reactions shows that, except in the reaction with Co_{aq}^{2+}, the apparent activation entropies are more negative for $CoOH_{aq}^{2+}$ than for Co_{aq}^{3+}; this is counter to the effect anticipated from increased entropy in the transition state due to the dissociation of a water molecule on formation of the bridge[26,28] and it may be that the mechanisms of these reactions of $CoOH_{aq}^{2+}$ have substantial SN2 character.[29] It is unfortunate that the relatively large uncertainty in the estimated[5,27] entropy of acid dissociation (eq 6) somewhat reduces the usefulness of this criterion[28] in cases involving aquocobalt(III) as a reactant, especially at high ionic strengths.

A plot of $\Delta G_{-1}^{\ddagger}$ *vs.* $\Delta G°_{estd}$ for the reactions of $CoOH_{aq}^{2+}$ with $0 \lesssim -\Delta G°_{estd} \lesssim 20$ kcal mol^{-1} is also approximately linear with a slope of $\sim$0.23. This average slope may be accounted for in the same general terms as were used above to interpret the corresponding deviations in the Co_{aq}^{3+} reactions. We note, however, that the reaction between $CoOH_{aq}^{2+}$ and Fe_{aq}^{2+} is slower (by about two orders of magnitude) than would be predicted on the basis of the free energy changes for the other reactions. This behavior is similar to that noted above in the corresponding reaction with Co_{aq}^{3+}. The observation of anomalously slow reactions with iron(II) points to the appearance of a new rate-determining step in the activation process as the overall free energy change increases through the series.[9a,28,30] It seems likely that precursor complex formation[9a,31] coupled with conversion of the $Co_{aq}^{3+}(t_{2g}^{6})$[5,25] to some high-spin form accounts for this insensitivity of rate to an increasing driving force for electron transfer. It would be of considerable interest to test this hypothesis in other cobalt(III) reactions involving comparatively large overall free energy changes.

The arguments presented above for reactions in general do not, of course, give any detailed information concerning the electronic and other changes accompanying the transfer of Co_{aq}^{3+} from the ground state to a configuration appropriate for electron transfer. However, any high-spin form of cobalt(III) involved in the reactions must be more strongly oxidizing than the ground-state $Co_{aq}^{3+}(t_{2g}^{6})$.[5,32,33] Available evidence[5,34] suggests that spin-multiplicity restrictions are only of minor importance in the energetics of outer-sphere reactions between cobalt complexes in which *small* overall free energy changes are involved, but the extent to which such restrictions contribute to the energetics of these reactions as a whole cannot be evaluated at the present time.

Acknowledgments.—We wish to thank Drs. R. D. Gillard, N. Sutin, and A. G. Sykes for valuable discussion.

(28) N. Sutin, *Electrochim. Acta*, **13**, 1175 (1968).

(29) B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, **6**, 1948 (1967); J. H. Espenspn, *ibid.*, **9**, 1380 (1970).

(30) R. C. Patel, R. E. Ball, J. F. Endicott, and R. G. Hughes, *ibid.*, **9**, 23 (1970), and references therein.

(31) (a) For recent discussions of the estimation of free energy changes in redox reactions see G. Davies, N. Sutin, and K. O. Watkins, *J. Amer. Chem. Soc.*, **92**, 1892 (1970), and ref 9a. (b) For an estimate of the equilibrium constant for precursor complex formation between $Ru(NH_3)_5H_2O_{aq}^{2+}$ and $CrCl^{2+}$ see W. G. Movius and R. G. Linck, *ibid.*, **92**, 2677 (1970).

(32) B. Warnqvist, *Inorg. Chem.*, **9**, 682 (1970).

(33) D. A. Johnson and A. G. Sharpe, *J. Chem. Soc. A*, 798 (1966).

(34) R. Farina and R. G. Wilkins, *Inorg. Chem.*, **7**, 514 (1968).

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada

Silicon–Transition Metal Chemistry. III. An Investigation of the Reaction between Trichlorosilane and Cyclopentadienyldicarbonyliron Dimer[1]

By W. JETZ and W. A. G. GRAHAM*

Received July 13, 1970

The reaction of $[C_5H_5Fe(CO)_2]_2$ with Cl_3SiH in the temperature range 110–180° yields four products: $Cl_3SiFe(CO)_2C_5H_5$ (**1**), $(Cl_3Si)_2FeH(CO)C_5H_5$ (**2**), $[C_5H_5Fe(CO)_3]^+[(Cl_3Si)_2Fe(CO)C_5H_5]^-$ (**3**), and $[C_5H_5Fe(CO)_3]^+[FeCl_4]^-$ (**4**). The critical dependence of relative yields on temperature has been investigated. Compound **2** is an acid in acetonitrile ($pK_a \simeq 2.6$) and is therefore a stronger acid in that solvent than the common mineral acids except perchloric. Compound **3** contains the anion of **2**, which has also been isolated as its tetraphenylarsonium salt. Methylcyclopentadienyl derivatives of **1**–**4** have also been prepared.

Introduction

There are innumerable cases in chemistry where the same reactants yield different products at different reaction conditions. Thus, the reaction between iron pentacarbonyl and trichlorosilane under ultraviolet irradiation below room temperature yields $Cl_3SiFeH(CO)_4$,[2] while heating these reagents in a sealed tube affords $(Cl_3Si)_2Fe(CO)_4$ at about 140° and $[Cl_2SiFe(CO)_4]_2$ above 160°.[3]

The reaction described in this paper yields four isolable products in amounts which are critically dependent upon reaction times and temperatures. Since these products were novel and inaccessable at the time by any other route, an extensive study of the reaction and the products was carried out.

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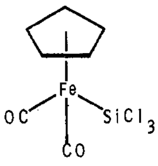
(1) Part II: W. Jetz and W. A. G. Graham, *Inorg. Chem.*, in press.

(2) W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 3375 (1969); *Inorg. Chem.*, **10**, 4 (1971).

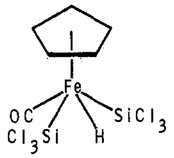
(3) W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **89**, 2773 (1967); a full paper will shortly be submitted.

