Tetrakis(1,8-dioxynaphthyl)cyclotetraphosphazene (IV).—A solution of 1,8-dihydroxynaphthalene (7.15 g, 0.044 mol) and triethylamine (13.0 ml, 0.093 mol) in dry tetrahydrofuran (250 ml) was added dropwise to a stirred solution of octachlorocyclotetraphosphazene (5.0 g, 0.0108 mol) in tetrahydrofuran (250 ml). The solution was stirred for 4 hr at 25° and the solid dispersion (8.4 g) was filtered off and was found to consist of triethylammonium chloride (8.2 g, 60%) and 0.2 g of a material which was recrystallized from cyclohexanone to give IV. The filtrate was boiled at reflux for an additional 8 hr and the solvent was removed in a rotary evaporator. The brown residue was washed with acetone (1000 ml) and the insoluble portion was recrystallized from cyclohexanone to yield an additional 3.2 g of **tetrakis(1,8-dioxynaphthyl)cyclotetraphosphazene** (IV) (total yield 3.4 g, 27%). The compound did not melt below 360°. *Anal.* Calcd for $C_{40}H_{24}O_8N_4P_4$: C, 59.2; H, 2.96; P, 15.25; mol wt 812. Found: C, 59.20; H, 2.92; P, 15.20; mol wt 808 (ultraviolet spectra), 812 (mass spectra). The use of sodium carbonate in place of triethylamine gave the same product but in much lower yields.

Tetrakis(2,2′-dioxybiphenyl)cyclotetraphosphazene (V).—A solution of 2,2′-dihydroxybiphenyl (8.2 g, 0.044 mol), octachlorocyclotetraphosphazene (5.0 g, 0.0108 mol), and triethylamine (12.5 ml, 0.09 mol) in dry tetrahydrofuran (300 ml) were stirred together at 0°. Triethylammonium chloride precipitated from solution immediately after the reactants were mixed. After a 2-hr reaction at 0°, the mixture was filtered to yield triethylammonium chloride (6.2 g, 50% yield), but continued stirring of the filtrate at 0° for 8 hr yielded no further precipitate. An additional 172-hr reaction at 25° yielded a white precipitate. This was dried in a vacuum oven at 30° and then sublimed at 165° (0.5 mm) for 100 hr. The sublimate was triethylammonium chloride, and the residue was recrystallized from dimethylacetamide to yield **tetrakis(2,2′-dioxybiphenyl)cyclotetraphosphazene (V)** (3.0 g, 30.2% yield). The compound did not melt below 340°. Use of sodium carbonate as a base in this reaction yielded no identifiable product. *Anal.* Calcd for $C_{48}H_{32}O_8N_4P_4$: C, 62.80; H, 3.49; N, 6.11; P, 13.55; mol wt 916. Found: C, 62.64; H, 3.69; N, 6.42; P, 13.22; mol wt 924 (ultraviolet spectra), 916 (mass spectra).

Influence of the Base.—In view of the similarities normally observed between phosphazene cyclic trimers and tetramers, it is surprising that bases such as triethylamine and sodium carbonate have specific influences for reactions of trimers and tetramers. Thus, while triethylamine gives high yields of tetramer IV, the use of sodium carbonate in place of triethylamine gave the same product but in much lower yields. By contrast, sodium carbonate is a good base for the formation of the analogous trimer III. Sodium carbonate was not effective for the synthesis of V, even though it is the preferred reagent for formation of the analogous trimer.[3] Sodium carbonate can be used to prepare I in higher yields than with triethylamine. Thus, it appears that sodium carbonate is an excellent reagent for the synthesis of spirocyclotriphosphazenes but that an organic base, such as triethylamine, is preferred for synthesis of the spirotetramers. These differences may be connected with the extreme insolubility of the aryloxyspiro tetramers and their uncyclized sodium salt precursors. This pattern does not extend to derivatives in which two independent substituents are present at phosphorus, where sodium carbonate is effective for both trimers and tetramers.

X-Ray Diffraction Data.—The following are *d* spacings (in Å), with estimated intensities in parentheses: III, 13.23 (vs), 10.61 (vs), 7.78 (m), 6.80 (s), 6.29 (vs), 5.82 (s), 5.25 (w), 4.71 (s), 4.56 (s), 4.37 (s), 4.00 (s), 3.89 (m), 3.80 (s), 3.59 (m), 3.49 (w), 3.40 (vs), 3.28 (m), 3.19 (s), 2.62 (w); IV, 10.59 (w), 9.49 (vs), 8.30 (w), 7.48 (s), 6.72 (vs), 5.41 (w), 5.15 (m), 4.85 (w), 4.57 (w), 4.14 (w), 3.97 (s), 3.82 (w), 3.72 (s), 3.59 (s), 3.45 (s), 2.61 (m), 2.52 (w), 2.42 (w), 2.32 (w), 2.21 (w), 2.09 (w), 1.98 (w), 1.88 (w), 1.77 (w), 1.66 (w), 1.40 (m), 1.37 (w), 1.23 (w), 1.14 (m); V, 10.49 (s), 8.80 (vs), 7.16 (vs), 6.24 (w), 5.78 (w), 5.01 (s), 4.77 (s), 4.55 (w), 4.32 (w), 4.12 (s), 3.88 (m), 3.70 (w), 3.57 (s), 3.48 (vs), 3.18 (vs), 2.98 (w), 2.66 (s), 2.51 (w), 2.06 w), 1.96 (w), 1.91 (w), 1.76 (m).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Silicon–Transition Metal Chemistry. II.[1] Anions Derived from Silyl(transition metal) Hydrides and Related Compounds

BY W. JETZ AND W. A. G. GRAHAM*

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The anions $Cl_3SiFe(CO)_4^-$, $(C_6H_5)_3SiFe(CO)_4^-$, $Cl_3SiMn(CO)_2C_5H_5^-$, and $Cl_3SiMn(CO)_2C_5H_4CH_3^-$ have been prepared from the parent hydrides as triethylammonium or tetraethylammonium salts. The acidity of the hydrides decreases in the order $Cl_3SiFeH(CO)_4 > (C_6H_5)_3SiFeH(CO)_4 > Cl_3SiMnH(CO)_2C_5H_5 > (C_6H_5)_3SiMnH(CO)_2C_5H_5$. Reactions of the anions with $(C_6H_5)_nSnCl_{4-n}$ (n = 0, 1, 2) lead to stable derivatives such as *cis*-$Cl_3Sn(Cl_3Si)Fe(CO)_4$ and *trans*-$C_6H_5Cl_2Sn(Cl_3Si)Mn(CO)_2C_5H_4CH_3$ as well as bis-substituted tin compounds. Bases such as $(C_2H_5)_3N$, CH_3CN, or Cl^- reversibly displace $Cl_3SiFe(CO)_4^-$ from $(Cl_3Si)_2Fe(CO)_4$.

Introduction

Transition metal hydrides, like the common mineral acids, are known to cover a wide range of acidities.[2] For example, cobalt tetracarbonyl hydride[3] and manganese pentacarbonyl hydride[4] have K_a values of 1.0 and 0.8×10^{-7}, respectively, and the anions of these acids are useful synthetic reagents. Furthermore, it has been shown that the acidity of metal carbonyl hydrides is markedly affected by altering the ligands.[5]

We have described the photochemical synthesis of a number of silyl-substituted transition metal hydrides which also exhibit a wide range of acidities.[1,6] Thus the compound $(Cl_3Si)_2FeH(CO)C_5H_5$ is a strong acid in acetonitrile.[7] We report here a study of the weaker

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(1) Part I: W. Jetz and W. A. G. Graham, *Inorg. Chem.*, **10**, 4 (1971).

