was a mixture of 1,1,6,6-tetraphenyl-2,5-dimethylhexa-1,5-diene (**19**, 5%) and *meso*-bis(1-methyl-2,2-diphenylcyclopropane) (**18**, 19%). The mixture was reacted with *m*-chloroperbenzoic acid in CH_2CH_2 for 0.5 h. The nonpolar fraction of the crude product was separated by preparative TLC, and it was identified as the bis(cyclopropane): mp 160 °C; $[\alpha]^{27}_{\mathrm{Hg}}$ 0.0°; IR (KBr) 3060–2850 (m), 1600, 1490, 1440, 1200–700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.72 (d, $J = 5$ Hz, 1 H), 1.13 (s, 3 H), 1.33 (d, $J = 5$ Hz, 1 H), 6.8–7.3 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 24.77 (t), 25.53 (q), 32.61 (s), 42.61 (s) 125.65 (d), 125.86 (d), 127.50 (d), 127.85 (d), 130.39 (d), 130.71 (d), 142.13 (s), 145.26 (s); mass spectrum (EI), *m/e* 414 ($M^{+}\cdot$).

Anal. Calcd for $C_{32}H_{30}$: C, 92.71; H, 7.29. Found: C, 92.59; H, 7.19.

Component 5. This fraction was (+)-(*R*,*R*)-bis(1-methyl-2,2-diphenylcyclopropane) (**17**) (0.22 g, 31%): mp 152–154 °C; $[\alpha]^{27}_{\mathrm{Hg}}$ +34.30 ± 0.71° (*c* 0.71, $CHCl_3$); IR (KBr) 3060–2850 (m), 1600, 1580, 1490, 1380, 1100–700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ AB quartet centered at 0.70 ($J = 5$ Hz, 2 H), 1.23 (s, 3 H), 6.95–7.5 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 23.43 (q), 25.17 (t), 29.58 (s), 40.59 (s), 125.72 (d), 127.96 (d), 128.12 (d, 2 C), 129.70 (d), 130.06 (d), 144.11 (s), 144.68 (s). On crystallization from CH_3OH, the melting point increased (165 °C) and a maximum rotation of +46.41 ± 0.72° was obtained on the Hg line. The NMR spectrum did not change.

The sample, isolated by HPLC, mp 152–154 °C with $[\alpha]^{27}_{\mathrm{Hg}}$ +34.3°, was recrystallized from methanol three times. Recrystallization gave a melting point of 165 °C $[\alpha]^{27}_{\mathrm{Hg}}$ +46.4°, whereas the solid isolated from the mother liquors gave a melting point of 120-135 °C, $[\alpha]$ +8.2°, whose NMR spectrum was identical with the pure sample.

Anal. Calcd for $C_{32}H_{30}$: C, 92.71; H, 7.29. Found: C, 92.64; H, 7.39.

Reaction of (*S*)-(1-Methyl-2,2-diphenylcyclopropyl)copper (4) with Dioxygen. To a solution of 2.0 g (6.96 mmol) of (*S*)-(+)-1-methyl-2,2-diphenylcyclopropyl bromide ($[\alpha]^{27}_{\mathrm{Hg}}$ +127.25 ± 0.70° (*c* 0.7, $CHCl_3$)) in 100 mL of dry THF at −78 °C (dry ice–acetone) under argon atmosphere was added 9.30 mL of 1.50 M *tert*-butyllithium over a period of 5–10 min. The resulting yellow solution was stirred for 15 min, and then 1.33 g (6.98 mmol) of dry cuprous iodide was added. A dark green suspension was obtained, and it was stirred for 15 min. The dry ice–acetone both was replaced by dry ice–acetonitrile bath (−42 °C), and a stream of oxygen (≃180 mL/min) was passed through the suspension. Within a few minutes a homogenous green solution was obtained. The passage of oxygen was continued at −42 °C for 4 h. The reaction mixture was quenched with D_2O and the poured into water and extracted with ether. The extract was washed with saturated NH_4Cl solution, dried over Na_2SO_4, filtered and evaporated to yield an oil.

The crude product was separated into four components by column chromatography (silica gel, hexane-ether).

Component 1. This was a mixture (0.134 g) of 1-methyl-2,2-diphenylcyclopropane (**14**) and 1-methylidene-2,2-diphenylcyclopropane (**15**) in 7.06% and 1.89% yields, respectively. The corrected rotation of cyclopropane (**14**), $[\alpha]^{27}_{\mathrm{Hg}}$ −102.09 ± 0.64° (*c* 0.78, $CHCl_3$), corresponds to 67.6% optical purity. The sample did not contain deuterium.

Component 2. This was (+)-(,*R*)-bis(1-methyl-2,2-diphenylcyclopropane) (**17**) (0.875 g, 60.7%); $[\alpha]^{27}_{\mathrm{Hg}}$ +42.22 ± 0.50° (*c* 1.0, $CHCl_3$).