Results and Discussion

Over a range of reaction conditions, π-cyclopentadienyldicarbonyliron dimer, $[C_5H_5Fe(CO)_2]_2$, reacts with trichlorosilane to form four products. Three of these are formulated as shown in formulas **1**–**3**, while **4** is the tetrachloroferrate salt of the cyclopentadienyltricarbonyl iron cation, $[C_5H_5Fe(CO)_3]^+[FeCl_4]^-$. The influence of reaction temperature on the yield of these products is discussed in the final section of this paper.



1



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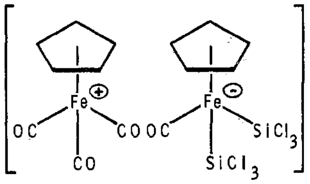

3

Compound **1**, $Cl_3SiFe(CO)_2C_5H_5$, was the anticipated product of the reaction, in analogy with the formation of $Cl_3SiMn(CO)_5$ from $Mn_2(CO)_{10}$, and has been reported previously.[3] It is very stable thermally, and undergoes no further reaction with trichlorosilane at temperatures up to 180°.

In the initial studies of this reaction, compound **2**, $(Cl_3Si)_2FeH(CO)C_5H_5$, was formed in only milligram quantities; a detailed study of the reaction was undertaken to obtain quantities sufficient to permit a full characterization and a more extensive study of its reactions and properties. The results of an X-ray crystallographic structure determination on **2** have recently been reported;[4] the hydridic hydrogen was not located, but the results are consistent with the idealized trans-square-pyramidal geometry depicted here and assumed earlier.[2] Compound **2** has also been formed from **1** in a photochemical reaction with trichlorosilane below room temperature.[2]

The very pale yellow crystalline compound is soluble in hydrocarbon solvents but ionizes in acetone to a 1:1 electrolyte. This unusual behavior in acetone is due to the formation of the $(Cl_3Si)_2Fe(CO)C_5H_5^-$ ion, as infrared studies described below will show. The tetraphenylarsonium salt of this anion can in fact be prepared from **2** by the reaction

$$(C_6H_5)_4As^+Cl^- + \mathbf{2} \longrightarrow [(C_6H_5)_4As]^+[(Cl_3Si)_2Fe(CO)C_5H_5]^- + HCl$$

Compound **3**, $[C_5H_5Fe(CO)_3]^+[(Cl_3Si)_2Fe(CO)C_5H_5]^-$ is sparingly soluble in dichloromethane but very soluble in acetone where it is a 1:1 electrolyte.[5,6] The relation

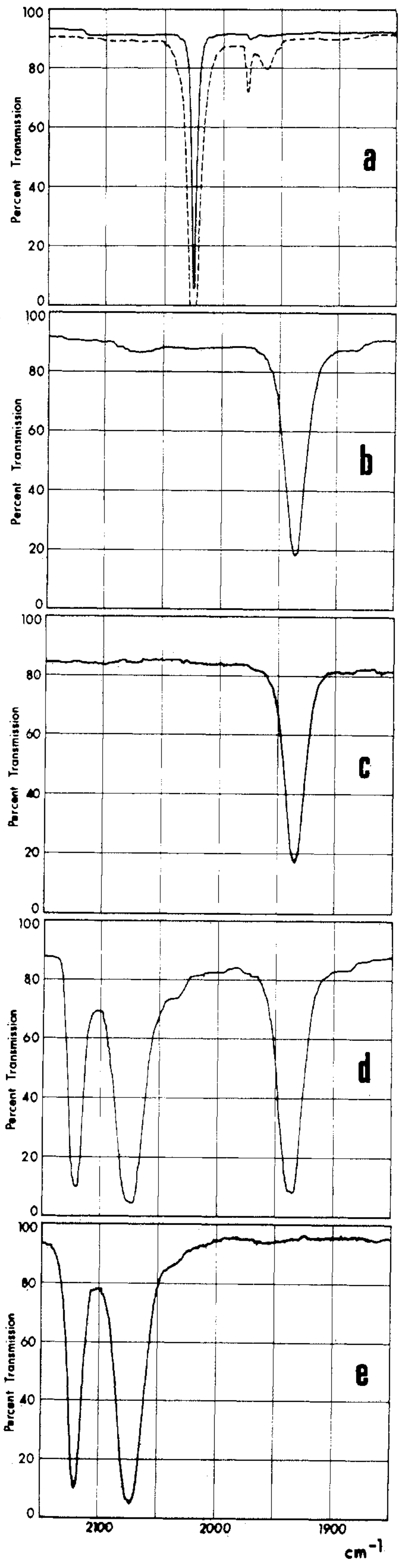

Figure 1.—Carbonyl stretching region of infrared spectra: (a) $(Cl_3Si)_2FeH(CO)C_5H_5$ (**2**) in *n*-hexane; (b) $(Cl_3Si)_2FeH(CO)C_5H_5$ (**2**) in acetone; (c) $[(C_6H_5)_4As]^+[(Cl_3Si)_2Fe(CO)C_5H_5]^-$ in acetone; (d) $[C_5H_5Fe(CO)_3]^+[(Cl_3Si)_2Fe(CO)C_5H_5]^-$ (**3**) in acetone; (e) $[C_5H_5Fe(CO)_3]^+[FeCl_4]^-$ (**4**) in acetone.

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[4] L. Manojlovic-Muir, K. W. Muir, and J. A. Ibers, *Inorg. Chem.*, **9**, 447 (1970).

[5] Compound **3** was initially wrongly formulated as having three carbonyl groups and an iron–iron bond.[6] We are grateful to Professor P. M. Treichel and Dr. K. W. Barnett for pointing out that the $C_5H_5Fe(CO)_3^+$ cation might be involved.

[6] W. A. G. Graham and W. Jetz, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. 82M.

of **3** to **2** is shown by the conversion of **3** to the same tetraphenylaronsium salt

$$(C_6H_5)_4As^+Cl^- + \mathbf{3} \longrightarrow$$
$$(C_6H_5)_4As^+[(Cl_3Si)_2Fe(CO)C_5H_5]^- + ClFe(CO)_2C_5H_5 + CO$$

This reaction requires 1 hr at room temperature in acetone, no doubt due to the slow displacement of carbon monoxide from $C_5H_5Fe(CO)_3^+$ by chloride ion.