(2) It is unfortunate from a semantic point of view that so many of the compounds formally classified as hydrides are in fact protonic acids.

(3) W. Hieber and W. Hübel, *Z. Elektrochem.*, **57**, 235, 331 (1953).

(4) W. Hieber and G. Wagner, *Z. Naturforsch. B*, **13**, 339 (1958).

(5) W. Hieber and E. Lindner, *Ber.*, **94**, 1417 (1961).

(6) W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 3375 (1969).

(7) The results of a detailed study of this compound will be submitted shortly. An nmr study has established $K_a = 2.6 \times 10^{-3}$ in acetonitrile, intermediate between the dissociation constants of perchloric and hydrobromic acids in that solvent.

acids $R_3SiFeH(CO)_4$ and $R_3SiMnH(CO)_2C_5H_5$ (R = Cl or C_6H_5) and of their anions. These silyl(transition metal) anions have important applications in synthesis, of which several examples are described. The characterization of these anions has also suggested an alternative interpretation for some recent results on other silyliron compounds.[8]

Results and Discussion

When triethylamine is added to a hexane solution of $Cl_3SiFeH(CO)_4$,[1] a white, microcrystalline, very air-sensitive salt precipitates quantitatively according to eq 1. The tetraethylammonium salt of this anion may

$$Cl_3SiFeH(CO)_4 + (C_2H_5)_3N = (C_2H_5)_3NH^+[Cl_3SiFe(CO)_4]^- \quad (1)$$

be prepared by sweeping hydrogen chloride from a dichloromethane solution of $(C_2H_5)_4N^+Cl^-$ and $Cl_3SiFeH(CO)_4$ using nitrogen (eq 2). The tetraethylam-

$$Cl_3SiFeH(CO)_4 + (C_2H_5)_4N^+Cl^- = (C_2H_5)_4N^+[Cl_3SiFe(CO)_4]^- + HCl \quad (2)$$

monium salt may be recrystallized from dichloromethane as white crystals which are moderately air stable, in contrast to the triethylammonium salt. The extreme air sensitivity of the latter can be attributed to the reversibility of eq 1 to form small amounts of the highly air-sensitive[1] parent hydride $Cl_3SiFeH(CO)_4$. The infrared spectra of $(C_2H_5)_3NH^+[Cl_3SiFe(CO)_4]^-$ and $(C_2H_5)_4N^+[Cl_3SiFe(CO)_4]^-$ in dichloromethane are identical, showing in the triethylammonium case no trace of $Cl_3SiFeH(CO)_4$; thus we conclude that the equilibrium 1 is far to the right.

A similar equilibrium in which the equilibrium constant is more nearly unity is observed in reaction 3.

$$Cl_3SiMnH(CO)_2C_5H_5 + (C_2H_5)_3N = (C_2H_5)_3NH^+[Cl_3SiMn(CO)_2C_5H_5]^- \quad (3)$$

This is clearly demonstrated by the infrared spectra of Figure 1. Figure 1b shows the presence of both parent hydride (Figure 1a) and the anion (Figure 1d). Addition of excess triethylamine further displaces the equilibrium in the direction of the anion (Figure 1c).[9]

The lower melting points of the triethylammonium salts relative to tetraethylammonium are probably the result of reversible formation of amine and hydride.

Triphenylsilyl(transition metal) hydrides[1] show lower acidities than their trichlorosilyl analogs. Thus, when triethylamine was added to a dichloromethane solution of $(C_6H_5)_3SiMnH(CO)_2C_5H_5$,[10] the infrared spectrum showed only unreacted hydride; a similar reaction in hexane did *not* result in precipitation of $(C_2H_5)_3NH^+[(C_6H_5)_3SiMn(CO)_2C_5H_5]^-$ which would have been expected on solubility grounds even for a weak acid.

On the other hand, addition of triethylamine to a hexane solution of $(C_6H_5)_3SiFeH(CO)_4$ quantitatively precipitates $(C_2H_5)_3NH^+[(C_6H_5)_3SiFe(CO)_4]^-$, and this salt in dichloromethane shows only the carbonyl bands of the anion. Equilibrium 4 is therefore far to the right.

$$(C_6H_5)_3SiFeH(CO)_4 + (C_2H_5)_3N = (C_2H_5)_3NH^+[(C_6H_5)_3SiFe(CO)_4]^- \quad (4)$$

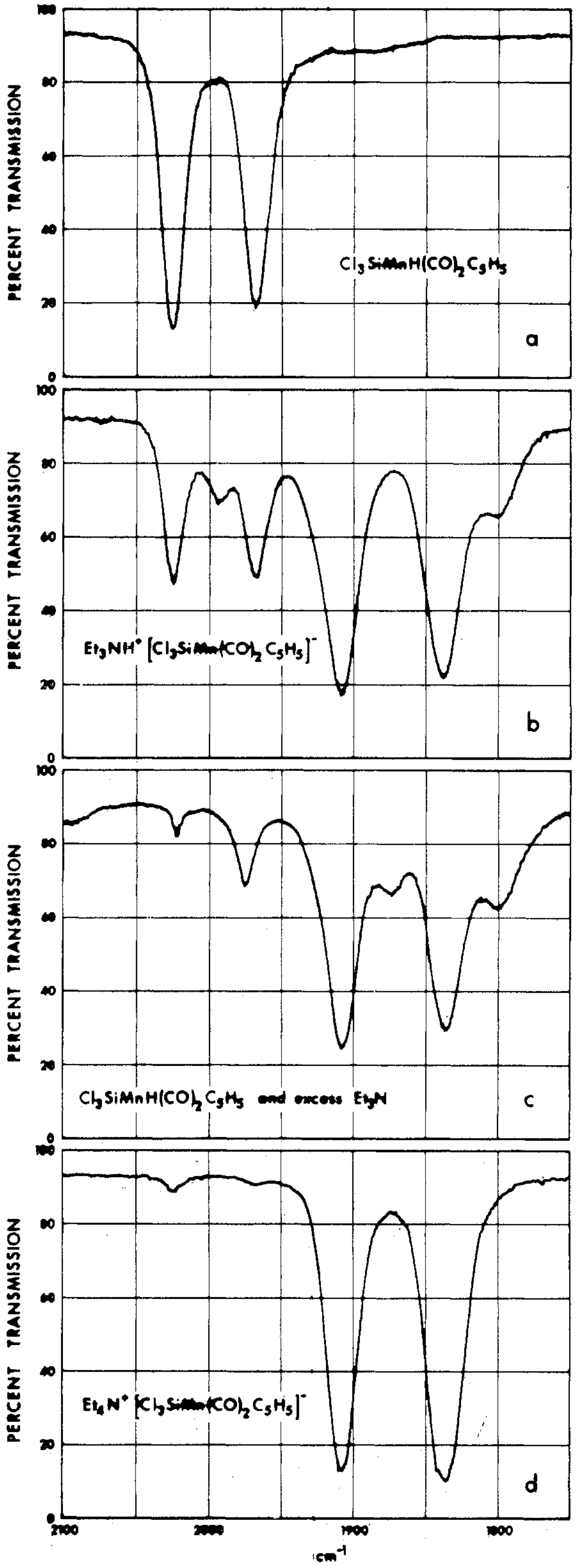

Figure 1.—Infrared spectra in dichloromethane solution: (a) $Cl_3SiMnH(CO)_2C_5H_5$; (b) the salt $(C_2H_5)_3NH^+[Cl_3SiMn(CO)_2C_5H_5]^-$, showing bands of both anion and free hydride and two small bands of unknown origin; (c) $Cl_3SiMnH(CO)_2C_5H_5$ with excess triethylamine, showing decrease in free hydride and additional weak bands and intensity changes indicative of other process as yet undetermined; (d) the salt $(C_2H_5)_4N^+[Cl_3SiMn(CO)_2C_5H_5]^-$.

