significantly more viscous as the amine content increases. Higher viscosity will tend to retard separation of the primary photoproducts formed in the reductive quenching step (eq 3) and thereby enhance the likelihood of unproductive back-electron transfer (eq 8). Additional information about the solution behavior of transient X will be required to decide which of these two properties of TEOA has greater importance.

$$[ReBr(CO)_3(bpy)]^- + TEOA^{+\cdot} \rightarrow ReBr(CO)_3(bpy) + TEOA \quad (8)$$

Summary

The results of the present study lead to several conclusions regarding the mechanism of CO_2 reduction in the $ReBr(CO)_3(bpy)/TEOA/DMF$ system. (1) The system is both efficient and specific for the photoinduced reduction of CO_2 to CO. Initial quantum yields reach 0.15 with 436-nm irradiation and may prove to be even higher when the optimum reaction conditions are established. (2) The initial photochemical step in the overall reaction sequence involves reductive quenching of photoexcited $ReBr(CO)_3(bpy)$ by TEOA. In contrast, the excited complex undergoes no discernible interaction with CO_2. (3) The reduced product of this quenching step, $[ReBr(CO)_3(bpy)]^-$, can be observed in the ns–μs time regime. In Ar-bubbled solutions, this species disappears via at least two pathways. (4) Scavenging of $[ReBr(CO_3(bpy)]^-$ by CO_2 leads to the appearance of a new species, Y. The identity of Y and its precise role in the mechanism of CO_2 reduction have yet to be ascertained.

Acknowledgment. We wish to thank Professor A. D. King, Mr. Neal Tonks, and Ms. Joan Corbin for valuable technical advice and assistance. We also acknowledge several fruitful discussions with Professor R. B. King. Financial support for this work was provided by the National Science Foundation (Grant CHE-8210558) and by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2683 from the Notre Dame Radiation Laboratory.

Registry No. TEOA, 102-71-6; DMF, 68-12-2; $ReBr(CO)_3(bpy)$, 40231-87-6; $[ReBr(CO)_3(bpy)]^-$, 98577-53-8; CO_2, 124-38-9; CO, 630-08-0.

Cyclosiloxanes as Frameworks for Multimetallic Compounds. 4. Synthesis and Characterization of Some Tricarbonylchromium-Substituted Methylphenylcyclosiloxanes

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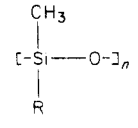
The cyclosiloxanes $D_n^{PhCr(CO)_3}$ (n = 3, cis,cis,cis and cis,trans,trans; n = 4, cis,trans,cis,trans and mixture of all possible isomers) have been prepared and characterized. Because the $Cr(CO)_3$ substituent renders the ortho and meta protons of the phenyl groups diastereotopic when the phenyl group is located on a chirotopic silicon atom, the structure of the pure n = 4 isomer can be unequivocally established by ^1H NMR. The catalytic properties of $D_3^{PhCr(CO)_3}$ for the hydrosilation of 1,3-pentadiene with triethoxysilane were compared to those of [(trimethoxysilyl)benzene]-, [(trimethylsilyl)benzene]-, and (benzene)chromium tricarbonyls. The lack of any significant difference in reactivity or specificity between the various catalysts supports the idea that catalysis is preceeded by dissociation of the $Cr(CO)_3$ from the arene ring. The absence of any significant specific intramolecular effects in the behavior of the cyclotrisiloxane catalyst is also mirrored in the mass spectral fragmentation behavior of the two cyclotrisiloxane isomers.

Introduction

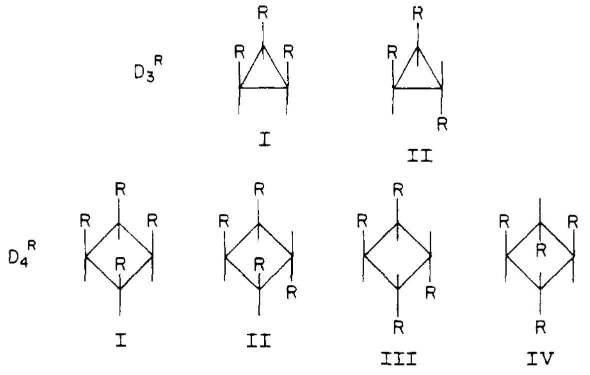
In the earlier papers of this series we described the preparation and characterization of some cyclosiloxanes of the general formula



$$[-\overset{CH_3}{\underset{R}{Si}}-O-]_n = D_n^R$$

where R is an organometallic function attached to the siloxane ring through a metal–Si bond.[1] These studies were directed toward exploring the suitability of the cyclosiloxane system as a framework for supporting catalytic functions in a closely defined spatial relationship to each other. In our initial studies we were mainly concerned with the stability of the cyclosiloxane ring system in the presence of organometallic functions and of developing methods for characterizing the different geometric isomers produced in the synthetic reactions. One of the main deficiencies of the systems studied was the failure to achieve complete separation of geometric isomers. Since the ultimate goal of this work is to take advantage of the