Component 3. This was identified as benzophenone (0.067 g, 5.3%).

Component 4. This fraction (0.075 g) was identified as 1,1-diphenylbutenone epoxide by comparison of its spectral properties with those of an authentic sample.

Preparation of 1,1-Diphenylbutenone Epoxide. 1,1-Diphenylbutenone[36] (prepared from benzophenone and *N*,*N*-dimethylhydrazone of acetone[37]) was reduced with an excess of $NaBH_4$ in ethanol.

The reduction product was stirred with an excess of *m*-chloroperbenzoic acid in CH_2Cl_2 over aqueous Na_2CO_2 for 3 h. The mixture was diluted with ether and the aqueous phase removed. The organic phase was washed with sodium bisulfite, Na_2CO_3, and water, dried over Na_2SO_4, and evaporated to obtain a quantitative yield of the epoxy alcohol: ^1H NMR ($CDCl_3$) δ 1.23 (d, 3 H), 2.15 (OH), 4.30 (m, 1 H), 5.98 (d, 1 H), 6.80–7.30 (m, 10 H).

The epoxy alcohol (1.0 g) was stirred with 7 equiv of pyridinium dichromate[38] in DMF over night. The reaction mixture was poured into water and extracted with ether and the ether solution dried and evaporated to get an oil. The crude product was chromatographed to obtain the pure epoxy ketone: IR (film) 3120–2960 (multiplets), 1710 and 1600–625 (multiplets) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.64 (s, 3 H), 3.77 (s, 1 H), 7.1–7.4 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 26.94 (q), 66.61 (s), 68.37 (d), 126.37 (d), 128.18 (d), 128.34 (d), 128.42 (d), 128.53 (d), 135.42 (s), 139.15 (s), 204.86 (s).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.73; H, 5.90.

Registry No. 3, 60164-98-9; **4**, 80502-07-4; **5**, 60164-94-5; **6**, 77764-43-3; **7**, 60164-99-0; **8**, 28835-97-4; **9**, 60164-97-8; **11**, 6526-76-7; **12**, 80502-08-05; **14**, 14275-48-0; **14-*d***, 80502-09-6; (*R*,*R*)-**17**, 80502-10-9; (±)-**17**, 80558-51-6; **18**, 80558-52-7; **19**, 988-38-5; (+)-(*S*)-(4-methylcyclohexylidene)ethanol, 80502-11-0; 1,1-diphenylbutenone epoxide, 80502-12-1; 3-hydroxy-4,4-diphenylbutan-2-one, 14035-54-2; 1,1-diphenylbutenone, 837-66-1.

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Communications

Hydroxymercuration—Reductive Coupling Route to δ-Lactones. Synthesis of Malyngolide, an Antibiotic from a Marine Blue-Green Alga

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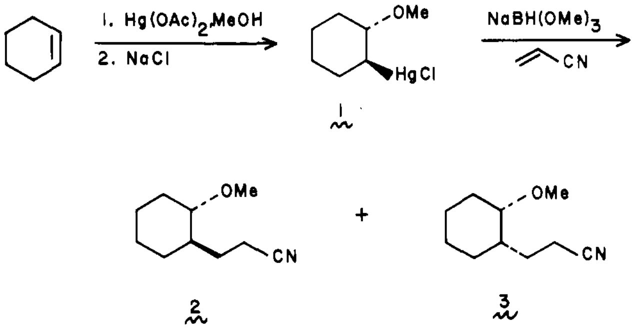
Summary: Radical intermediates can be generated from the hydroxymercuration products of alkenes by reduction with sodium trimethoxyborohydride. These β-hydroxyalkyl radicals react with electron-deficient olefins (methyl acrylate and acrylonitrile to provide δ-hydroxy esters and nitriles which can in turn be cyclized to 5-substituted δ-lactones. Such lactones comprise important part structures of numerous naturally occurring products. The utility of this new hydroxymercuration–reductive coupling route to δ-lactones has been demonstrated through a simple synthesis of malyngolide, an antibiotic isolated from a marine blue-green alga.