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[8] B. J. Aylett, J. M. Campbell, and A. Walton, *J. Chem. Soc. A*, 2110 (1969); *Inorg. Nucl. Chem. Lett.*, **4**, 79 (1968).

[9] The presence of a few additional bands in Figure 1b and 1c suggests that processes other than simple proton transfer are involved; this complication is being investigated.

[10] This compound was first prepared in this laboratory by J. K. Hoyano and details will be reported shortly. The X-ray structure of the compound has been described in *Chem. Eng. News*, **48**, 75 (June 8, 1970).

TABLE I

CARBONYL STRETCHING BANDS OF HYDRIDES AND BASE ADDUCTS

$(C_6H_5)_3SiFeH(CO)_4$[a]	2097 m	2036 m	2026 s	2018 s	...	...	...	...
$(C_6H_5)_3SiFeH(CO)_4 \cdot N(C_2H_5)_3$[b]	...	...	...	...	1994 s	1904 m	1876 vs	1864 sh
$(C_2H_5)_4N^+[(C_6H_5)_3SiFe(CO)_4]^-$[b]	...	...	...	...	1995 s	1907 m	1879 vs	1865 sh
$Cl_3SiFeH(CO)_4$[a]	2124 m	2069 m	2058 s	2053 s	...	...	...	...
$(C_2H_5)_4N^+[Cl_3SiFe(CO)_4]^-$[b]	...	...	...	...	2031 s	1950 m	1916 vs	1904 sh
$(Cl_3Si)_2Fe(CO)_4$[b]	2131 m	2083 m	2073 s	2064 s	...	...	...	...
$(Cl_3Si)_2Fe(CO)_4$–$N(C_2H_5)_3$[b,c]	2131 m	2083 m, sh	2073 s	2064 s	2027 m	1941 m	1910 vs	...
$(Cl_3Si)_2Fe(CO)_4$–$(C_2H_5)_4NCl$[b,d]	2131 m	2083 m, sh	2073 s	2063 s	2028 m	1945 m	1910 vs	...
$(Cl_3Si)_2Fe(CO)_4$–CH_3CN[e]	2135 ms	2086 m	...	2059 s	2031 m	1950 m	1905 s	...
$(C_2H_5)_4N^+[HFe(CO)_4]^-$[f]	...	...	...	...	2000 w	1910 m	1878 s	...

[a] Hexane solution. [b] Dichloromethane solution. [c] $(C_2H_5)_3N:(Cl_3Si)_2Fe(CO)_4$ molar ratio 100. [d] $(C_2H_5)_4NCl:(Cl_3Si)_2Fe(CO)_4$ molar ratio 1.3. [e] Acetonitrile solution. [f] Values in dichloromethane measured by Dr. R. P. Stewart, University of Alberta.

Triethylamine is thus not a suitable base to differentiate between the acidity of the trichlorosilyl- and triphenylsilyliron derivatives. To establish the relative acid strengths, a competition reaction (eq 5) was carried out

$$(C_2H_5)_4N^+[(C_6H_5)_3SiFe(CO)_4]^- + Cl_3SiFeH(CO)_4 = (C_6H_5)_3SiFeH(CO)_4 + (C_2H_5)_4N^+[Cl_3SiFe(CO)_4]^- \quad (5)$$

in dichloromethane. Infrared spectroscopy showed that the reaction proceeded quantitatively to the right, establishing that $Cl_3SiFeH(CO)_4$ is the stronger acid. We may thus write the following order of relative acid strengths in dichloromethane solution with triethylamine as the reference base: $Cl_3SiFeH(CO)_4 > (C_6H_5)_3SiFeH(CO)_4 > Cl_3SiMnH(CO)_2C_5H_5 > (C_6H_5)_3SiMnH(CO)_2C_5H_5$.

In both iron and manganese compounds, the greater acidity of the trichlorosilyl derivatives can be ascribed to the more electronegative chlorine substituents. Substituent effects in these compounds are likely to be more complicated than the inductive effect leading to increased acidity in trichloroacetic acid, for example, and further investigation is required. It may be noted, however, that a recent discussion of the bonding in manganese pentacarbonyl derivatives concluded that $(C_6H_5)_3Si$ and Cl_3Si groups differed substantially in their σ-withdrawing properties but were quite comparable insofar as π bonding was concerned.[11]

The anion $(C_6H_5)_3SiFe(CO)_4^-$ was recently obtained by a different route by Kruck, *et al.*, from the reaction of $(C_6H_5)_3SiLi$ and $Fe(CO)_5$.[12a] Cleavage of $[(CH_3)_3SiRu(CO)_4]_2$ by sodium amalgam has also led to the $(CH_3)_3SiRu(CO)_4^-$ anion.[12b]

It is necessary to comment at this point on the results of Aylett and his coworkers, who prepared the compounds $H_3SiFeH(CO)_4$ and $(H_3Si)_2Fe(CO)_4$ and investigated their behavior with trimethylamine.[8] These authors, in view of the formation of "adducts" such as $[H_3Si \cdot 2N(CH_3)_3]^+[Mn(CO)_5]^-$ from $H_3SiMn(CO)_5$,[13] formulated the trimethylamine adduct of $H_3SiFeH(CO)_4$ as $[H_3Si \cdot nN(CH_3)_3]^+[HFe(CO)_4]^-$.

A similar formulation in the present work would require that eq 4 be rewritten as eq 6. Such a possibility for the triphenylsilyl or trichlorosilyl derivatives examined here can be definitely excluded by the infrared data of Table I. First, the carbonyl bonds of the species present in the triethylamine "adducts" do not correspond in position or intensity with those of authentic $HFe(CO)_4^-$. Second, the spectra of the tetraethylammonium salts, for which only one reasonable formulation is possible, are identical with those of the triethylamine "adducts." Unfortunately, the spectra reported[8] for "$H_3SiFeH(CO)_4 \cdot nN(CH_3)_3$" were taken in the solid state, and a comparison with the values reported here is not meaningful. While it is not impossible that the silyl complex reacts differently from the trichlorosilyl or triphenylsilyl analogs, we feel that the reported spectra[8] are not inconsistent with the formulation of the silyliron adduct as $[(CH_3)_3NH]^+[H_3SiFe(CO)_4]^-$.

$$(C_6H_5)_3SiFeH(CO)_4 + (C_2H_5)_3N = [(C_2H_5)_3NSi(C_6H_5)_3]^+[HFe(CO)_4]^- \quad (6)$$

Some closely related chemistry stems from the reaction of the stable and readily available *cis*-$(Cl_3Si)_2Fe(CO)_4$[14] with bases. Reaction 7 takes place (where

$$(Cl_3Si)_2Fe(CO)_4 + nB = Cl_3Si \cdot nB^+ + Cl_3SiFe(CO)_4^- \quad (7)$$

$B = (C_2H_5)_3N$, CH_3CN, or Cl^-).[15] An examination of the infrared data of Table I shows that this reaction *involves an equilibrium that is not displaced fully to the right even by a large excess of base.* The reaction presumably proceeds *via* a nucleophilic displacement on silicon by the base. We suggest that a similar formulation is likely for the reported adduct $(H_3Si)_2Fe(CO)_4 \cdot 2N(CH_3)_3$.[8]