Chart I



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[1] (a) Pelletier, E.; Harrod, J. F. *Can. J. Chem.* **1983**, *61*, 762. (b) Pelletier, E. Harrod, J. F. *Organometallics* **1984**, *3*, 1064,1070.

Table I. Reaction Conditions for Preparation of $D_n^{PhCr(CO)_3}$ (n = 3, 4)

compd	reactn time, h	% yield
$D_3^{PhCr(CO)_3}$ (I, II)	68	86
$D_3^{PhCr(CO)_3}$ (I)	70	97
$D_3^{PhCr(CO)_3}$ (II)	90	66
$D_4^{PhCr(CO)_3}$ (mixture of isomers)	122	79
$D_4^{PhCr(CO)_3}$ (III)	155	66

different spatial constraints exhibited by the different isomers to influence catalytic activity, the separation of the isomers is crucial. A schematic representation of the geometrical isomers of D_n^R together with their numerical identification is shown in Chart I.

In this paper we describe the synthesis, characterization, and catalytic activity of some tricarbonylchromium-substituted methylphenylcylclosiloxanes. The choice of this system was based on the knowledge that at least some of the isomers of the dimer and trimer cyclosiloxanes can be obtained in the pure state[2,3] and that (arene)tricarbonylchromium complexes exhibit catalytic activity for the hydrogenation of dienes[4,5] and for the hydrosilation of dienes.[6]

Results and Discussion

Synthesis of Complexes. Using conventional synthetic procedures we were able to obtain a number of fully substituted $D_n^{PhCr(CO)_3}$ (n = 3 and 4) complexes in an isomerically pure state. Some details of reaction conditions and products are listed in Table I. Some of the yields are very high, indicating essentially quantitative conversion. This is remarkable since there must be three or four stepwise substitutions to achieve the final products.

There is a notable difference in reactivity between the all-cis and the trans,trans,cis isomers of D_3^{Ph} and between the cis,trans,cis,trans isomer and the isomer mixture of D_4^{Ph}. These differences were found to be reproducible and are probably due to significant steric effects slowing down the final substitution steps in reactants with cis substituents. Such steric effects have already been observed in other systems.[1b]

^{1}H Spectra of $D_n^{PhCr(CO)_3}$. The proton NMR spectra of the phenyl groups of $D_3^{PhCr(CO)_3}$ (I and II) are shown in Figure 1. In the methyl region the spectra are as expected, a single methyl resonance for the all-cis isomer and two resonances in a ratio of 2:1 for isomer II. In the phenyl regions the spectra are much more informative than is usually the case due to the adventitious spreading of the spectrum by the attached $Cr(CO)_3$ moiety. In the spectrum of isomer I the ortho (doublet, two protons), meta (triplet, two protons), and para (triplet, one proton) signals are clearly resolved. The additional fine structure is attributed to small long-range couplings. The phenyl spectrum of isomer II is more complicated, as would be expected from the presence of two geometrically inequivalent types of silicon substituent. However, the spectrum shows more than the doubling of each resonance expected on the grounds of geometrical inequivalence. A 2D homonuclear decoupling experiment showed that each of the ortho- and meta- resonances is tripled in isomer II, to doublets and triplets of equal intensity, while the para-resonance is doubled to triplets of intensity ratio 2:1. The reason for this behavior is evident when the detailed structure of the molecule is examined (see Figure 2). The two silicon atoms bearing cis phenyl substituents are chirotopic, and the attachment of the $Cr(CO)_3$ to one face of the phenyl rings attached to these silicons renders the ortho- and meta-proton pairs diastereotopic. Thus, there are three kinds of ortho- and meta-protons (H_A, $H_{A'}$, H_B, and H_C, $H_{C'}$, H_D in Figure 2) but only two kinds of paraprotons in the molecule.