Giese and co-workers have reported over the past several years in a number of articles that the radicals formed on reduction of organomercurials can be trapped with electron-deficient olefins to produce coupled products.[1] Of these reports, the most exciting was Giese's demonstration that even the mercurial produced by methoxymercuration of an olefin could be employed in this reduction–radical coupling scheme.[2] Thus, the methoxymercuration product of cyclohexene 1 on reduction with sodium trimethoxyborohydride in the presence of a large excess of acrylonitrile produced a 65:35 *trans*/*cis* stereoisomeric mixture of the substituted cyclohexanes 2 and 3 in 77% yield. An extensive investigation of the effect of variation in the nature of the olefin used to trap the radical intermediate has been made. Reactivities and selectivities have been explained in terms of frontier molecular orbital theory.[3]



Since the process does represent a tremendously versatile new method for producing vicinally functionalized molecular systems, we felt that additional studies were warranted. Specifically, we were concerned with the question of whether the organomercurial generated from *hydroxymercuration* of an olefin could be used in this coupling scheme. We believed that if the coupling step still proceeded in good yield with the hydroxyl group unprotected, then a very useful route to 5-substituted δ-lactones would be at hand, for the product of the coupling process would merely have to be exposed to acid (or base and then acid) to effect lactonization. The 5-substituted δ-lactones do, of course, represent fairly ubiquitous structure types in nature (e.g., malyngolide, compactin lactone, pestalotin, and massoilactone).[4]

Table I. Preparation of δ-Lactones from Alkenes via Their Hydroxymercurials

starting alkene	coupling yield,[a] %	lactone yield, %/ method[a,b]
1-octene	50[c]	70/b
2-methyl-2-pentene	43[c]	88/b
cyclohexene	78[c]	95/b
allyl benzyl ether	50[c]	65/b
styrene	37[c]	100/a
1-octene	60[d]	50/a
2-methyl-2-pentene	70[d]	97/a
cyclohexene	74[d]	62/a
allyl benzyl ether	94[d]	60/b
styrene	72[d]	65/b

[a] The products were purified by silica gel chromatography and characterized by ^{1}H NMR, IR, and mass spectral analysis. [b] a = refluxing with *p*-TSA; b = hydrolysis with 10% aqueous sodium hydroxide and then acidification with 3 N HCl. [c] With methyl acrylate. [d] With acrylonitrile.

A number of different olefins (1-octene, 2-methyl-2-pentene, cyclohexene, allyl benzyl ether, and styrene) were thus hydroxymercurated [$Hg(OAc)_2$, H_2O][5] and converted to their generally crystalline chloromercuri derivatives by ligand exchange with chloride ion.

Reduction of these mercurials was carried out in methylene chloride by using 3 equiv of sodium trimethoxyborohydride as the reducing agent.[3] Both acrylonitrile and methyl acrylate were examined as trapping agents. In general, both of these acceptors did, in fact, give fair to good yields of coupled products. In the majority of cases, however, acrylonitrile proved to be the more efficient trapping agent (Table I).

Having substantiated the first stage of the alkene to lactone conversion, the final stage required that we now cyclize the δ-hydroxy esters or δ-hydroxy nitriles. This was accomplished easily by use of one of two general procedures: (a) refluxing the nitrile or ester with *p*-TSA in DME or (b) hydrolysis with 10% aqueous NaOH at room temperature and then acidification with 3 N HCl.

The results obtained for the lactonization methods are displayed in Table I. While no special efforts were taken to optimize these reactions, the yields range from fair to excellent.

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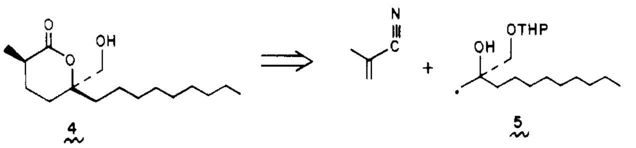
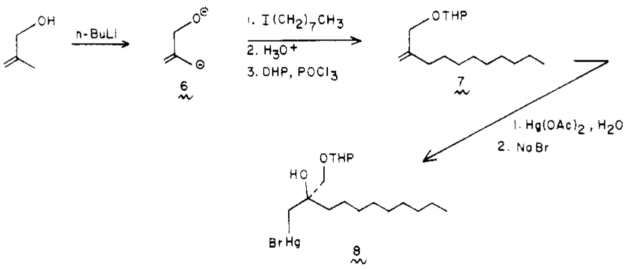
(1) Giese, B.; Meister, J. *Chem. Ber.* **1977**, *110*, 2588.
(2) Giese, B.; Heuck, K.; Lüning, U. *Tetrahedron Lett.* **1981**, *22*, 2155. Giese, B.; Heuck, K. *Ibid.* **1980**, *21*, 1829. Giese, B.; Heuck, K. *Chem. Ber.* **1979**, *112*, 3759.
(3) Giese, B.; Kretzschmar, G.; Meisner, J. *Chem. Ber.* **1980**, *113*, 2787.
(4) Chmielewski, M.; Jurczak, J. *J. Org. Chem.* **1981**, *46*, 2230 and references cited therein.
(5) Brown, H. C.; Lynch, G. J. *J. Org. Chem.* **1981**, *46*, 531 and references cited therein.