There is no evidence for displacement of a second trichlorosilyl group by excess base, and it is of interest to compare this with the great difference between the first and second acid dissociation constants of $H_2Fe(CO)_4$.[16]

When the base B of eq 7 is chloride ion, the product would presumably be silicon tetrachloride. In a further investigation of this particular reaction, the equilibrium was approached from the opposite direction, starting with silicon tetrachloride and the trichlorosilyltetracarbonyliron anion as in eq 8.

$$(C_2H_5)_4N^+[Cl_3SiFe(CO)_4]^- + SiCl_4 = (C_2H_5)_4N^+Cl^- + (Cl_3Si)_2Fe(CO)_4 \quad (8)$$

An infrared study (in dichloromethane) of the carbonyl stretching region showed the well-resolved highest frequency band of $(Cl_3Si)_2Fe(CO)_4$, which was much less intense than the bands of $Cl_3SiFe(CO)_4^-$ even at a $SiCl_4:Cl_3SiFe(CO)_4^-$ molar ratio of 20:1. Assuming similar extinction coefficients for the two species, we

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[11] W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968); for $(C_6H_5)_3Si$, $\sigma = -0.55$, $\pi = 0.40$; for Cl_3Si, $\sigma = 0.06$, $\pi = 0.41$.

[12] (a) T. Kruck, E. Job, and U. Klose, *Angew. Chem., Intern. Ed. Engl.*, **7**, 374 (1968); (b) S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 2559 (1969).

[13] B. J. Aylett and J. M. Campbell, *Chem. Commun.*, 159 (1967); B. J. Aylett, J. M. Campbell, and A. Walton, *J. Chem. Soc. A*, 1920 (1969).

[14] W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **89**, 2773 (1967).

[15] In eq 7 (for $B = (C_2H_5)_3N$ or CH_3CN) it is assumed that $n = 2$ since 2 mol of $(CH_3)_3N$ normally is associated with the H_3Si^+ cation.[13]

[16] P. Krumholz and H. M. A. Stettiner, *J. Amer. Chem. Soc.*, **71**, 3035 (1949).

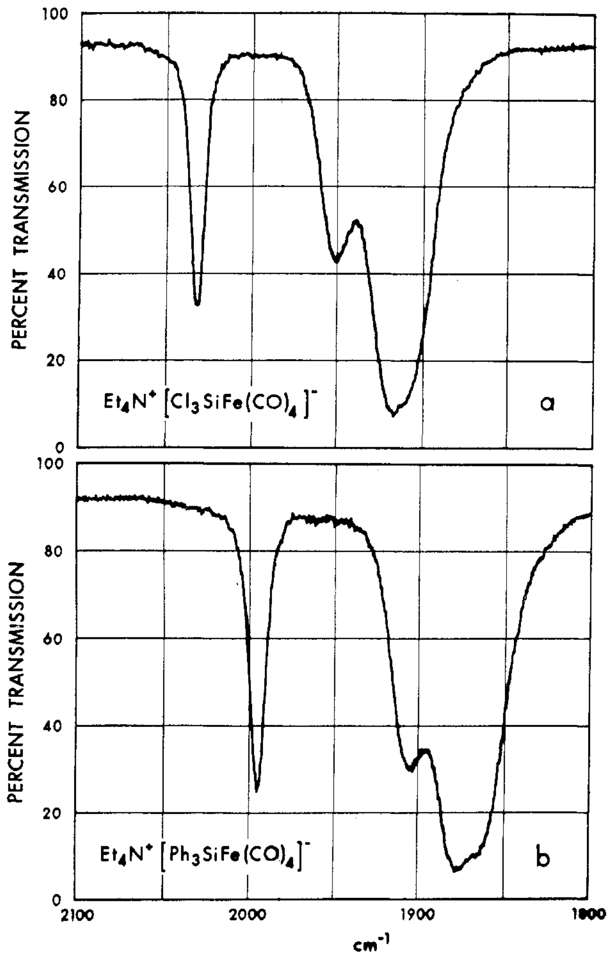


Figure 2.—Infrared spectra in dichloromethane solution: (a) $(C_2H_5)_4N^+[Cl_3SiFe(CO)_4]^-$; (b) $(C_2H_5)_4N^+[(C_6H_5)_3SiFe(CO)_4]^-$ showing incipient splitting of the low-frequency band (see text).

may conclude that the equilibrium constant in (8) is substantially less than unity.

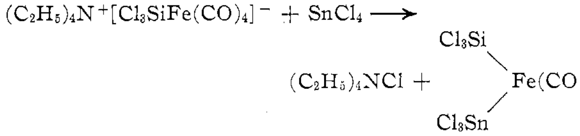
In more general terms, eq 8 represents the reaction of a metal carbonyl anion with a main group halide, often used in the synthesis of metal–metal bonds. The small equilibrium constant for $SiCl_4$ implies that this is not an attractive route for the preparation of $(Cl_3Si)_2Fe(CO)_4$. However, as reported below, a similar reaction with $SnCl_4$ affords a quantitative yield of the mixed derivative $Cl_3Sn(Cl_3Si)Fe(CO)_4$. Clearly, a quantitative study of equilibria such as (7) and (8) will have important applications in synthetic chemistry.

Infrared Spectra and Structure of the Anions.—The carbonyl stretching bands of $Cl_3SiMn(CO)_2C_5H_5^-$ as the tetraethylammonium salt lie at 1910 and 1837 cm^{-1} as shown in Figure 1d. The structure is presumed to be similar to that of the neutral species $X_3SnFe(CO)_2C_5H_5$.[17] The *isoelectronic* neutral compound $Cl_3SiFe(CO)_2C_5H_5$[14] shows bands shifted to 2039 and 1995 cm^{-1}, as expected.

The anion $Cl_3SiFe(CO)_4^-$ is isoelectronic with neutral $Cl_3SiCo(CO)_4$, known to have a trigonal-bipyramidal structure.[18] For C_{3v} symmetry, three infrared-active carbonyl stretching bands are expected, and neutral molecules of the $X_3MCo(CO)_4$ type exhibit three bands in a medium–medium–strong pattern, assigned as A_1, A_1, and E, respectively.[19] Grossly, the spectra of $Cl_3SiFe(CO)_5^-$ and $(C_6H_5)_3SiFe(CO)_4^-$ shown in Figure 2 follow a similar pattern. Closer examination reveals appreciable asymmetry in the low-frequency band of Figure 2a, which has developed in Figure 2b to an incipient splitting. The effective symmetry of the ions has evidently been lowered. We suggest that this is a result of ion pairing, which, as Edgell, *et al.*, have shown, takes place in tetrahydrofuran solutions of $Na^+[Co(CO)_4]^-$.[20]

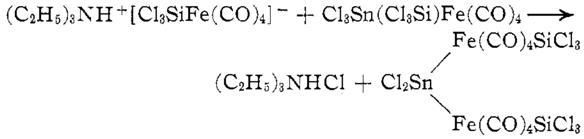
It has been established that the lowered symmetry of molecules such as $CH_3SiH_2Co(CO)_4$[21] or $C_6H_5GeCl_2Co(CO)_4$[19] removes the degeneracy of the E mode, which splits into two well-resolved bands in the gas phase or in cyclohexane. A close approach of the tetraethylammonium cation to the silyliron anion in any of several configurations would result in a lower symmetry for the ion pair; owing to the broadness of the bands in dichloromethane solution (the salts are completely insoluble in hydrocarbon solvents), the two components of the lower band are poorly resolved.