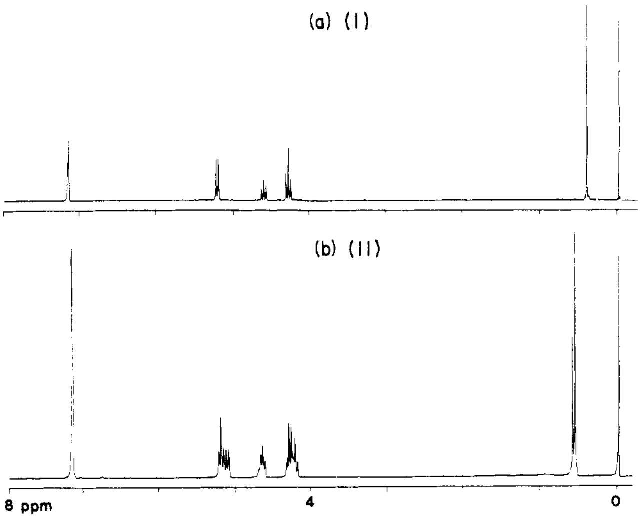

Figure 1. ^{1}H NMR spectra of the phenyl groups of the two isomers of $D_3^{PhCr(CO)_3}$ in C_6D_6 at room temperature: (a) the all-cis isomer; (b) the c,t,t isomer.

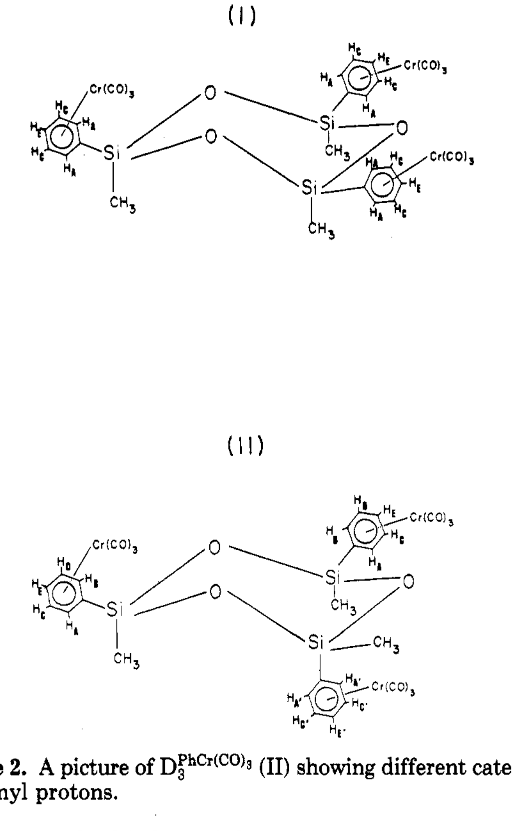

Figure 2. A picture of $D_3^{PhCr(CO)_3}$ (II) showing different categories of phenyl protons.

Whereas the phenyl resonances in the ^{1}H NMR spectrum of $D_3^{PhCr(CO)_3}$ are interesting, no new structural information is revealed. However, analysis of this region of the ^{1}H NMR spectrum for the pure isomer obtained from $D_4^{PhCr(CO)_3}$ permits its structure to be assigned. Since only one methyl resonance is observed, isomer II may be eliminated since it has a set of three methyl resonances in the ratio 2:1:1. The remaining three isomers each have only

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(2) Richards, R. E.; Thompson, H. W. *J. Chem. Soc.* **1949**, 124.

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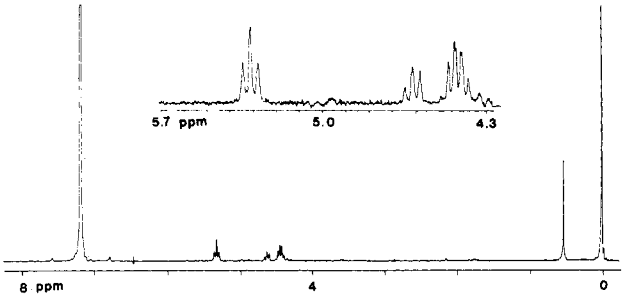

Figure 3. ^{1}H NMR spectrum of $\mathrm{D}_4^{\mathrm{PhCr(CO)_3}}$ in C_6D_6 at room temperature.