The operational simplicity of this new method for δ-lactone construction was further demonstrated through a synthesis of malyngolide (4), the major antibiotic found in the lipid extract of *L. majuscula* Gomont from Kahala Beach, Oahu.[6a] Malyngolide has been shown to be active against *M. Smegmatis* and *Streptococcus pyogenes* and somewhat less active against *Staphylococcus aureus* and *Bacillus subtilis*.[6b]

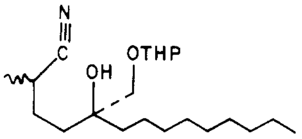


As can be seen from the retrosynthetic analysis of this substance, the radical 5 must be generated from the corresponding organomercurial and coupled with methacrylonitrile.

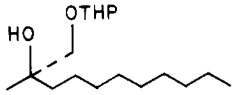
The olefin required for the initial hydroxymercuration reaction was assembled from the dianion 6 of methallyl alcohol.[7] Protection of the hydroxyl group as its tetrahydropyranyl ether, and hydroxymercuration of the olefin delivered 8 after ligand exchange with sodium bromide (45% overall yield). The mercurial 8 proved to be a fairly unstable substance. When left standing for several hours, it turned from a clear to an opaque oil.



For the coupling step, the freshly prepared mercurial 8 was dissolved in methylene chloride containing a large excess (30 equiv) of methacrylonitrile. To this mixture was added a 1 M solution (5 equiv) of sodium trimethoxyborohydride in tetrahydrofuran. The reaction mixture was stirred for 14 h and then quenched with water. An easily separable 4:1 mixture of the desired δ-hydroxy nitrile 9 plus the reduction product 10 was isolated. While the yield of coupled product was modest (49%) the synthesis was completed merely by refluxing the δ-hydroxy nitrile with p-toluenesulfonic acid in THF for 17 h. As in previously reported syntheses of 1,[8] a 1:1 mixture of diastereoisomeric lactones was obtained which could be separated readily by gravity chromatography. The spectral properties of the synthetic compound were identical with those reported for the natural product.[6a,9]



9



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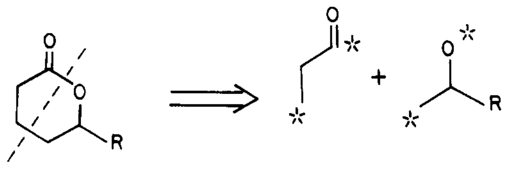
The hydroxymercuration–reductive coupling sequence does thus expand greatly the importance of mercurials in organic chemistry. The use of this "3 + 3" technology for the preparation of other δ-lactone systems is currently being investigated.



The experimental procedures for the preparation of 8 and 9 are representative.

Hydroxymercuration. To a stirred solution of olefin 7 (0.25 g, 0.93 mmol) in 6 mL of THF was added 0.30 g (0.93 mmol) of mercuric acetate and 2 mL of water. After 3 h the reaction mixture was diluted with aqueous sodium bromide and extracted with dichloromethane. The organic layer was dried and concentrated to yield 0.48 g (91%) of the mercurial 8 as an oil: IR (thin film) 3430, 2950, 2870, 1470, 1210, 1130, 1080, 1040, 980, 920 cm^{-1}; NMR (CDCl$_3$) δ 4.57 (two dd, 1 H), 4.01–3.34 (m, 4 H), 2.15–1.33 (m, 9 H), 1.24 (br s, 16 H), 0.85 (t, 3 H); mass spectrum (15 eV), *m/e* 467, 465 (^{202}Hg^{81}Br, ^{202}Hg^{79}Br).

Reductive Coupling. To a solution of 0.95 g (1.68 mmol) of mercurial 8 and 3.8 g (50 mmol) of methacrylonitrile in 25 mL of dichloromethane was added by syringe pump (flow rate = 0.15 mL/min) 1.1 g (8.4 mmol) of sodium trimethoxyborohydride (1 M in THF). The reaction mixture darkened, and a thick gray precipitate formed. After 14 h at room temperature, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was dried (MgSO$_4$) and concentrated, and the resultant oil was chromatographed on silica gel with 14% ethyl acetate–hexanes as eluent to furnish 0.08 g (18%) of the reduction product 10 and 0.29 g (49%) of coupled product 9: IR (thin film) 3480, 2950, 2890, 2280, 1465, 1215, 1135, 1080, 1040, 990, 925 cm^{-1}; NMR (CDCl$_3$) δ 4.52 (br s, 1 H), 3.82 (m, 1 H), 3.55 (m, 2 H), 2.77 (m, 1 H), 2.57 (q, 1 H, J = 6.9 Hz), 1.90–1.38 (m, 12 H), 1.29 (d, 3 H, J = 6.9 Hz), 1.23 (br s, 14 H), 0.84 (t, 3 H); mass spectrum (15 eV) *m/e* 323.

Acknowledgment. This work was supported in part by the National Institutes of Health (Grant No. AI 16138-03. The 300-MHz Brücker NMR instrument used in the studies was purchased through funds provided by the National Science Foundation (Grant No. CHE-79-05-185).