Reactions of the Anions.—The chemistry of silyl carbonylate salts has been little investigated. The work of Knox and Stone[12b] on $(CH_3)_3SiRu(CO)_4^-$ indicates that this particular anion undergoes a number of metathetical reactions leading to metal–metal bands. Our initial investigations on the anions reported here involve their reactions with tin halides and suggest that they will undergo many of the reactions of the established anions such as $Mn(CO)_5^-$. Some representative reactions are given in eq 9–12.



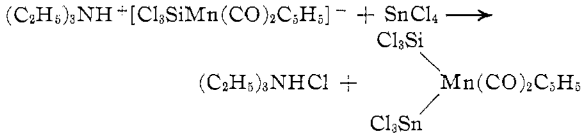
$$(C_2H_5)_4N^+[Cl_3SiFe(CO)_4]^- + SnCl_4 \longrightarrow (C_2H_5)_4NCl + \underset{Cl_3Sn}{\overset{Cl_3Si}{\quad}}\!\!>Fe(CO)_4 \qquad (9)$$

1



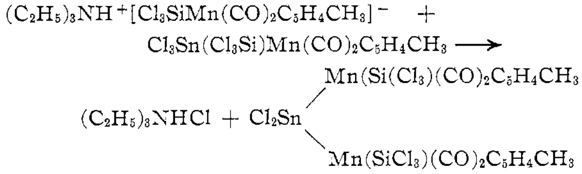
$$(C_2H_5)_3NH^+[Cl_3SiFe(CO)_4]^- + Cl_3Sn(Cl_3Si)Fe(CO)_4 \longrightarrow (C_2H_5)_3NHCl + Cl_2Sn<\!\!\underset{Fe(CO)_4SiCl_3}{\overset{Fe(CO)_4SiCl_3}{\quad}} \qquad (10)$$

2



$$(C_2H_5)_3NH^+[Cl_3SiMn(CO)_2C_5H_5]^- + SnCl_4 \longrightarrow (C_2H_5)_3NHCl + \underset{Cl_3Sn}{\overset{Cl_3Si}{\quad}}\!\!>Mn(CO)_2C_5H_5 \qquad (11)$$

3



$$(C_2H_5)_3NH^+[Cl_3SiMn(CO)_2C_5H_4CH_3]^- + Cl_3Sn(Cl_3Si)Mn(CO)_2C_5H_4CH_3 \longrightarrow (C_2H_5)_3NHCl + Cl_2Sn<\!\!\underset{Mn(SiCl_3)(CO)_2C_5H_4CH_3}{\overset{Mn(Si(Cl_3)(CO)_2C_5H_4CH_3}{\quad}} \qquad (12)$$

4

These reactions are carried out in dichloromethane.[22]

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[17] R. F. Bryan, P. T. Greene, G. A. Melson, P. F. Stokely, and A. R. Manning, *Chem. Commun.*, 722 (1969).

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[20] W. F. Edgell, M. T. Yang, and N. Koizumi, *J. Amer. Chem. Soc.*, **87**, 2563 (1965).

[21] A. P. Hagen and A. G. MacDiarmid, *Inorg. Chem.*, **6**, 686 (1967).

[22] Dichloromethane slowly reacts with amines to form ammonium salts. These reactions, however, are much slower than the anion reactions and do not interfere significantly.

TABLE II

ANALYTICAL DATA, COLORS, AND MELTING POINTS OF HYDRIDE DERIVATIVES

Compd	Mp, °C	Color	% calcd			% found		
			C	H	Cl	C	H	Cl
$(C_2H_5)_3NH^+[Cl_3SiMn(CO)_2C_5H_5]^-$ [a]	28–31	Pale yellow	37.75	5.12	25.71	37.84	5.59	26.32
$(C_2H_5)_4N^+[Cl_3SiMn(CO)_2C_5H_5]^-$ [b]	>190 dec	Yellow	40.88	5.72	24.13	40.78	6.31	24.36
$(C_2H_5)_4N^+[Cl_3SiFe(CO)_4]^-$ [c]	>260 dec	White	33.32	4.66	24.59	32.45	4.62	24.95
$(C_2H_5)_4N^+[(C_6H_5)_3SiFe(CO)_4]^-$	. . .	White	64.63	6.33	0.00	64.20	6.42	0.50
$Cl_3Sn(Cl_3Si)Mn(CO)_2C_5H_5$	161–163	Pale yellow	15.70	0.94	39.72	15.67	1.06	38.90
$Cl_3Sn(Cl_3Si)Mn(CO)_2C_5H_4CH_3$	115–117	Yellow	17.48	1.28	38.71	17.56	1.31	38.74
$Cl_2Sn[Cl_3SiMn(CO)_2C_5H_4CH_3]_2$ [d]	>180 dec	Yellow	25.00	1.86	32.80	24.89	1.90	32.93
$C_6H_5Cl_2Sn(Cl_3Si)Mn(CO)_2C_5H_4CH_3$	111–112 dec	White	28.41	2.18	29.94	27.84	2.07	30.46
$C_6H_5)_2ClSn(Cl_3Si)Mn(CO)_2C_5H_4CH_3$	>145 dec	White	37.96	2.71	22.41	38.36	2.93	22.43
$Cl_3Sn(Cl_3Si)Fe(CO)_4$	114–115	White	9.11	0.00	40.33	9.13	0.00	40.73
$Cl_2Sn[Cl_3SiFe(CO)_4]_2$	>160 dec	Orange	9.10	0.00	35.71	12.04	0.15	35.73
$C_6H_5Cl_2Sn(Cl_3Si)Fe(CO)_4$	<25	White	21.11	0.88	31.15	22.05	1.26	28.79

[a] Nitrogen: calcd, 3.39; found, 3.95. [b] Nitrogen: calcd, 3.18; found, 3.26. [c] Nitrogen: calcd, 3.24; found, 3.38. [d] Crystallizes with benzene: analysis calculated for $Cl_2Sn[Cl_3SiMn(CO)_2C_5H_4CH_3]_2\cdot{}^1/_3C_6H_6$.