Table II. Assignments of Peaks Observed in Mass Spectra of $\mathrm{D}_3^{\mathrm{PhCr(CO)_3}}$ (I and II)

		% relative intensity	
m/e	assignt	$\mathrm{D}_3^{\mathrm{PhCr(CO)_3}}$ (I)	$\mathrm{D}_3^{\mathrm{PhCr(CO)_3}}$ (II)
816	M^+	8.0	11.2
732	$M^+ - 3CO$	57.3	69.6
704	$M^+ - 4CO$	6.1	50.5
648	$M^+ - 6CO$	43.1	15.1
620	$M^+ - 7CO$	46.1	81.6
596	$M^+ - Cr(CO)_3 - 3CO$	54.8	19.9
564	$M^+ - 9CO$	51.6	45.5
460	$M^+ - 2Cr(CO)_3 - 3CO$	100.0	100.0
393	$M^+ - 3Cr(CO)_3 - CH_3$	24.0	23.6
315	$M^+ - 3Cr(CO)_3 - CH_3 - C_6H_5$	33.2	32.7

one type of methyl group. Although an assignment of the $\mathrm{D}_4^{\mathrm{Ph}}$ has been carried out by Hickton et al.,[7] and by Jancke et al.,[8] using a chemical shift correlation, this cannot be considered a definitive proof of structure. In the present experiment the pure isomer exhibits two types of ortho and meta protons, but only one type of para proton (Figure 3). This was verified by a 2D homonuclear decoupling experiment. Isomers I and IV have no chirotopic centers and should give only one resonance each for the ortho-, meta-, and para-protons. In isomer III, with four magnetically equivalent chirotopic centers, the ortho- and meta-protons exist as two sets of diastereotopic pairs, while the para-protons form a single set. Thus, we can unambiguously assign the structure of the pure isomer of $\mathrm{D}_4^{\mathrm{PhCr(CO)_3}}$ which we have prepared as that of isomer III. For completion is should be pointed out that isomer IV has three geometrically distinct ring positions and two positions that are chirotopic. This would give rise to four types of ortho- and meta-protons in equal numbers: three geometric species, one of which gives rise to diastereotopic pairs.

In the isomer mixture of $\mathrm{D}_4^{\mathrm{PhCr(CO)_3}}$, the relative simplicity of the methyl region allows the presence of four isomers and their relative concentrations to be established, but the phenyl region is too complex and unresolved to yield any useful information. In the resolved isomers, the relative usefulness of the two regions is reversed due to the excessive simplicity of the methyl spectra of three of the isomers.

Mass Spectra of Tricarbonylchromium-Substituted Methylphenylcyclosiloxanes. Our earlier studies of cyclosiloxanes included a detailed investigation of their MS fragmentation behavior.[1a] It was therefore of interest to extend that enquiry to the compounds prepared in the present study. The mass spectra of the two isomers of $\mathrm{D}_3^{\mathrm{PhCr(CO)_3}}$ are listed in Table II. The spectra are in general very similar, as expected, the only significant difference being a reversal in the relative abundances of the ($M^+ - 4CO$) and ($M^+ - 6CO$). The values are 6:43 for the all-cis isomer and 50:15 for the other. Our measurements on the other silyl-substituted (arene)tricarbonylchromium complexes used in this work, and the reported spectrum of the unsubstituted benzene complex[9] indicate that the loss of all three carbonyl groups is very facile, the ($M^+ - 3CO$) peak being the most important in each case. The remarkable similarity of the two trimer spectra in all regions other than those referred to above seems to prove that there are no significant specific intramolecular interactions affecting the early stages of the fragmentation. The relative importance of partially CO depleted fragments in the spectra of the cyclosiloxane compounds is probably a reflection of statistical rather than chemical effects. The major peaks in the spectrum of $\mathrm{D}_4^{\mathrm{PhCr(CO)_3}}$ (III) are listed in Table III.