Compound **4**, $[C_5H_5Fe(CO)_3]^+[FeCl_4]^-$, is insoluble in dichloromethane but dissolves in acetone, in which it decomposes rapidly. The compound was rather intractable, but its methylcyclopentadienyl analog could be isolated in a purer form, and the latter was characterized by analysis and magnetic measurements in preference to **4**. Methylcyclopentadienyl derivatives of **1**, **2**, and **3** were also prepared.

Infrared Spectra.—The spectra of **2** in hexane (Figure 1a) and in acetone (Figure 1b) reflect the dissociation of the compound in acetone solution. Comparison of Figures 1b and 1c shows that the $(Cl_3Si)_2Fe(CO)C_5H_5^-$ anion is produced in both cases; the ionization of **2** is thus due to transfer of the iron-bonded hydrogen as a proton to the relatively basic solvent. Figures 1d and 1e are consistent with the formulations of **3** and **4**, respectively. Band positions in Figure 1 show the expected trend of increasing frequency in moving from anionic to neutral to cationic species.

A more concentrated solution of **2** (dashed line in Figure 1a) shows a sharp band at 1976 cm^{-1} assigned as a ^{13}CO vibration; the isotopic shift of 49 cm^{-1} may be compared with the calculated shift of 45 cm^{-1}. The broader band at 1960 cm^{-1} in the same spectrum has been assigned as ν(Fe–H), and this has been confirmed by observation of ν(Fe–D) in $(Cl_3Si)_2FeD(CO)_2C_5H_5$ at 1414 cm^{-1}.[7]

Carbonyl stretching frequencies for all compounds are listed in Table I. A point worth comment is the occurrence of additional bands in the neutral methylcyclopentadienyl compounds; such shoulders or small band splittings could not be observed in the ionic compounds due to band broadening in the polar solvent which was required to dissolve them. Two bands separated by 4 cm^{-1} were observed in $(Cl_3Si)_2FeH(CO)C_5H_4CH_3$, for example. The most reasonable explanation for this, we suggest, is the presence of conformational isomers having the methyl group in different locations with respect to the rest of the molecule. The splitting would thus be of similar origin to that postulated in related molecules such as $Cl_2CH_3SiFe(CO)_2C_5H_5$ having different substituents on the silicon atom.[3,8] We are unable to account for the extra shoulder in the well-known compound $ClFe(CO)_2C_5H_5$,[9] which we had occasion to prepare in this work, but are convinced that it is genuine.

TABLE I

INFRARED CARBONYL STRETCHING FREQUENCIES[a] AND NMR DATA[b]

Compound	ν(CO), cm^{-1}			$\tau(C_5H_5)$, ppm
$Cl_3SiFe(CO)_2C_5H_5$ (**1**)	2039 s	1995 vs	. . .	4.87
$(Cl_3Si)_2FeH(CO)C_5H_5$ (**2**)	2025[c]	. . .	. . .	4.57[d]
$[C_5H_5Fe(CO)_3]^+[(Cl_3Si)_2Fe(CO)C_5H_5]^-$ (**3**)	2121 s	2074 vs	1936 s	4.25, 5.37[e]
$[C_5H_5Fe(CO)_3]^+[FeCl_4]^-$ (**4**)	2121 s	2074 vs	. . .	. . .
$[C_5H_5Fe(CO)_3]^+[B(C_6H_5)_4]^-$[f]	2121 s	2074 vs	. . .	3.87[g]
$[(C_6H_5)_4As]^+[(Cl_3Si)_2Fe(CO)C_5H_5]^-$	. . .	. . .	1936	5.40
$ClFe(CO)_2C_5H_5$	2055 s	2050 sh	2013 vs	4.99
$Cl_3SiFe(CO)_2C_5H_4CH_3$[h]	2034 s	1992 vs	. . .	. . .
$(Cl_3Si)_2FeH(CO)C_5H_4CH_3$[i]	2023 ms	2019 s	. . .	. . .[k]
$[C_5H_4CH_3Fe(CO)_3]^+[(Cl_3Si)_2Fe(CO)C_5H_4CH_3]^-$[j]	2118 s	2070 vs	1934 s	. . .[l]
$[C_5H_4CH_3Fe(CO)_3]^+[FeCl_4]^-$[j]	2118 s	2070 vs	. . .	. . .
$ClFe(CO)_2C_5H_4CH_3$	2051 s	2047 sh	2008 vs	. . .

[a] Infrared spectra of covalent compounds in *n*-hexane; ionic compounds in acetone. [b] In acetonitrile except as noted. [c] At 1936 cm^{-1} in acetone (*cf.* Figure 1a and b). [d] With a singlet of *ca.* 7% intensity at 5.38 ppm and a high-field proton at 21.64 ppm (*cf.* Figure 2 and text). In acetone, no high-field proton was observed and $\tau(C_5H_5)$ varied with time over the range τ 5.3–5.4. [e] Integrating 1:1; shifting in acetone to 3.85 and 5.40 ppm. [f] Prepared by the method of A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961). [g] In acetone. [h] Infrared in *n*-hexane showed two medium shoulders at 2040 and 1996 cm^{-1} presumed due to a conformational effect of the substituted cyclopentadienyl ring. The compound melted below room temperature and was not analyzed. [i] Extra band assumed to be due to conformational effect; see text. [j] In dichloromethane. [k] In CCl_4, $\tau(CH_3)$ at 7.8 ppm; ring protons as triplets centered at τ 4.7 and 5.0 ppm. [l] In acetone-d_6, $\tau(CH_3)$ at 8.3 (slightly broad) and 8.65 ppm (sharp); ring protons as a broad singlet at τ 4.6 ppm and two triplets centered at τ 6.0 and 6.25 ppm.

Nmr Spectra.—Chemical shift data for the cyclopentadienyl derivatives are given in Table I. One observes a shift to higher τ values for the C_5H_5 protons in passing from cationic through neutral to anionic complexes; higher electron density in the complex is delocalized and results in greater shielding of ring protons. Other workers have noted a similar trend in a neutral[10] or cationic[11] species as carbon monoxide is replaced by phosphines or other ligands which are presumed to be poorer π acceptors (and also better σ donors[12]). With this interpretation in mind, it is instructive to consider the following series of compounds with their $\tau(C_5H_5)$ values: $Cl_3SiFe(CO)_2C_5H_5$, 4.87; $ClFe(CO)_2C_5H_5$, 4.99; $(CH_3)_3SiFe(CO)_2C_5H_5$, 5.33.[13] This emphasizes the contrast in electronic properties of trihalo- and trialkyl-group IV elements as ligands, a conclusion reached also from infrared studies.[12] The strongly acid character of **2**, to be discussed shortly, can be rationalized if the trichlorosilyl ligand is regarded as extremely efficient in withdrawing electron density from the metal.