TABLE III

INFRARED DATA FOR CARBONYL STRETCHING VIBRATIONS[a]

$(C_2H_5)_4N^+[Cl_3SiFe(CO)_4]^-$	2031 s	1950 m	1916 vs	1940 s, sh				
$(CH_3)_4N^+[Cl_3SiFe(CO)_4]^-$	2032 s	1953 m	1919 vs	1902 s, sh				
$(C_2H_5)_3NH^+[(C_6H_5)_3SiFe(CO)_4]^-$	1994 s	1904 m	1876 vs	1864 s, sh				
$(C_2H_5)_4N^+[(C_6H_5)_3SiFe(CO)_4]^-$	1995 s	1907 m	1879 vs	1865 s, sh				
$(C_2H_5)_3NH^+[Cl_3SiMn(CO)_2C_5H_5]^-$ [b]	2026 m	1969 m	1907 s	1839 s				
$(C_2H_5)_4N^+[Cl_3SiMn(CO)_2C_5H_5$			1910 s	1839 s				
$Cl_3Sn(Cl_3Si)Mn(CO)_2C_5H_5$	2022 m	1981 s						
$Cl_3Sn(Cl_3Si)Mn(CO)_2C_5H_4CH_3$	2018 m	1978 s						
$Cl_2Sn[Cl_3SiMn(CO)_2C_5H_4CH_3]_2$	2010 m	1988 s	1966 s, sh	1961 vs	1939 m			
$C_6H_5Cl_2Sn(Cl_3Si)Mn(CO)_2C_5H_4CH_3$	2000 m	1957 s						
$(C_6H_5)_2ClSn(Cl_3Si)Mn(CO)_2C_5H_4CH_3$	1990 m	1939 s						
$Cl_3Sn(Cl_3Si)Fe(CO)_4$	2127 m	2086 m	2077 vs	2067 s				
$Cl_2Sn[Cl_3SiFe(CO)_4]_2$	2111 s, sh	2108 s	2082 w	2077 m	2068 vs	2063 m, sh	2045 w	2032 w
$C_6H_5Cl_2Sn(Cl_3Si)Fe(CO)_4$	2118 s	2078 m	2066 s	2049 s				

[a] Hexane solution for nonionic compounds; dichloromethane for ionic complexes. Values in wave numbers. Additional bands at 1993 and 1800 cm^{-1}; *cf.* Figure 1b.

Silyl(transition metal)tin derivatives which have thus far been synthesized are listed in Table II. In reactions of $(C_2H_5)_3NH^+[Cl_3SiMn(CO)_2C_5H_5CH_3]^-$ with the $Cl_{3-n}Sn(C_6H_5)_n$ series, the reaction becomes progressively more difficult with increase in n. When $n = 2$, the yield of the product is very low, and for $n = 3$ no product has yet been isolated.

If the orange-yellow crystalline product from reaction 10 is allowed to remain in solution with the ammonium salt, $Cl_2Sn[Fe(CO)_4SiCl_3]_2$ slowly redissolves with evolution of carbon monoxide, resulting in a dark red, transparent solution. After removal of the solvent, a red, viscous oil remains which crystallizes after several weeks in a dichloromethane–hexane mixture. This analyzes approximately as the ionic complex $(C_2H_5)_3NH^+[Fe_2(CO)_7Si_2SnCl_9]^-$. This compound probably has a structure similar to that of **2**, in which chloride ion has replaced a carbonyl group.

Stereochemistry of the Derivatives.—The octahedral iron derivative **1** has silicon and tin in cis positions. This is clear in the case of **1** from its four carbonyl stretching bands. The solution infrared spectrum of **2** is quite complex and does not permit a choice among the three possible geometrical isomers. However, crystallographic data require molecular twofold symmetry[23] which excludes a cis,trans isomer but is consistent with either cis,cis or trans,trans geometries.

Molecules such as **3** and its methylcyclopentadienyl analogs show two carbonyl stretching bands with the more intense band at lower frequency. This may be taken to support a trans-square-pyramidal structure[24] and may be contrasted with the cis arrangement in the hydrido analogs such as $Cl_3SiMnH(CO)_2C_5H_5$.[1] The trans arrangement in $Cl_3Sn(Cl_3Si)Mn(CO)_2C_5H_5$ (**3**) is presumed to result largely from the steric requirements of the bulky Cl_3Si and Cl_3Sn ligands; as noted above, the same two ligands occupy cis positions in the octahedral $Fe(CO)_4$ derivative. In the latter case, the (idealized) angle between cis groups is 90° but would decrease from this value as the equatorial groups are bent downward in the square-pyramidal arrangement. Thus steric repulsion would be greater in the manganese case. A similar argument would account for the cis-octahedral geometry of $(Cl_3Si)_2Fe(CO)_4$[14] and the idealized trans-square-pyramidal arrangement in $(Cl_3Si)_2FeH(CO)C_5H_5$.[1,6,25]

Experimental Section

Synthesis of hydrides has been described in the preceding paper.[1] All other reagents are commercially available. Reactions were carried out under a nitrogen atmosphere, and products were similarly isolated and purified. Apparatus of the Schlenk type was used in nearly all cases. Filtrations were normally carried out by use of nitrogen pressure in preference to suction. Microanalyses were carried out in the microanalytical laboratory of this department by Mrs. Darlene Mahlow, with results as given in Table II. Infrared carbonyl stretching bands (Table III) were recorded and calibrated as previously described.[1]

$(C_2H_5)_4N^+[Cl_3SiFe(CO)_4]^-$.—Nitrogen was bubbled for 1 hr through a solution of 16.3 g of $Cl_3SiFeH(CO)_4$ (54.0 mmol) and 8.57 g of $(C_2H_5)_4NCl$ (52.0 mmol) in 70 ml of dichloromethane.

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[23] Professor M. J. Bennett and Mrs. K. A. Simpson have kindly provided the following crystal data: orthorhombic, a = 11.82, b = 10.41, c = 9.86 Å; space group $P2_1/2_12$; density 2.15 g cm^{-3}, two molecules per unit cell; site symmetry C_2.

[24] A. R. Manning, *J. Chem. Soc. A*, 1984 (1967); A. Bainbridge, P. J. Craig, and M. Green, *ibid.*, *A*, 2715 (1968).

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

After the reaction appeared complete, solvent was removed at reduced pressure resulting in a cream-colored, crystalline material. This crude product was washed with several aliquots of hexane, yielding 21.1 g of $(C_2H_5)_4N^+[Cl_3SiFe(CO)_4]^-$ (48.5 mmol, 93% based on $(C_2H_5)_4NCl$ employed). This was dissolved in a minimum amount of dichloromethane and filtered, and the clear, colorless filtrate was placed in the refrigerator. After several hours coarse, platelike, white crystals formed.

$(C_2H_5)_3NH^+[Cl_3SiFe(CO)_4]^-$.—A solution of $Cl_3SiFeH(CO)_4$ (from the reaction of 20 ml of $Fe(CO)_5$ (0.148 mol) and 30 ml of Cl_3SiH in 180 ml of heptane irradiated for 14 hr) was reduced in volume to 120–140 ml under vacuum and filtered. With the clear filtrate cooled to approximately −50°, triethylamine was slowly added, while the reaction mixture was magnetically stirred. A dense, white, microcrystalline material precipitated immediately. When the addition of triethylamine precipitated no further product, the solution was decanted and the crystalline material was washed with several aliquots of pentane containing small amounts of triethylamine. The resulting product (30.9 g, 0.077 mol, 52% based on $Fe(CO)_5$ employed) was extremely air sensitive. Occasionally the compound becomes mushy at room temperature. This salt has not been analyzed.

$(CH_3)_4N^+[Cl_3SiFe(CO)_4]^-$.—Nitrogen was bubbled for 90 min through a solution containing 24 g of $Cl_3SiFeH(CO)_4$ (0.079 mol) and 8.8 g of $(CH_3)_4NCl$ (0.080 mol) in 70 ml of dichloromethane. The $(CH_3)_4NCl$ had been dried under high vacuum for several days. After the reaction appeared complete, solvent was removed at reduced pressure, leaving a white, crystalline material. This was washed with several aliquots of pentane, dissolved in a minimum amount of dichloromethane, and filtered. The colorless, clear filtrate was placed in the refrigerator. After several hours white, platelike, crystalline $(CH_3)_4N^+[Cl_3SiFe(CO)_4]^-$ formed; this compound was quite air sensitive and a satisfactory elemental analysis was not obtained.