Registry No. 1, 5274-83-9; 2, 72887-19-5; 3, 72886-98-7; 4, 71582-80-4; 7, 80697-28-5; 8, 80697-29-6; 9, 80719-00-2; 10, 80697-30-9; 1-octene, 111-66-0; 2-methyl-2-pentene, 625-27-4; cyclohexene, 110-83-8; allyl benzyl ether, 14593-43-2; styrene, 100-42-5; methyl acrylate, 96-33-3; acrylonitrile, 107-13-1; 1-octene δ-hydroxynitrile, 80697-31-0; 2-methyl-2-pentene δ-hydroxynitrile, 80697-32-1; cyclohexene δ-hydroxynitrile, 63714-95-4; allyl benzyl ether δ-hydroxynitrile, 80697-33-2; styrene δ-hydroxynitrile, 80697-34-3; 1-octene δ-hydroxyester, 80697-35-4; 2-methyl-2-pentene δ-hydroxyester, 80697-36-5; cyclohexene δ-hydroxyester, 21197-34-2; allyl benzyl ether δ-hydroxyester, 80697-37-6; styrene δ-hydroxyester, 80697-38-7; 1-octene δ-lactone, 710-04-3; 2-methyl-2-pentene δ-lactone, 80697-39-8; cyclohexene δ-lactone, 4430-31-3; allyl benzyl ether δ-lactone, 80697-40-1; styrene δ-lactone, 80697-41-2.

Supplementary Material Available: Spectral data for organic compounds (2 pages). Ordering information is given on any current masthead page.

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(6) (a) Structure: Cardllina, J. H.; Moore, R. E.; Arnold, E. V.; Clardy, J. *J. Org. Chem.* **1979**, *44*, 4039. (b) Biological activity: Starr, T. J.; Dieg, E. F.; Church, K. K.; Allen, M. B. *Tex. Rep. Biol. Med.* **1962**, *20*, 271. Burkholder, P. R.; Burkholder, L. M.; Almodovar, L. R. *Bot. Mar.* **1960**, *2*, 149.

(7) Carlson, R. M. *Tetrahedron Lett.* **1978**, 111.

(8) Cardillo, G.; Orena, M.; Porzi, G.; Sandri, S. *J. Org. Chem.* **1981**, *46*, 2439.

(9) Satisfactory NMR, IR, and mass spectral data were obtained for all new compounds.

Book Reviews

Methoden der Organischen Chemie (Houben-Weyl), 4th Edition, Volume IV/1c, Reduktion, Part I, H. Kropf, volume editor, A. W. Frahm, J. Lehmann, W. Meise, H. Muth, P. Pachaly, E. Reimann, H.-J. Rimek, M. Sauerbier, P. Tinapp, and F. Zymalkowski, volume authors. 1980. xxxi + 912 pages, DM 780. Volume IV/1d, Reduktion, Part II, H. Kropf, volume editor, J. Bracht, A. Hajós, P. Hartter, H. Muth and M. Sauerbier, volume authors. 1981. xliii + 1000 pages. DM 860. Georg Thieme Verlag, Stuttgart/New York.

Reduction is one of the key processes in organic chemistry, and we have here nearly 2000 pages devoted to all aspects of the reduction of organic compounds. The Houben-Weyl series, we remind the reader, is complementary to the Beilstein handbook. The properties of individual organic compounds are not given here; rather the Houben-Weyl volumes focus on the *chemistry—what* has been done and *how* it was done. The chemistry is brought systematically and critically in well-organized discussions that are very thorough and which are backed up by an abundance of references to the original and the review literature. Both text and many tables bring a wealth of information. Detailed experimental procedures from the literature also are provided. There are many equations and figures, and these will be helpful to the reader.

Volume IV/1c covers catalytic hydrogenation in all its many aspects. A 90-page section brings general discussions of heterogeneous and homogeneous catalytic hydrogenation, catalytic transfer hydrogenation, and the stereochemistry of catalytic hydrogenations. The applications of various metal catalyst systems, all of which are familiar to the organometallic chemist, are discussed in the section devoted to homogeneous catalysis: chromium carbonyl complexes, pentacyanocobaltate(II), dicobalt octacarbonyl $(Ph_3P)_3RuCl_2$, $(Ph_3P)_3RhCl$, and other rhodium complexes, iridium complexes, including $(Ph_3P)_2Ir(CO)Cl$, $H_2PtCl_6/SnCl_2$, $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$, and soluble Ziegler catalysts. Here, as is usual in the Houben-Weyl series, the emphasis is on practical aspects of the chemistry to the almost complete exclusion of mechanistic considerations. So there is no mention of the catalytic cycles involved in which organometallic intermediates play an important role. Nonetheless, for the organic chemist whose aim is the hydrogenation of a given organic compound these general sections will be useful and informative. However, it is the following sections which provide the really useful information for the synthetic organic chemist: over 450 pages in which the applications of catalytic hydrogenation are detailed in a discussion which is organized according to the organic functions which are reduced.