Table III. Assignments of Peaks Observed in Mass Spectrum of $\mathrm{D}_4^{\mathrm{PhCr(CO)_3}}$ (III)

m/e	assignt	% rel intensity
1088	M^+	8.0
1004	$M^+ - 3CO$	19.5
732	$M^+ - 2Cr(CO)_3 - 3CO$	22.5
700	$M^+ - Cr(CO)_3 - 9CO$	17.5
648	$M^+ - 2Cr(CO)_3 - 6CO$	69.2
596	$M^+ - 3Cr(CO)_3 - 3CO$	100.0
529	$M^+ - 4Cr(CO)_3 - CH_3$	41.0
451	$M^+ - 4Cr(CO)_3 - CH_3 - C_6H_6$	10.0

A number of peaks at the low mass end of the $\mathrm{D}_n^{\mathrm{PhCr(CO)_3}}$ spectra correspond to major peaks of the mass spectra of the unsubstituted methylphenylcyclosiloxanes, e.g., *m/e* 393 ($M^+ - CH_3$) and 315 ($M^+ - CH_3 - C_6H_5$). It therefore seems that the major sequence in the fragmentation of the tricarbonylchromium-substituted molecules is the loss of the tricarbonylchromium fragments followed by a conventional fragmentation of the phenylcyclosiloxane residue. As will be seen below, the results of the catalytic studies conform to a similar picture, in which the liberated tricarbonylchromium fragments express themselves catalytically while the cyclosiloxane residue has no influence on the reaction.

Hydrosilation Catalyzed by Silyl-Substituted (Arene)chromium Tricarbonyl Complexes. Although (arene)chromiumtricarbonyl complexes have been extensively studied as catalysts for the hydrogenation of dienes,[4,5] apart from the casual reference by Wrighton et al. there has been no report in the literature of their activity as catalysts for hydrosilation.[6] A preliminary study in our laboratory revealed that not only are they active for the thermal catalysis of the hydrosilation of 1,3-dienes but also their activity is considerably higher than suggested by the observations of Wrighton and co-workers. Whereas the latter workers cite a temperature range of 170–180 °C for a reasonable turnover rate, we found convenient rates at 80–100 °C under the same concentration conditions.

The main goal of our study was not simply to study new catalysts for hydrosilation but to demonstrate rate and specificity effects arising from the peculiar properties of multifunctional catalytic molecules. To do this we compared the activity and specificity of $\mathrm{D}_3^{\mathrm{PhCr(CO)_3}}$ (I) as a catalyst for the addition of triethoxysilane to *trans*-1,3-pentadiene with the activities and specificities of (η^6-benzene)-, [η^6-(trimethylsilyl)benzene]-, and [η^6-(trimethoxysilyl)benzene]chromium tricarbonyl catalysts for the same reaction. The trimethoxysilyl and trimethyl com-

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[7] Hickton, H. J.; Holt, A.; Homer, J.; Jarvie, A. W. *J. Chem. Soc.* **1966**, C149; *J. Chem. Soc. B* **1967**, 67.

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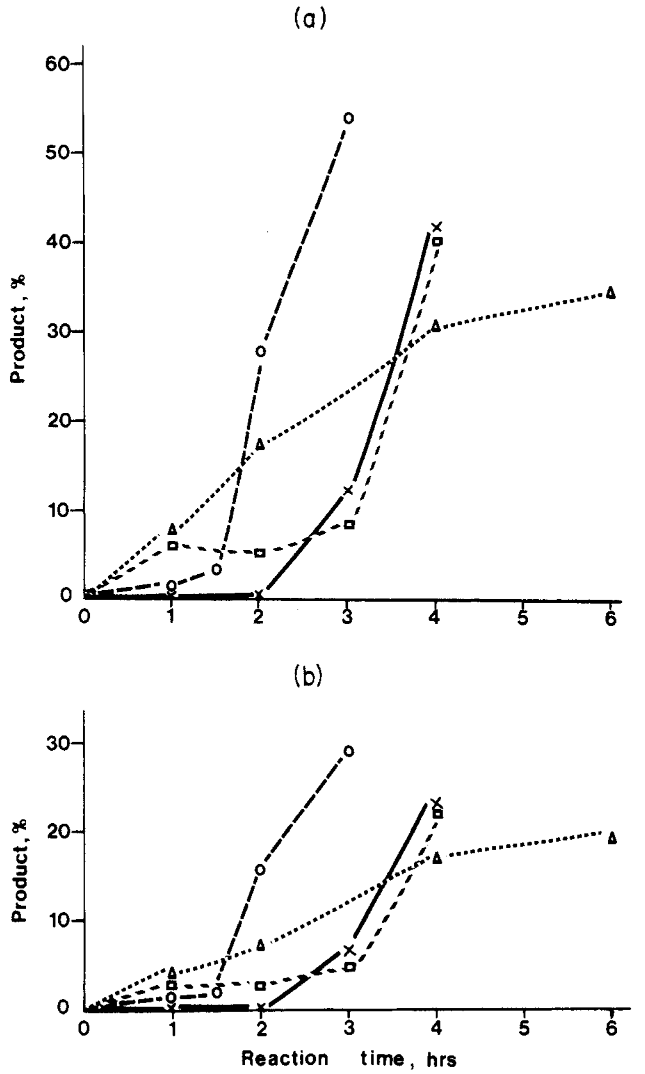
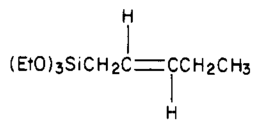