The high-field region of the nmr spectrum of **2** is shown in expanded form in Figure 2. The satellites flanking the main resonance at τ 21.64 are of particular interest. The nuclei of spin $^1/_2$ to which the unique proton might couple are ^{13}C (1.11% natural abundance), ^{29}Si (4.70%), and ^{57}Fe (2.25%). The 20-Hz coupling in Figure 2 is taken as $J(^{29}Si–Fe–H)$

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[7] The deuteride was prepared by ultraviolet irradiation of $Cl_3SiFe(CO)_2C_5H_5$ with Cl_3SiD.

[8] In the case of $(Cl_3Si)_2FeH(CO)C_5H_4CH_3$, the possibility of cis and trans isomers might be invoked to explain the splitting. We consider this unlikely, since it would be equally possible in **2** where a single sharp band is observed; furthermore, the cis–trans explanation would not account for the shoulders in $Cl_3SiFe(CO)_2C_5H_4CH_3$.

[9] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

[10] R. B. King, *Inorg. Chim. Acta*, **2**, 454 (1968).

[11] P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, **5**, 1177 (1966). These authors report $\tau(C_5H_5)$ of $[C_5H_5Fe(CO)_3]^+[PF_6]^-$ as 3.86 in acetone-d_6, in excellent agreement with the values of Table I *in the same solvent*. However, τ for the cation increases by 0.40 ppm in acetonitrile, indicative of an appreciable change in solvent–solute interaction. In contrast, τ for $(Cl_3Si)_2Fe(CO)C_5H_5^-$ decreases by 0.03 ppm when acetonitrile is substituted for acetone.

[12] W. A. G. Graham, *ibid.*, **7**, 315 (1968).

[13] The value for the $(CH_3)_3Si$– derivative was measured in CH_2Cl_2 and compares well with the value 5.36 recently reported in $CHCl_3$: R. B. King and K. H. Pannell, *ibid.*, **7**, 1510 (1968).

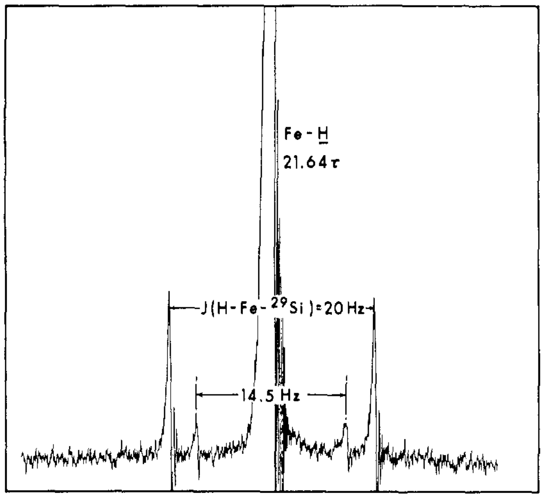

Figure 2.—High-field region of the 100-MHz nmr spectrum of $(Cl_3Si)_2FeH(CO)C_5H_5$ (**2**) in acetonitrile at room temperature. On intensity grounds, the 20-Hz coupling is assigned as $J(^{24}Si\text{–}Fe\text{–}H)$ and the 14.5-Hz coupling as $J(^{57}\mathrm{Fe\text{–}H})$.

and the 14.5-Hz coupling as $J(^{57}\mathrm{Fe\text{–}H})$. The observation of a single proton–silicon coupling does not establish that the two silicons in the molecule are magnetically equivalent, since a second coupling constant might be too small to detect. A consideration of satellite intensities is required to establish the point. The spectrum in fact approximates the intensity ratio 4.7:1.1:88.4:1.1:4.7 calculated for the above assignment assuming magnetic equivalence of the silicon atoms. This suggests (but does not prove) that the silicons are symmetrically equivalent as well, and is thus consistent with a trans structure in solution (as seems likely in the solid state[4]). Moreover, the trans structure is found in the structurally related $Cl_3Sn(Cl_3Si)Mn(CO)_2C_5H_5$ in solution.[1]

Although there is no reason to suppose that **2** does not have the trans structure in solution, it should be noted that the spectrum of Figure 2 could also arise from a cis isomer by rapid averaging of the couplings, in a fashion similar to that in $HW(CO)_3C_5H_5$.[14]

Acidic Character of $(Cl_3Si)_2FeH(CO)C_5H_5$.—The first indication of the acidity of **2** was the absence of a high-field nmr signal in acetone. The signal is observed in hydrocarbon solvents or in acetonitrile, a weakly basic solvent that has been used in the study of strong acids;[15] acetonitrile was therefore used for further studies of the acidity of **2**.

An acetonitrile solution of **2** shows resonances at τ 4.57 and 21.64 in a 5:1 intensity ratio, with a third weak absorption (relative intensity *ca.* 0.3) at τ 5.38. The latter value agrees almost exactly with the C_5H_5 resonance (τ 5.40) observed in the salt $[(C_6H_5)_4As]^+[(Cl_3Si)_2Fe(CO)C_5H_5]^-$ and is considered to be due to the dissociation of **2** according to the equation,

$$(Cl_3Si)_2FeH(CO)C_5H_5 + B \rightleftharpoons BH^+ + (Cl_3Si)_2Fe(CO)C_5H_5^- \quad (1)$$

where B is the solvent. As successive small aliquots of pyridine are added to a solution of **2** in CH_3CN, the τ 4.57 band decreases in intensity (finally disappearing) while the τ 5.38 band increases, confirming the interpretation above. The equilibrium constant for eq 1 is the acid dissociation constant, K_a, for **2** in CH_3CN; since concentrations of the acid and its anion are proportional to peak intensities, pK_a can be estimated as 2.6.[16] It is thus stronger than HBr or H_2SO_4 in CH_3CN ($pK_a = 5.5$ and 7.3, respectively[15]) but weaker than perchloric acid, which is reported to be completely dissociated.[15] Conductivity measurements of **2** in acetonitrile led to a similar pK_a value.[17]

The hydride **2** is thus second in strength to perchloric acid among the acids so far measured in acetonitrile.[18,19] It appears to be unique as a stable, crystalline, nonoxidizing acid that is soluble even in hexane. It is of course unsuitable for use in protic solvents, which attack the trichlorosilyl groups.