Volume IV/1c concludes with the first two sections of the chapter on reductions with inorganic reducing agents. The remaining three sections of this chapter are found in Volume IV/1d. Included in this chapter are the following inorganic reducing agents: nonmetal compounds (I^-, HI, $S_2O_4^{2-}$, N_2H_4, $(RO)_3P$, H_3PO_2, etc.); metals; simple and complex metal hydrides; metal salts (Sn(II), Ti(II), Ti(III), V(II), Cr(II), etc.) and metal carbonyls; so there is much organometallic chemistry in this chapter. (This will not be apparent to the uninformed reader since, as noted before, mechanisms are not discussed.) Further chapters in Volume IV/1d deal with the few examples of reductions using organometallic compounds as reducing agents, with electrochemical reductions, and with biochemical reductions which utilize microorganisms.

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Each volume contains an author index and a compound index. The latter is organized in seven categories, each of these alphabetically. This index, together with the very detailed table of contents, allows one to find just about anything one might be looking for. For the chemical public at large it is unfortunate that this outstanding, definitive account of reduction in organic chemistry is written in German, not in English. The Houben-Weyl series is now nearly complete; however, since the earliest volumes date from the 1950s, it may be hoped that supplementary volumes will be issued to bring the topics covered earlier up-to-date. If this done, we hope that Houben-Weyl will follow the lead of Beilstein and Gmelin and bring out such books in English.

The price of these volumes largely precludes individual ownership. However, all academic, industrial, government chemistry libraries should have these excellent books on their shelves.

Dietmar Seyferth, *Massachusetts Institute of Technology*

Handbook of High Resolution Multinuclear NMR. By C. Brevard and P. Granger. John Wiley and Sons, New York. 1981. xvii + 229 pages. $24.50.

This handbook is divided into two parts. Part One (four chapters, 77 pages) includes a chapter on NMR parameters (i.e., sensitivity, receptivity, chemical shifts, coupling constants, relaxation times, and relaxation mechanisms), a chapter on the Fourier transform method (the rotating frame, pulse angles, the free induction decay, the digitalization process, and display of the spectrum), a chapter on the nuts and bolts of spectrum acquisition (sample preparation, lock systems, references, spectral manipulations, decoupling procedures, special pulse sequences, sensitivity enhancement, and resolution enhancement), and finally a chapter concerning dynamic measurements (T_1 and T_2 measurements and spin-locking measurements).

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This book will not compete with "Practical NMR Spectroscopy" by Martin, Delpuech, and Martin or with "NMR and the Periodic Table" by Harris and Mann, but any laboratory doing multinuclear NMR will find it useful.

J. D. Odom, *University of South Carolina*

Gmelin Handbook of Inorganic Chemistry. 8th Edition. Fe, Organoiron Compounds. Part C3, Binuclear Compounds 3. G. Dettlaf, U. Krüerke, N. Kuhn, and M. Mirbach, volume authors, U. Krüerke, volume editor. 1980. ii + 196 pages. DM 456, $269.10. Organoiron Compounds, Part C4, Binuclear Compounds 4. U. Krüerke, N. Kuhn, E. Luther, M. Mirbach, and B. Wöbke, volume authors, U. Krüerke, volume editor. 1981. ii + 285 pages. DM 787, $374.70. Gmelin Institut für Anorganische Chemie der Max-Planck-Gesellschaft zur Förderung der Wissenschaften and Springer-Verlag, Berlin/Heidelberg/New York.

These volumes are the latest additions to the Gmelin organoiron series which now numbers 15 volumes. In Part C3 are included dinuclear iron compounds with organic ligands bonded by four carbon atoms (mostly acyclic and cyclic dienes), with or without Fe–Fe bonds and dinuclear iron compounds containing one or two η^5-C_5H_5 ligands. The treatment of the latter class is continued and concluded in Part C4. A great diversity of organoiron compounds is found in these books, and the empirical formula and ligand formula indexes at the end of each volume will be indispensible to the user. The way the iron atoms are connected in these dinuclear complexes varies widely: direct Fe–Fe bonds and single bridges and double bridges of all kinds. Among the dinuclear η^5-C_5H_5Fe complexes, $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ has received much attention, and 86 pages are devoted to this compound and to others containing alkyl and other substituents on the C_5 ligand. In Part C3, among the complexes with L^4 ligands, the ferracyclopentadiene complexes of type $C_4R_4Fe_2(CO)_6$ play an important role, with many known examples of this class.