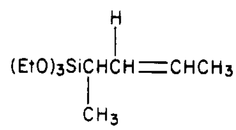
Figure 4. Product yields (based on reactant diene) vs. time for the catalytic addition of triethoxysilane to 1,3-pentadiene (T = 80 °C; catalyst concentration ca. 35 mM): (a) product 1; (b) product 2. Catalyst: ×, $D_3^{PhCr(CO)_3}$; ○, $(CH_3O)_3SiC_6H_5Cr(CO)_3$; □, $(CH_3)_3SiC_6H_5Cr(CO)_3$; △, $C_6H_6Cr(CO)_3$.

pounds were chosen to bracket the electronic properties of the cyclosiloxane compound. The result of a set of reactions are summarized in Figure 4.

The structures of the two isomeric hydrosilation products were established by two-dimensional ^1H NMR spectroscopy to be 1 and 2. The two products were produced


$(EtO)_3SiCH_2\overset{H}{C}{=}\underset{H}{C}CH_2CH_3$

1


$(EtO)_3Si\underset{CH_3}{C}H\overset{H}{C}H{=}CHCH_3$

2

in a ratio of 1.82 ± 0.01 for the whole range of catalysts and with no significant variation over the course of the reaction. Both products 1 and 2 are likely the result of 1,4-addition to the diene, but the product 2 is unconventional. Metal complex catalyzed hydrosilations usually result in terminal silylation, even when the reactant alkene is internal. Several exceptions to this rule are known,[10-13] and it is interesting to note that two of them involve triethoxysilane.[12,13]

The main conclusion to be drawn from these results is that neither the activities nor the specificities of this series of catalysts varies to any significant degree. In the first place this observation supports the mechanism proposed by Cais for the analogous hydrogenation reaction, in which the initial steps in the reaction involve displacement of the tricarbonylchromium moiety from the arene.[5] Provided this process is not dominantly rate determining, the specific structure of the arene would not therefore be expected to have a strong influence on either rate or specificity. It is perhaps a little surprising that the highly congested cyclosiloxane compound does not manifest a dramatically different rate of displacement of $Cr(CO)_3$ and hence a noticeably different acceleration in the early stages of the reaction when the presumed active free $Cr(CO)_3$ species is being produced. This may reflect the adoption of a configuration by the phenyltricarbonylchromium units in which their interaction is not very great.

Since the reaction rates and induction periods were found to be extremely sensitive to traces of moisture, we hesitate to place much significance on the relatively minor differences in the activities of the various catalysts. However, the more pronounced autoacceleration in the case of the substituted arenes as compared to the benzene complex was observed consistently and may be due to a slight change in mechanism on going from unsubstituted to substituted complexes.

Although a number of novel properties are exhibited by the compounds and reactions described herein, it is clear that a definitive test of the principle of cooperative interactions between catalytically active function supported on cyclosiloxane frameworks has yet to be demonstrated. The search for more suitable catalytic models is continuing in our laboratories.

Experimental Section

All reactions were carried out under prepurified Linde nitrogen. Reagent grade di-*n*-butyl ether was purified by distillation from sodium and tetrahydrofuran was distilled from sodium/benzophenone. Other solvents were freshly distilled under nitrogen before use. Chromium hexacarbonyl was purchased from Aldrich Chemical Co. and used without further purification. trans-1,3-Pentadiene, triethoxysilane, and trimethylsilane were obtained from the same company and purified by distillation immediately before use. Phenyltrimethoxysilane was purchased from Peninsular Chem Research and distilled before use. (Trimethylsilyl)phenylchromium tricarbonyl was prepared according to a literature procedure[14] as was the unsubstituted benzene compound. The preparation and separation of the isomers of D_n^{Ph} were done according to procedures in the literature.[7,8] Whereas both isomers of the trimer were obtained in a pure state, only the cis,trans,cis,trans isomer II of the tetramer was successfully isolated as a pure compound by crystallization from a methanol solution of the mixed isomers.