We have recently reported the acidic character of several other silyl transition metal hydrides, of which the strongest acid was $Cl_3SiHFe(CO)_4$.[1] The position of **2** in the series of acids previously given was established by the displacement reaction in dichloromethane

$$(Cl_3Si)_2FeH(CO)C_5H_5 + (C_2H_5)_4N^+[Cl_3SiFe(CO)_4]^- = (C_2H_5)_4N^+[(Cl_3Si)_2Fe(CO)C_5H_5]^- + Cl_3SiFeH(CO)_4 \quad (2)$$

When the compounds on the left-hand side were mixed in dichloromethane solution with the salt in slight excess, infrared spectroscopy showed that **2** was converted quantitatively to its anion. When solutions of the product of eq 2 were mixed, there was no change. The stronger acid is thus **2**, and the previous order of acid strengths can be extended as

$$(Cl_3Si)_2FeH(CO)C_5H_5 > Cl_3SiFeH(CO)_4 > (C_6H_5)_3SiFeH(CO)_4 > Cl_3SiMnH(CO)_2C_5H_5 > (C_6H_5)_3SiMnH(CO)_2C_5H_5$$

A further point of interest is apparent from Figure 2 but should be mentioned specifically. The observation of coupling constants involving the high-field proton requires that reversible proton transfer to the solvent, as in eq 1, be slow on the nmr time scale.

Temperature Dependence of the Products.—As noted previously, yields of the products **1**–**4** are very sensitive to reaction times and temperatures. All reactions were carried out in sealed Carius tubes in view of the low boiling point of Cl_3SiH (32°), and it is likely that high pressures of carbon monoxide and hydrogen are generated which are important in stabilizing and interconverting various intermediates and products.

In a reaction at 130° for 30 min, all $[C_5H_5Fe(CO)_2]_2$ is consumed, as indicated by the color change from brown to yellow. The products from this reaction contain mainly **3**, a considerable amount of **2**, and a small quantity of **1**. If a similar reaction mixture is heated at the same temperature for a prolonged

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(14) J. W. Faller, A. S. Anderson, and C. Chen, *Chem. Commun.*, 719 (1969).

(15) I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.*, **83**, 3927 (1961).

(16) The pK_a value of 2.6 is based on an experiment in which a 100-mg sample of **2** in 0.40 ml of CH_3CN gave a ratio of 154:9.5 for the intensities of the C_5H_5 resonances of **2** and its anion.

(17) We thank Professor B. Kratochvil and Dr. H. Yeager of this department for carrying out these measurements. The conductivity of these solutions exhibited noticeable drift over the extended times required for thermal equilibration. The drift is attributed to the polymerization of CH_3CN known to be brought about by strong acids. Acetone solutions of **2** become very viscous on standing due to a similar process.

(18) Although another carbonyl hydride, $HCo(CO)_4$, is known to be a strong acid in aqueous solution ($pK_a \simeq 0$),[19] it has not been examined in acetonitrile. Its dissociation in the less basic solvent should decrease, as does that of HBr and H_2SO_4.

(19) W. Hieber and W. Hubel, *Z. Elektrochem.*, **57**, 235 (1953).

TABLE II

MICROANALYTICAL DATA, COLORS, AND MELTING POINTS

Compound	Mp,[a] °C	Color	% calcd C	% calcd H	% calcd Cl	% found C	% found H	% found Cl
$Cl_3SiFe(CO)_2C_5H_5$ (**1**)	128–130	Yellow	27.00	1.62	34.15	27.06	1.89	34.49
$(Cl_3Si)_2FeH(CO)C_5H_5$ (**2**)	130–131	Pale yellow	17.21	1.44	50.78	17.27	1.78	50.28
$[C_5H_5Fe(CO)_3]^+[(Cl_3Si)_2Fe(CO)C_5H_5]^-$ (**3**)[c]	>220[b] dec	Yellow	27.00	1.62	34.15	27.03	1.73	34.17
$[(C_6H_5)_4As]^+[(Cl_3Si)_2Fe(CO)C_5H_5]^-$ [d]	142–145	Yellow	44.97	3.14	26.55	44.99	3.19	26.70
$ClFe(CO)_2C_5H_5$	88–92	Red	39.58	2.37	16.69	38.94	2.33	16.28
$(Cl_3Si)_2FeH(CO)C_5H_4CH_3$	121–122	White	19.42	1.86	49.14	19.49	1.99	48.57
$[CH_3C_5H_4Fe(CO)_3]^+[(Cl_3Si)_2Fe(CO)C_5H_4CH_3]^-$	>105 dec	Yellow	29.53	2.17	32.68	29.59	2.17	32.61
$[CH_3C_5H_4Fe(CO)_3]^+[FeCl_4]^-$	. . .	Yellow	24.94	1.70	34.03	26.42	2.03	34.05
$ClFe(CO)_2C_5H_4CH_3$	49–51	Red	42.43	3.12	15.65	42.47	3.11	15.97

[a] Kofler hot stage. [b] Sealed capillary. [c] Calcd: Fe, 17.93; Si, 9.02. Found: Fe, 17.49; Si, 8.27. [d] Calcd: O, 2.00; Fe, 6.97. Found: O, 2.11; Fe, 6.86.

period of time, the products are mainly **1**, trace amounts of **2**, and some **3**. In a very narrow range of reaction conditions (*e.g.*, 120–130° for 15 min), the products contain considerable amounts of unreacted $[C_5H_5Fe(CO)_2]_2$, but compound **4**, $[C_5H_5Fe(CO)_3]^+[FeCl_4]^-$, may be isolated in appreciable quantities. There is evidence for the presence of other products which have not been characterized. For example, when excess unreacted Cl_3SiH is distilled from the reaction mixture under vacuum and stored in a closed container at room temperature, the solution becomes slowly brown and eventually precipitates flaky insoluble material, which may result from decomposition of $HFe(CO)_2C_5H_5$. Above 170° the solid products, after removal of Cl_3SiH, contain an oily material which does not show carbonyl bands; it may be a polysilane or polycyclopentadiene compound.