The presentation of the many different types of dinuclear iron compounds, many with complex structures, is greatly helped by the many formulas and figures. All available data for each compound are provided, either in text or tables: preparation, physical and spectroscopic properties, structure, and chemical conversions, along with the pertinent references. These include citations of the original literature, reviews, theses, conference reports, and a few patents, through the end of 1977 for Part C3 and the end of 1978 for Part C4. A few later references have been added.

For anyone working in the area of organoiron chemistry these books, as well as the rest of the Gmelin organoiron series, will be very useful indeed. They provide a wealth of information and are as exhaustive in their coverage as "Chemical Abstratcts" permits, and they are well organized and up-to-date. A final volume in which the remaining dinuclear iron compounds are treated, those with organic ligands bonded to Fe through six or more carbon atoms, will conclude the "C" series.

Dietmar Seyferth, *Massachusetts Institute of Technology*

Advances in Catalysis. Volume 28. Edited by D. D. Eley, H. Pines, and P. B. Weisz. Academic Press, New York. 1979. x + 403 pages. $52.00.

This recent volume of Advances in Catalysis contains chapters by T. Engel and G. Ertl, "Elementary Steps in the Catalytic Oxidation of Carbon Monoxide on Platinum Metals", by R. Eisenberg and D. E. Hendriksen, "The Binding and Activation of CO, CO_2 and NO and Their Homogeneously Catalyzed Reactions", by M. I. Temkin, "The Kinetics of Some Industrial Heterogeneous Catalytic Reactions", by S. M. Csicsery, "Metal-Catalyzed Dehydrocyclization of Alkylaromatics", and by J. J. Villafranca and F. M. Raushel, "Metalloenzyme Catalysis".

It is often true that a review significantly reflects the vantage point and background of the reviewer—and the present is no exception. For this reviewer the gem of the volume is the article by Csicsery, surveying an important but as yet little recognized area of hydrocarbon chemistry, the cyclization reactions of alkylaromatics which lie at or just beyond the gasoline boiling range. Although somewhat documentary (rather than interpretive or projective) in nature, the article clearly surveys an area which (in my view) has not yet received the attention it merits within the industry.

Three chapters deal with reactions of small molecules, CO, CO_2, NO, NH_3, and the like, each directed at a distinct audience. The article by Engel and Ertl catalogs, in considerable detail, the state-of-the-art in CO adsorption and oxidation on Pt-group metal surfaces; Eisenberg and Hendriksen write for a general audience in their somewhat elementary overview chapter on reactive inorganic complexes of CO, CO_2, and NO; and Temkin seeks the engineering community in his kinetic analysis of reaction rates.

At the other extreme in complexity is the brief but very specific and very up-to-date review by Villafranca and Raushel on catalysis by three metalloenzymes: thermolysin, a Zn- and Ca-containing peptidase; yeast hexokinase, catalyzing reaction between hexose and MgATP; and glutamine synthetase, which requires divalent cations such as Mn^{2+}.

Overall Volume 28 of Advances in Catalysis is characterized by authors of recognized ability and by a wide breadth of subject material, ranging from highly analytical chapters on small molecule conversion and synthesis to the provocative articles on dehydrocyclization and on metalloenzymes.

L. D. Rollmann, *Mobil R&D Corporation*

Aspects of Homogeneous Catalysis. Volume 4. Edited by R. Ugo. D. Reidel Publishing Co., Dordrecht. 1981. viii + 204 pages. $58.00, Dfl. 110.

This is the fourth volume of a series which is concerned with different areas of homogenous catalysis. The previous volumes have contained some useful reviews and the present one continues in this tradition.

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In summary, Volume 4 will be of interest to organic and inorganic chemists, particularly those working on metal complex catalyzed reactions of olefins.

Howard Alper, *University of Ottawa* constant and relaxation time values are listed. Several references are then given. A close examination of several nuclei revealed some problems. For example, only one value of a ^{11}B–^{11}B coupling constant (18.9 Hz) is given while literature values of J_{BB} range from 12 to 106 Hz. A remark under ^{77}Se states that no NOE is observed except when a proton is directly bound to Se. All relaxation studies to date have shown essentially no contribution to T_1 from the dipole–dipole mechanism even when Se–H bonds are present. Also, in the chemical shift scale figure for tin, Sn(IV) is listed for three different classes of compounds although it is fairly obvious that Sn(VI) and Sn(V) should be listed.

This book will not compete with "Practical NMR Spectroscopy" by Martin, Delpuech, and Martin or with "NMR and the Periodic Table" by Harris and Mann, but any laboratory doing multinuclear NMR will find it useful.