$(C_2H_5)_4N^+[(C_6H_5)_3SiFe(CO)_4]^-$.—Nitrogen was bubbled through a solution of $(C_6H_5)_3SiFeH(CO)_4$[1] (0.50 g, 1.2 mmol) and $(C_2H_5)_4NCl$ (0.20 g, 1.2 mmol) in 15 ml of dichloromethane for 1 hr. Solvent was removed under vacuum, leaving a cream-colored crystalline solid which was extracted with several portions of nitrogen-saturated water and finally dried under vacuum (the water extraction was intended to remove small amounts of unreacted $(C_2H_5)_4NCl$, which tended to follow the product through dichloromethane recrystallization). The dried crystals were dissolved in dichloromethane and *n*-hexane was added to produce slight cloudiness. The solution was cooled at −20° to produce white crystals of $(C_2H_5)_4N^+[(C_6H_5)_3SiFe(CO)_4]^-$ (0.46 g, 0.82 mmol, 69%).

$(C_2H_5)_3NH^+[(C_6H_5)_3SiFe(CO)_4]^-$.—Triethylamine (0.15 g, 1.5 mmol) was added dropwise to a stirred solution of $(C_6H_5)_3SiFeH(CO)_4$[1] (0.34 g, 0.79 mmol) in 20 ml of hexane. A cream-colored oily solid formed. The mother liquor was decanted, and the solid residue was dried under vacuum. Recrystallization from dichloromethane–*n*-hexane at −20° afforded off-white crystals of $(C_2H_5)_3NH^+[(C_6H_5)_3SiFe(CO)_4]^-$ (0.35 g, 0.66 mmol, 84%). The solid compound decomposed rapidly in air, and analysis was not possible. Dichloromethane solutions under nitrogen decomposed slowly at room temperature.

$(C_2H_5)_4N^+[Cl_3SiMn(CO)_2C_5H_5]^-$.—A mixture of 0.50 g of $Cl_3SiMnH(CO)_2C_5H_5$ (1.6 mmol) and 0.26 g of $(C_2H_5)_4NCl$ (1.5 mmol) was stirred magnetically at room temperature in dichloromethane. The reaction mixture slowly gave off hydrogen chloride, which escaped through a bubbler. Nitrogen was passed through the solution to sweep out the hydrogen chloride. After filtration, hexane was carefully added to the top of the clear, yellow filtrate, forming two layers. As the hexane slowly diffused into the dichloromethane, large yellow crystals of the product formed on the wall of the vessel.

$(C_2H_5)_3NH^+[Cl_3SiMn(CO)_2C_5H_5]^-$.—Triethylamine was added dropwise to a hexane solution containing 0.69 g of $Cl_3SiMnH(CO)_2C_5H_5$ (2.2 mmol). The solution became cloudy immediately and a yellow material oiled out, finally solidifying to a pale yellow powder. This was dissolved in 15 ml of dichloromethane and filtered. Hexane was added slowly and the product oiled out of solution. After vigorous shaking, the oily material crystallized to a pale yellow solid, melting at 28–31°.

$Cl_3Sn(Cl_3Si)Mn(CO)_2C_5C_5$.—To a stirring dichloromethane solution containing 0.25 ml of $SnCl_4$ (0.55 g, 2.1 mmol), 0.35 g of $(C_2H_5)_3NH^+[SiMn(CO)_2C_5H_5]^-$ in 10 ml of dichloromethane was added dropwise. The reaction mixture was kept at room temperature for 30 min after the addition was complete and then the solvent was removed at reduced pressure. The resulting pale yellow solid was dissolved in hexane and filtered, and the clear solution was refrigerated to produce coarse, pale yellow crystals.

$Cl_3Sn(Cl_3Si)Mn(CO)_2C_5H_4CH_3$.—A solution of 10 ml of $CH_3C_5H_4Mn(CO)_3$ (0.061 mol) and 10 ml of Cl_3SiH in 180 ml of hexane was irradiated for 12 hr. Extensive decomposition was observed. The reaction mixture was filtered and the clear, yellow solution cooled to −78°, precipitating a dense, cream-colored material. The cold solvent was decanted and the remaining hexane and unreacted Cl_3SiH were removed at reduced pressure. The oily material was dissolved in pentane, yielding a clear, yellow solution. Excess $(C_2H_5)_3N$ was slowly added until no additional material precipitated from solution. (This precipitate, $(C_2H_5)_3NH^+[Cl_3SiMn(CO)_2C_5H_4CH_3]^-$, was not analyzed but was used directly in the succeeding step in the preparation of derivatives.) This oily product was washed with several aliquots of pentane containing small quantities of $(C_2H_5)_3N$. It was dissolved in 15 ml of dichloromethane and slowly added to a dichloromethane solution containing 1.5 ml of Cl_4Sn (excess). After addition was complete, the reaction mixture was stirred at room temperature for 30 min. The dichloromethane was removed at reduced pressure, leaving a yellow residue. This was extracted with hot hexane and filtered. A considerable quantity of yellow material remained undissolved (see below). The clear, yellow filtrate was cooled slowly in the refrigerator, affording large, yellow crystals.

$Cl_2Sn[Cl_3SiMn(CO)_2C_5H_4CH_3]_2$.—The hexane-insoluble residue from the above reaction was dissolved in 15 ml of benzene and filtered, yielding a clear, orange-yellow solution. To this, hexane was slowly added until the mixture became cloudy. This was placed in the refrigerator, and at 1–2-hr intervals small aliquots of additional hexane were added. Fine orange-yellow crystals precipitated. Note the analytical values in Table II. This complex precipitated with one benzene molecule per three complex molecules, $\mathbf{Cl_2Sn[Cl_3SiMn(CO)_2C_5H_4CH_3]_2\cdot{}^1/_3C_6H_6}$. The nmr spectrum in deuterated dichloromethane showed the benzene proton absorption at τ 2.68. A sample kept under high vacuum for a prolonged period of time showed no change in composition.

$C_6H_5Cl_2Sn(Cl_3Si)Mn(CO)_2C_5H_4CH_3$.—A stirred dichloromethane solution containing 2.05 g of $(C_2H_5)_3NH^+[Cl_3SiMn(CO)_2C_5H_4CH_3]^-$ (4.8 mmol) was cooled to −78°. To this, 3.0 ml of $C_6H_5SnCl_3$ (excess) was added and the mixture was warmed slowly to room temperature. After 1 hr at room temperature, solvent was removed at reduced pressure, leaving an oily residue. The residue was washed with 20 ml of cold hexane to remove most of the excess $C_6H_5SnCl_3$. The remaining residue was then extracted with several aliquots of hot hexane and filtered. The combined filtrate was slowly cooled in the refrigerator yielding the pale yellow, crystalline product.

$(C_6H_5)_2ClSn(Cl_3Si)Mn(CO)_2C_5H_4CH_3$.—A solution of 2.30 g of $(C_2H_5)_3NH^+[Cl_3SiMn(CO)_2C_5H_4CH_3]^-$ (5.40 mmol) in 50 ml of dichloromethane was cooled to −78°. To this stirring mixture 1.78 g of $(C_6H_5)_2SnCl_2$ (5.2 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirring was continued overnight. The solvent was removed at reduced pressure, leaving a light-brown, oily material which was extracted with a minimum amount of hot hexane and filtered. At refrigerator temperature the pale yellow, microcrystalline product precipitated. This compound was sparingly soluble in hexane at room temperature.