A study of reaction products as a function of temperature for a fixed reaction time of 30 min was carried out. By careful standardization of all details, reproducible results were obtained for the heterogeneous reaction. Each reaction involved 5.65 mmol of $[C_5H_5Fe(CO)_2]_2$ and a measured excess of trichlorosilane, which served also as the solvent. Yields of products were determined by infrared spectroscopy and are as shown in Figure 3. Between 130 and 150°, compounds **1**–**3** accounted for 70–80% by weight of the nonvolatile reaction products; the figure dropped to 50% at 180°. The balance was dichloromethane-insoluble solid material without carbonyl groups and an oily substance.

It is important to realize that Figure 3 does *not* represent a normal kinetic study and that the conclusions that can be drawn from it are much more limited. The main purpose of this study, in which equal amounts of starting materials reacted for a constant period of time at different temperatures, was to determine the temperature range for the optimum yields of the individual components at reasonable reaction times. However, several significant points emerge from Figure 3. First, the use of 5.65 mmol of $[C_5H_5Fe(CO)_2]_2$ yields a combined molar quantity of 5.2–5.6 mmol of compounds **1**–**2** at all temperatures above 130°. Below 130° a considerable amount of unreacted $[C_5H_5Fe(CO)_2]_2$ is present. Second, there appears to be no simple additive relationship between any two components. Third, irregularities in all three curves coincide in the same temperature range. It is not profitable to speculate on the mechanism by which **2** and **3** are ultimately converted to **1**. In a separate experiment, it was shown that **1** and **2** were not formed when **3** was allowed to react with Cl_3SiH at 180°; the processes involved are far from straightforward.

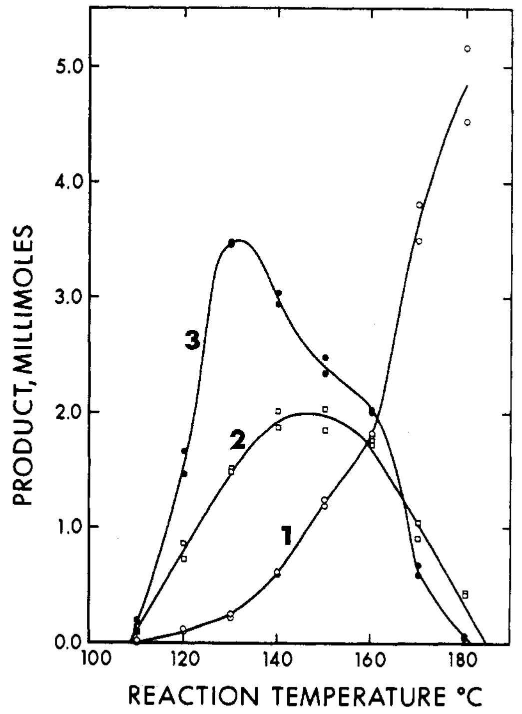

Figure 3.—Product variation with temperature in 30-min reactions between $[C_5H_5Fe(CO)_2]_2$ (5.65 mmol) and Cl_3SiH (excess). Each point represents a separate reaction carried out in a sealed Carius tube. Product **1** is $Cl_3SiFe(CO)_2C_5H_5$, product **2** is $(Cl_3Si)_2FeH(CO)C_5H_5$, and product **3** is $[C_5H_5Fe(CO)_3]^+[(Cl_3Si)_2Fe(CO)C_5H_5]^-$.

With other silanes such as CH_3Cl_2SiH, $(CH_3)_2ClSiH$, and $(CH_3)_3SiH$, $[C_5H_5Fe(CO)_2]_2$ does not yield methylsilyl analogs of **2** and **3**. These reactions become progressively slower with the increase in the number of methyl groups on the silane. If these reactions do proceed by a similar mechanism, then the reaction of the intermediates in subsequent steps is more rapid than their formation, and only the end products are obtained (*e.g.*, $CH_3Cl_2SiFe(CO)_2C_5H_5$, $(CH_3)_2ClSiFe(CO)_2C_5H_5$, and $(CH_3)_3SiFe(CO)_2C_5H_5$).[3]

Experimental Section

Cyclopentadienyldicarbonyliron dimer and the methylcyclopentadienyl analog were purchased from Alfa Inorganics, Inc., Beverly, Mass. Trichlorosilane was purchased from Pierce Chemical Co., Rockford, Ill.

Infrared spectra were measured by means of a Perkin-Elmer Model 337 spectrometer, and the carbonyl region was expanded by means of an external recorder (1 cm of chart paper $\approx$ 10 cm^{-1}, scanning rate 39 cm^{-1} min^{-1}, CO–DBr calibration). Nmr spectra were recorded at 60 MHz using a Varian A-56-60 instrument, with the exception of the high-field region of **2** (Figure 2) which was obtained at 100 MHz on a Varian HA 100 spectrometer. Peak areas were measured using the integrating feature of the instruments.

All reactions involving trichlorosilane at elevated temperature were carried out in Carius tubes of 60–70-ml volume. The reactants were sealed in these under vacuum at liquid nitrogen temperatures. The Carius tubes were carefully constructed and annealed; *sizable pressures are developed in the reactions, and appropriate precautions should be taken.* Analyses are given in Table II and were carried out in the microanalytical laboratory of this department and by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, West Germany.

Conductivities as listed in Table III were measured at room temperature using a Philips Type PR-9500 bridge and a cell with a constant of 0.28 cm^{-1}. The solvent was acetone which was dried over sodium carbonate and distilled from potassium permanganate.

TABLE III

CONDUCTIVITIES IN ACETONE SOLUTION

Compound	Concn, m*M*	Conductance, mhos cm^2 mol^{-1}
$Cl_3SiFe(CO)_2C_5H_5$ (**1**)[a]	1.26	3.1
	2.72	2.5
$(Cl_3Si)_2FeH(CO)C_5H_5$ (**2**)	1.01	150
	2.25	138
$[C_5H_5Fe(CO)_3]^+[(Cl_3Si)_2Fe(CO)C_5H_5]^-$ (**3**)	1.05	139
	2.35	127
$[(C_6H_5)_4As]^+[(Cl_3Si)_2Fe(CO)C_5H_5]^-$	1.05	119
	2.96	118
$[C_5H_5Fe(CO)_3]^+[B(C_6H_5)_4]^-$	1.07	125
	2.27	114
$ClFe(CO)_2C_5H_5$[a]	1.17	1.2
	3.91	0.6

[a] Values changed rapidly for 10 sec after dilution.