J. D. Odom, *University of South Carolina*

Gmelin Handbook of Inorganic Chemistry. 8th Edition. Fe, Organoiron Compounds. Part C3, Binuclear Compounds 3. G. Dettlaf, U. Krüerke, N. Kuhn, and M. Mirbach, volume authors, U. Krüerke, volume editor. 1980. ii + 196 pages. DM 456, $269.10. Organoiron Compounds, Part C4, Binuclear Compounds 4. U. Krüerke, N. Kuhn, E. Luther, M. Mirbach, and B. Wöbke, volume authors, U. Krüerke, volume editor. 1981. ii + 285 pages. DM 787, $374.70. Gmelin Institut für Anorganische Chemie der Max-Planck-Gesellschaft zur Förderung der Wissenschaften and Springer-Verlag, Berlin/Heidelberg/New York.

These volumes are the latest additions to the Gmelin organoiron series which now numbers 15 volumes. In Part C3 are included dinuclear iron compounds with organic ligands bonded by four carbon atoms (mostly acyclic and cyclic dienes), with or without Fe–Fe bonds and dinuclear iron compounds containing one or two η^5-C_5H_5 ligands. The treatment of the latter class is continued and concluded in Part C4. A great diversity of organoiron compounds is found in these books, and the empirical formula and ligand formula indexes at the end of each volume will be indispensible to the user. The way the iron atoms are connected in these dinuclear complexes varies widely: direct Fe–Fe bonds and single bridges and double bridges of all kinds. Among the dinuclear η^5-C_5H_5Fe complexes, $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ has received much attention, and 86 pages are devoted to this compound and to others containing alkyl and other substituents on the C_5 ligand. In Part C3, among the complexes with L^4 ligands, the ferracyclopentadiene complexes of type $C_4R_4Fe_2(CO)_6$ play an important role, with many known examples of this class.

The presentation of the many different types of dinuclear iron compounds, many with complex structures, is greatly helped by the many formulas and figures. All available data for each compound are provided, either in text or tables: preparation, physical and spectroscopic properties, structure, and chemical conversions, along with the pertinent references. These include citations of the original literature, reviews, theses, conference reports, and a few patents, through the end of 1977 for Part C3 and the end of 1978 for Part C4. A few later references have been added.

For anyone working in the area of organoiron chemistry these books, as well as the rest of the Gmelin organoiron series, will be very useful indeed. They provide a wealth of information and are as exhaustive in their coverage as "Chemical Abstratcts" permits, and they are well organized and up-to-date. A final volume in which the remaining dinuclear iron compounds are treated, those with organic ligands bonded to Fe through six or more carbon atoms, will conclude the "C" series.

Dietmar Seyferth, *Massachusetts Institute of Technology*

Advances in Catalysis. Volume 28. Edited by D. D. Eley, H. Pines, and P. B. Weisz. Academic Press, New York. 1979. x + 403 pages. $52.00.

This recent volume of Advances in Catalysis contains chapters by T. Engel and G. Ertl, "Elementary Steps in the Catalytic Oxidation of Carbon Monoxide on Platinum Metals", by R. Eisenberg and D. E. Hendriksen, "The Binding and Activation of CO, CO_2 and NO and Their Homogeneously Catalyzed Reactions", by M. I. Temkin, "The Kinetics of Some Industrial Heterogeneous Catalytic Reactions", by S. M. Csicsery, "Metal-Catalyzed Dehydrocyclization of Alkylaromatics", and by J. J. Villafranca and F. M. Raushel, "Metalloenzyme Catalysis".

It is often true that a review significantly reflects the vantage point and background of the reviewer—and the present is no exception. For this reviewer the gem of the volume is the article by Csicsery, surveying an important but as yet little recognized area of hydrocarbon chemistry, the cyclization reactions of alkylaromatics which lie at or just beyond the gasoline boiling range. Although somewhat documentary (rather than interpretive or projective) in nature, the article clearly surveys an area which (in my view) has not yet received the attention it merits within the industry.

Three chapters deal with reactions of small molecules, CO, CO_2, NO, NH_3, and the like, each directed at a distinct audience. The article by Engel and Ertl catalogs, in considerable detail, the state-of-the-art in CO adsorption and oxidation on Pt-group metal surfaces; Eisenberg and Hendriksen write for a general audience in their somewhat elementary overview chapter on reactive inorganic complexes of CO, CO_2, and NO; and Temkin seeks the engineering community in his kinetic analysis of reaction rates.

At the other extreme in complexity is the brief but very specific and very up-to-date review by Villafranca and Raushel on catalysis by three metalloenzymes: thermolysin, a Zn- and Ca-containing peptidase; yeast hexokinase, catalyzing reaction between hexose and MgATP; and glutamine synthetase, which requires divalent cations such as Mn^{2+}.

Overall Volume 28 of Advances in Catalysis is characterized by authors of recognized ability and by a wide breadth of subject material, ranging from highly analytical chapters on small molecule conversion and synthesis to the provocative articles on dehydrocyclization and on metalloenzymes.

L. D. Rollmann, *Mobil R&D Corporation*

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