$Cl_3Sn(Cl_3Si)Fe(CO)_4$.—A magnetically stirred solution containing 14.0 ml of Cl_4Sn (0.12 mol) in 100 ml of dichloromethane was cooled to −78°. Slowly 30.9 g of $(C_2H_5)_3NH^+[Cl_3SiFe(CO)_4]^-$ (0.077 mol) dissolved in 40 ml of dichloromethane was added. After addition was complete, the reaction mixture was maintained at −78° for an additional 5 min and then warmed slowly to room temperature where stirring was continued for 20 min. The solvent was removed at reduced pressure, resulting in a cream-colored powdery product, which was extracted with five 60-ml aliquots of dry, oxygen-free benzene. The combined, colorless, clear filtrate was cooled until it solidified to prevent bumping. At reduced pressure the benzene was slowly removed, leaving the white microcrystalline product (26.0 g, 0.050 mol, 65% based on $(C_2H_5)_3NH^+[Cl_3SiFe(CO)_4]^-$ employed). A small portion was recrystallized from hexane for analysis.

$Cl_2Sn[Fe(CO)_4SiCl_3]_2$.—A magnetically stirred solution containing 29.3 g of $Cl_3Sn(Cl_3Si)Fe(CO)_4$ (0.055 mol) in 100 ml of dichloromethane was cooled to −78°. Slowly, 22.5 g of $(C_2H_5)_3NH^+[Cl_3SiFe(CO)_4]^-$ (0.056 mol) in 30 ml of dichloromethane was added. All crystalline material dissolved slowly forming an intensely orange-red solution. After addition was complete, the reaction mixture was allowed to warm to room temperature. As the temperature gradually increased, a dense, orange-yellow crystalline material precipitated. At room temperature, evolution of gas became pronounced. The dichloromethane was quickly decanted and the crystalline material was washed with two 30-ml aliquots of cool dichloromethane. A small portion of the product was dissolved in a minimum amount of warm dichloromethane and filtered. Coarse orange crystals formed slowly at refrigerator temperature.

When this product is not immediately isolated after its formation and is allowed to remain in the reaction mixture at room temperature, it redissolves with evolution of carbon monoxide. The resulting reaction mixture is a deep red, transparent solution.

Reaction of $Cl_2Sn[Fe(CO)_4SiCl_3]_2$ with $(C_2H_5)_4NCl$.—A mixture of 0.88 g of $Cl_2Sn[Fe(CO)_4SiCl_3]_2$ (1.1 mmol) and 0.18 g of $(C_2H_5)_4NCl$ (1.1 mmol) in 20 ml of dichloromethane was stirred at room temperature until evolution of gas ceased. The solution changed slowly from yellow to red and a total of 29.4 cm^3 of gas at 25° and 695 mm pressure (at STP 24.5 cm^3, 1.1 mmol) was collected. The solvent was removed at reduced pressure leaving a red, oily material which was washed with several aliquots of pentane. The transparent, red, oily residue was dissolved in 40 ml of dichloromethane. Hexane was added to the top of the dark red solution, resulting in two liquid layers. Over a period of 3–4 weeks the hexane diffused into the dichloromethane and some red crystals, surrounded by an oily material formed. These were isolated and dried. When this crystalline material was heated, it slowly turned yellow. At 145° some melting activity was observed and above 160° it decomposed. Its infrared spectrum showed bands at 2096 (m), 2045 (s), 2030 (ms), and 1938 cm^{-1} (w) (dichloromethane).

Anal. Calcd for $C_{15}H_{20}Cl_9Fe_2NO_7SnSi_2$: C, 19.3; H, 2.2; Cl, 34.2; N, 1.5. Found: C, 19.9–20.2; H, 3.4–3.5; Cl, 35.6–36.3; N, 2.0–2.5.

$C_6H_5Cl_2Sn(Cl_3SiFe)Fe(CO)_4$.—A solution of 42.7 g of $(C_2H_5)_3NH^+[Cl_3SiFe(CO)_4]^-$ (1.06 mol) in 50 ml of dichloromethane was slowly added to a magnetically stirred solution of 50 ml of dichloromethane containing 36.2 g of $C_2H_5SnCl_3$ (0.120 mol) at −78°. After addition was complete, the reaction mixture was allowed to warm to room temperature. The solvent was removed at reduced pressure, leaving a yellow, oily material. This was extracted with hexane and filtered. The clear, yellow filtrate was cooled to −78° to form a cream-colored, microcrystalline material.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Kinetics and Mechanism of Oxidative Addition Reactions. II. Reactions of Benzyl and Allyl Halides with π-Cyclopentadienyl(triphenylphosphine)carbonylrhodium[1]

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The oxidative addition reactions of benzyl and allyl halides to $C_5H_5Rh(CO)P(C_6H_5)_3$ (**1**) yield products of the form $C_5H_5RhX(COR)P(C_6H_5)_3$. The reactions of the benzyl halides $C_6H_5CH_2X$ display simple kinetics, first order with respect to each reagent, and become progressively faster in the order $Cl \ll Br < I$. Reactions of allyl halides are more complex, but a mechanism is proposed to account for both the kinetics and the structures of the products. Investigation of a number of other electrophiles suggests that **1** will react cleanly only with reactive alkyl halides which lack other complicating functional groups.

Introduction

The oxidative additions of CH_3I and C_2H_5I to the compound $C_5H_5Rh(CO)P(C_6H_5)_3$ were shown[1] to involve a nucleophilic attack by the metal atom on the alkyl halide, the reactions being first order in each reagent. We have now extended this reaction to a number of other electrophiles. In this paper we describe these reactions and report the kinetics of the reactions with benzyl and allyl halides.

Experimental Section

Alkyl halides (Aldrich, Eastman, or BDH) were distilled under vacuum before use in kinetic runs. No impurities were detected by nmr. Dichloromethane was fractionated twice under nitrogen before use. All reactions were performed under an atmosphere of nitrogen. The preparation of $C_5H_5Rh(CO)P(C_6H_5)_3$ (**1**) has been described.[1] Products were prepared by one of two methods as follows.

Method A.—Compound **1** (100–200 mg) was dissolved with a stoichiometric amount of alkyl halide in 1–2 ml of CH_2Cl_2 and 1–2 ml of hexane. The mixture was allowed to stand at room temperature for a suitable time (Table I). Some of the products crystallized slowly from the reaction mixture, giving a useful preliminary purification. Recrystallization from CH_2Cl_2–hexane gave the product as red prisms or needles.

Method B.—Compound **1** (100–200 mg) was dissolved in CH_2Cl_2 (1–2 ml) with a large excess (1–2 ml) of alkyl halide. After a suitable reaction time the solvent and excess alkyl halide were removed under vacuum and the product was recrystallized as above.

Infrared data were obtained with a Perkin-Elmer Model 337 spectrophotometer, equipped with a Hewlett-Packard Model 7127A external recorder. Nmr spectra were recorded on Varian A56/60A and HA100 instruments and data are presented in Table II. Analytical data (Table I) were obtained by the microanalytical laboratory of this department.

Kinetics were based on the disappearance of the infrared carbonyl stretching band of **1** (at 1942 cm^{-1} in CH_2Cl_2).[1] All kinetics were carried out under pseudo-first-order conditions, using at least a tenfold excess of alkyl halide. Rate data are listed in Table III.

Results and Discussion

Compound **1** reacts with benzyl and allyl halides and

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[1] Part I: A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, **9**, 2658 (1970).