Trichlorosilyl(cyclopentadienyl)dicarbonyliron (1).—A sample of 2.0 g of $[C_5H_5Fe(CO)_2]_2$ (5.65 mmol) in 7.0 ml of Cl_3SiH (excess) was heated at 140° for 30 min, during which the reddish brown color of the reaction mixture changed to yellow. Excess Cl_3SiH was removed at reduced pressure and the residue was transferred to a Schlenk tube where it was extracted with several aliquots of warm pentane. The pentane was evaporated at reduced pressure and the yellow crystalline residue was sublimed at room temperature (0.01 mm) onto a water-cooled probe. This sublimation was slow and extended over several days. When sublimation ceased at room temperature, the combined sublimate was dissolved in a minimum of hot hexane, filtered, and cooled slowly in the refrigerator to form the crystalline product in 11% yield.

Hydridobis(trichlorosilyl)cyclopentadienylcarbonyliron (2).—The above sublimation was continued at 60° (0.01 mm). An off-white microcrystalline material sublimed slowly. Recrystallization of the sublimate from a minimum amount of *n*-hexane afforded pure crystalline **2** in 35% yield. Larger crystals were very pale yellow.

$[C_5H_5Fe(CO)_3]^+(Cl_3Si)_2Fe(CO)C_5H_5]^-$ (3).—The pentane-insoluble residue from the above reaction was extracted with hot dichloromethane under slight pressure, and the supersaturated solution was filtered hot. Slow cooling afforded crystalline **3** (53% yield), which is sparingly soluble in cold dichloromethane.

Reaction of 2 with $(C_6H_5)_4As^+Cl^-$.—Dry acetone (10 ml) was added to **2** (0.70 g, 1.67 mmol) and $(C_6H_5)_4AsCl$ (0.70 g, 1.67 mmol), and the solution was stirred until dissolution was complete. Acetone was then removed at reduced pressure to leave an oily solid which crystallized on washing with *n*-hexane. These crystals were dissolved in 10 ml of dichloromethane and filtered. Hexane (20 ml) was carefully added to the top of the clear yellow filtrate so as to form a layer over the dichloromethane. This was set aside in the refrigerator, and as the two layers slowly diffused into one another, large yellow crystals formed on the wall of the vessel. After crystallization was complete, the product was washed with hexane, yielding 1.20 g of $[(C_6H_5)_4As]^+$-$[(Cl_3Si)_2Fe(CO)C_5H_5]^-$ (1.50 mmol, 90% yield).

Reaction of 3 with $(C_6H_5)_4As^+Cl^-$.—A 50-ml three-neck flask was charged with 0.845 g of $(C_6H_5)_4AsCl$ (2.02 mmol) and 15 ml of dry acetone. The reaction was attached to a gas buret and 1.20 g of **3** (1.93 mmol), dissolved in 10 ml of dry acetone, was slowly added from an addition funnel into the stirring reaction mixture. The solution turned slowly from yellow to orange and finally to red, with slow evolution of carbon monoxide. Over a period of 1 hr, 50.5 cm^3 of gas (shown by infrared spectrum to be carbon monoxide) was evolved at room temperature (690–700 mm). This corresponds to approximately 42 cm^3 at STP (1.88–1.90 mmol). Acetone was removed at reduced pressure to leave an oily red material which crystallized on addition of a small quantity of pentane. The pentane was evaporated and the residue was sublimed at 45° (0.01 mm) onto a water-cooled probe, affording red, crystalline $ClFe(CO)_2C_5H_5$ as the sublimate (0.327 g, 1.54 mmol, 80% based on compound **3** employed).

The cream-colored powdery residue was washed with several small aliquots of pentane, dissolved in 20 ml of dichloromethane, and filtered. Hexane (30 ml) was carefully added to the top of the yellow filtrate and the resulting two-layer system was set aside in the refrigerator. Crystals of $[(C_6H_5)_4As]^+[(Cl_3Si)_2Fe(CO)C_5H_5]^-$ slowly formed on the wall of the vessel (yield 1.36 g, 1.70 mmol, 88% based on **3** taken).

Temperature–Yield study.—A sample of 40 g of coarse, crystalline $[C_5H_5Fe(CO)_2]_2$ was finely ground to a powdery material of uniform appearance. Employing this material, two Carius tubes of approximate volume of 60–70 ml were each charged with 2.00 ± 0.01 g of $[C_5H_5Fe(CO)_2]_2$ (5.65 mmol) and 7.7 ± 0.1 ml of Cl_3SiH. These were sealed under vacuum with the sample at liquid nitrogen temperature. The tubes were immersed in an oil bath thermostated at 110°. The tubes were attached to a reciprocating shaker and allowed to react for 30 min. This procedure was repeated at 10° intervals to 180°. At the end of the reaction time the tubes were cooled to −196° and opened to release CO and H_2. Trichlorosilane was removed at reduced pressure and the crude powdery product from each reaction was weighed. An accurately weighed sample of the crude product (25–50 mg) was placed in a 25-ml volumetric flask and hexane was added. The infrared spectrum of this solution showed carbonyl bands of **1** and **2**, and concentrations were determined from peak heights using a working curve prepared from the pure compounds. The hexane-insoluble residue in the volumetric flask was washed with two or three portions of pentane and dried in a nitrogen stream, and 10 ml of dry acetone was pipetted in; the concentration of **3** in this solution was determined from its infrared band intensity referred to a suitable working curve. From the accumulated data the curves of Figure 3 were prepared.