IR spectra were recorded on a Perkin-Elmer Model 297 spectrometer. NMR spectra were measured on a Varian XL-200 FT spectrometer with a 4-s pulse width, 4-s acquisition time, and a probe temperature of 19 °C. Medium-resolution mass spectra were recorded on a Hewlett-Packard 5980A instrument (electron energy 70 eV, source temperature 210 °C) and high resolution spectra on a Kratos MS50TCTA using a DS55 data system under FAB conditions (ion current 50 μA at 6 V).

Microanalyses were performed by Guelph Chemical Laboratories.

Preparation of $D_3^{PhCr(CO)_3}$ and Other Tricarbonylchromium Complexes. The following method was used for the synthesis of all of the new tricarbonylchromium compounds prepared in this study.

Under a N_2 atmosphere D_3^{Ph} (I) (2.0 g, 5 mmol) and $Cr(CO)_6$ (5.0 g, 22.5 mmol) were dissolved in dry dibutyl ether (120 mL)

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[12] Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 000.

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[14] Seyferth, D.; Alleston, D. L. *Inorg. Chem.* **1963**, *2*, 417.

containing a little tetrahydrofuran (15 mL) and the solution was heated under reflux for 120 h. The solution was cooled and passed through a short column of Florisil/Celite to remove the small amount of insoluble decomposition product. Volatile materials were removed under vacuum, and the yellow residue was recrystallized from benzene: yield 3.95 g, 97%; mp 148–150 °C (under N_2); IR (Nujol) 1970 (s), 1890 (s), 1260 (sh), 1020 (s), 775 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 0.42 (3 H), 4.26–5.25 (5 H); mass spectrum, selected *m/e* (relative abundance) 816 (M^+, 8.0), 732 (M^+ – 3CO, 57.3), 596 (M^+ – Cr $(CO)_6$, 54.8), 460 (M^+ – $Cr_2(CO)_9$, 100). Anal. Calcd for $C_{30}H_{24}O_{12}Si_3Cr_3$: C, 44.12; H, 2.94; Si, 10.29; Cr, 19.12. Found: C, 43.15; H, 2.93; Si, 9.63; Cr, 18.88.

Physical Data for Other New Compounds. $D_3^{PhCr(CO)_3}$ (II): mp 218–220 °C; IR (Nujol) 1970 (s), 1890 (s), 1260 (sh), 1020 (s), 785 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 0.56 (2 H), 0.59 (1 H), 4.12–5.23 (5 H); mass spectrum, selected *m/e* (relative abundance) 816 (M^+, 11.2), 732 (M^+ – 3CO, 70), 620 (M^+ – 7CO, 81.6), 460 (M^+ – $Cr_2(CO)_9$, 100).

$D_4^{PhCr(CO)_3}$ (III): mp 244–248 °C; IR (Nujol) 1965 (s), 1880 (s), 1265 (sh), 1095 (s), 780 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 0.60 (3 H), 4.37–5.32 (5 H); mass spectrum, selected *m/e* (relative abundance) 1088 (M^+, 8), 732 (M^+ – $Cr_2(CO)_9$, 22.5), 648 (M^+ – $Cr_2(CO)_{12}$, 69), 596 (M^+ – $Cr_3(CO)_{12}$, 100). Anal. Calcd for $C_{40}H_{42}O_{16}Si_4Cr_4$: C, 44.12; H, 2.94; Si, 10.29; Cr, 19.12. Found: C, 43.6; H, 2.99; Si, 10.03; Cr, 18.84.

$(CH_3O)_3SiC_6H_5Cr(CO)_3$: mp 42 °C; IR (Nujol) 1985 (s), 1912 (s), 1090 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 3.42 (9 H), 4.16–5.14 (5 H); mass spectrum, selected *m/e* (relative abundance) 334 (M^+, 30.4), 250 (M^+ – 3CO, 100). Anal. Calcd for $C_{12}H_{14}O_6SiCr$: C, 43.11; H, 4.19; Cr, 15.57. Found: C, 43.61; H, 4.38; Cr, 15.53.