The Reaction of $[CH_3C_5H_4Fe(CO)_2]_2$ and Cl_3SiH.—A mixture of 2.44 g of $[CH_3C_5H_4Fe(CO)_2]_2$ (6.38 mmol) and 12 ml of Cl_3SiH (excess) was heated at 115° for 10 hr in a Carius tube. After removal of excess Cl_3SiH, the reaction mixture was extracted with two 40-ml portions of hexane, leaving a bright yellow, powdery residue. The hexane was evaporated at reduced pressure leaving an oily, brown material which was washed into a sublimer with pentane. After removal of the pentane, the oily residue was sublimed onto a water-cooled probe at room temperature (0.01 mm). A yellow liquid identified spectroscopically as **$Cl_3SiFe(CO)_2C_5H_4CH_3$** slowly deposited on the probe. After no additional liquid $Cl_3SiFe(CO)_2C_5H_4CH_3$ deposited, sublimation was continued at 60° (0.01 mm) onto a clean probe. A white, crystalline material slowly deposited and was recrystallized from a small quantity of hexane at refrigerator temperature yielding a needlelike, white, crystalline product, **$(Cl_3Si)_2FeH(CO)C_5H_4CH_3$**.

The hexane-insoluble yellow residue was extracted with 40 ml of dichloromethane and filtered. Hexane was slowly added to the top of the dichloromethane filtrate. Coarse needlelike crystals rapidly formed at the interface as the two liquid layers were gently agitated. The product **$[(CH_3C_5H_4Fe(CO)_3]^+$-$[(Cl_3Si)_2Fe(CO)C_5H_4CH_3]^-$** decomposed slowly above 105°.

The undissolved residue from the dichloromethane extraction was extracted with more dichloromethane. After the first two extractions, the dichloromethane was only faintly yellow. The infrared spectra of succeeding extracts showed no bands due to $(Cl_3Si)_2Fe(CO)C_5H_4CH_3^-$ in the carbonyl region, while those due to $CH_3C_5H_4Fe(CO)_3^+$ were of medium intensity. The remaining undissolved yellow residue analyzed as **$[CH_3C_5H_4Fe$-**

$(CO)_3]^+[FeCl_4]^-$. The measured gram-susceptibility of the material was 34.8 cgsu; the spin-only value calculated for five unpaired electrons of the tetrachloroferrate(III) anion is 35.4 cgsu.[20]

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[20] We are indebted to Mr. E. D. Day, of this department, who determined the susceptibility for us using a Faraday apparatus.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Cyclopentadienyl(triphenylphosphine)ethylenerhodium and Related Compounds

BY A. J. OLIVER AND W. A. G. GRAHAM*

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Sodium cyclopentadienide reacts with $(CH_3COCHCOCH_3)RhP(C_6H_5)_3(C_2H_4)$ to form $C_5H_5RhP(C_6H_5)_3(C_2H_4)$ and with $[As(C_6H_5)_3]_2Rh(C_2H_4)Cl$ to yield $C_5H_5RhAs(C_6H_5)_3(C_2H_4)$. Some oxidative addition reactions of halogens and alkyl halides have been carried out on these cyclopentadienylrhodium compounds and are consistent with the formation of ionic intermediates. The tetrafluoroethylene compound $C_5H_5RhP(C_6H_5)_3(C_2F_4)$ has been prepared by abstraction of bromine from $C_5H_5RhP(C_6H_5)_3(C_2F_4Br)Br$ using metallic zinc.

Introduction

It has been shown in earlier work of this laboratory[1,2] that the compounds C_5H_5MLY (M = Rh or Ir, L = a phosphine, and Y = CO) can undergo oxidation (i) with retention of Y to give an ionic compound, (ii) with insertion of Y into a newly formed bond, and (iii) with complete elimination of Y. Ligands other than CO might behave similarly but in order that the three modes of reaction can remain, Y must be capable of acting as an insertion reagent.[3,4] The other possibilities for Y are then almost limited to isocyanides,[5] sulfur dioxide,[6] or olefins.[7-10]

The compounds chosen for study were C_5H_5RhL-(olefin) since reactions of one olefin derivative have implications for a large number of others. Such compounds might also have applications in the field of catalysis.[11]

Results and Discussion

By analogy with the preparation of $C_5H_5Rh(CO)P(CH_3)_2C_6H_5$ from $C_5H_5Rh(CO)_2$,[1,12] it might be considered that a ligand could displace ethylene from the known $C_5H_5Rh(C_2H_4)_2$ to afford the prototype of the required olefin compounds, $C_5H_5RhL(C_2H_4)$. However, as Cramer has shown,[13] this reaction only takes place if L has some Lewis acid character, presumably because there is no mechanism for attack if L is a base such as triphenylphosphine. In a 16-electron rather than an 18-electron system there is a means of attack, for an 18-electron complex could form as an intermediate. Thus displacement of ethylene by triphenylphosphine was attempted in acetylacetonatobisethylenerhodium. Substitution of one ethylene ligand was achieved in similar fashion to the substitution of carbon monoxide in acetylacetonatodicarbonylrhodium.[14] Subsequent reaction of $(CH_3COCHCOCH_3)Rh(C_2H_4)$-$P(C_6H_5)_3$ with sodium cyclopentadienide gave the required compound $C_5H_5RhP(C_6H_5)_3(C_2H_4)$ (**1**) in moderate yield.

$$(CH_3COCHCOCH_3)Rh(C_2H_4)_2 \xrightarrow{P(C_6H_5)_3} (CH_3COCHCOCH_3)RhP(C_6H_5)_3(C_2H_4) \xrightarrow{C_5H_5Na} \underset{\mathbf{1}}{C_5H_5RhP(C_6H_5)_3(C_2H_4)}$$

Attempts to prepare the analogous triphenylarsine complex by this method were without success; this seems to be attributable to incomplete replacement of a single ethylene ligand from $(CH_3COCHCOCH_3)Rh(C_2H_4)_2$ at temperatures where general decomposition was minimal.

Another possible method of obtaining the compound $C_5H_5RhP(C_6H_5)_3(C_2H_4)$ is by a route found applicable to $C_5H_5RhP(C_6H_5)_3(CO)$.[2] Displacement of triphenylphosphine from Wilkinson's compound, $[(C_6H_5)_3P]_3RhCl$, gives $[(C_6H_5)_3P]_2Rh(C_2H_4)Cl$ (**2**), which might react with sodium cyclopentadienide. The ethylene in **2** is very labile[15a] and appears to be lost so easily that it is not retained in the latter reaction.[15b] In the arsine complex analogous to **2**[16] the ethylene is not as labile and we have found that the corresponding reaction

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