Hydrosilation Reactions. Reactions were carried out in batches in thick walled tubes, sealed under vacuum. Each tube was filled with nitrogen and then charged with triethoxysilane (0.46 mL, 2.5 mmol), *trans*-1,3-pentaidene (0.25 mL, 2.5 mmol), and catalyst (0.025 mmol for the monomeric catalysts and 0.008 mmol for the trimer). After being sealed under vacuum, the tubes were heated in a temperature controlled oil bath at 80 °C. Several identical tubes were prepared for each catalyst, and one tube of each catalyst was removed at intervals for analysis. Unconsumed reactants were removed by distillation under vacuum at room temperature, and then the product mixture was stripped off under vacuum at 80 °C and collected for quantitative analysis. Product analysis was effected by GC on a 6% Chrom W column (3 m × 3 mm) at an initial temperature of 90 °C and increasing at 16 °C/min.

The structures of the products were established by 2D ^1H NMR, at 200 MHz on the product mixture dissolved in C_6D_6. Compound 1: CH_3CH_2 (triplet, δ 0.09); $SiCH_2$ (doublet of doublets, δ 1.68); CH_3CH_2 (pseudoquintet of doublets, δ 2.05); CCH_2CH= (quartet of triplets, δ 5.61); $SiCH_2CH$= (multiplet overlapping with analogous peaks from compound 2, δ 5.40). Compound 2: $CH_3CH(Si)$ (doublets, δ 1.30); CH_3CH= (doublet of triplets, δ 1.63); $SiCH(CH_3)$ (quintet of quintets, δ 1.85); $Si(CH_3)CHCH$= (see compound 1, δ 5.40); CH_3CH= (doublet of doublets of quartets, δ 5.76).

The identity of the products was further confirmed by GC–MS. Mass spectra, selected *m/e* (relative abundance): compound 1, 232 (M^+, 2.98), 217 (M^+ – CH_3, 5); compound 2, 232 (1.46), 217 (0.40).

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Registry No. 1, 40962-01-4; **2**, 40962-06-9; D_3^{Ph} (I), 3424-57-5; D_3^{Ph} (II), 6138-53-0; D_4^{Ph} (I), 4885-37-4; D_4^{Ph} (II), 5131-04-4; D_4^{Ph} (III), 15331-54-1; D_4^{Ph} (IV), 4885-39-6; $D_3^{PhCr(CO)_3}$ (I), 98679-12-0; $D_3^{PhCr(CO)_3}$ (II), 98719-22-3; $D_4^{PhCr(CO)_3}$ (I), 98679-13-1; $D_4^{PhCr(CO)_3}$ (II), 98719-23-4; $D_4^{PhCr(CO)_3}$ (III), 98719-24-5; $D_4^{PhCr(CO)_3}$ (IV), 98719-25-6; $Cr(CO)_6$, 13007-92-6; $(C_6H_6)Cr(CO)_3$, 12082-08-5; $(CH_3)_3SiC_6H_5Cr(CO)_3$, 33248-13-4; $(CH_3O)_3SiC_6H_5Cr(CO)_3$, 98679-14-2; $PhSi(CH_3O)_3$, 2996-92-1; $(EtO)_3Si$, 998-30-1; *trans*-1,3-pentadiene, 2004-70-8.

Carbonyl Insertion Reactions. 2. Alkali Ion Effect on Hydride Migration in $(HFe(CO)_4)^-$

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Molecular orbital calculations indicate that alkali ion coordination to a carbonyl ligand of $(HFe(CO)_4)^-$ will promote hydride migration to that carbonyl ligand to form a formyl. Coordination of the alkali removes charge from the parent complex and alters the nature of the highest occupied molecular orbital in the formyl so as to lower its energy relative to other molecular orbitals and to remove its C–H antibonding character. The properties of the highest occupied molecular orbital are primarily responsible for the great instability of the formyl structure $((CO)_3FeCHO)^-$. In order to be effective the alkali must be coordinated to the formyl oxygen. Li^+ coordinates more strongly with an equatorial oxygen than with an axial oxygen.

Introduction

The rearrangement of a transition-metal hydride to a formyl has not been observed although alkyls readily migrate to an adjacent carbonyl to form an acyl.[1-4] This is often referred to as a carbonyl insertion reaction. Carbonyl insertion reactions are important in heterogeneous and homogeneous catalysis as well as in stoichiometric organometallic synthesis. Transition-metal formyls have been prepared by other routes,[5] but they are generally of only marginal stability with room-temperature half-lives of seconds to a few days.[2] None-the-less the catalytic reduction of CO by H_2 has been proposed to proceed via formyl intermediates.[6-8]

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