

TABLE III
 CALCULATION OF $\Delta H_f^\circ_{298.15}(\text{BrO}_3\text{F}(l))^{a,b}$

1. $\text{HBrO}_4 \cdot \text{HF} \cdot 1724\text{H}_2\text{O} \rightarrow \text{BrO}_3\text{F}(l) + 1725\text{H}_2\text{O}(l)$	$\Delta H_1 = 32.18 \pm 0.18 \text{ kcal mol}^{-1}{}^c$
2. $\text{HBrO}_4 \cdot 1723\text{H}_2\text{O} + \text{HF} \cdot 1.237\text{H}_2\text{O} \rightarrow \text{HF} \cdot \text{HBrO}_4 \cdot 1724.237\text{H}_2\text{O}$	$\Delta H_2 = -0.80 \pm 0.05 \text{ kcal mol}^{-1}{}^c$
3. $0.5\text{F}_2(\text{g}) + 0.5\text{H}_2(\text{g}) + 1.237\text{H}_2\text{O}(l) \rightarrow \text{HF} \cdot 1.237\text{H}_2\text{O}$	$\Delta H_3 = -76.17 \pm 0.06 \text{ kcal mol}^{-1}{}^d$
4. $0.5\text{Br}_2(l) + 2\text{O}_2(\text{g}) + \infty \text{H}_2\text{O}(l) \rightarrow \text{BrO}_4^- \cdot \infty \text{H}_2\text{O}$	$\Delta H_4 = 3.19 \pm 0.15 \text{ kcal mol}^{-1}{}^e$
5. $\text{BrO}_4^- \cdot \infty \text{H}_2\text{O} + 0.5\text{H}_2(\text{g}) \rightarrow (\text{H}^+ + \text{BrO}_4^-) \cdot \infty \text{H}_2\text{O}$	$\Delta H_5 = 0 \pm 0 \text{ kcal mol}^{-1}{}^f$
6. $(\text{H}^+ + \text{BrO}_4^-) \cdot \infty \text{H}_2\text{O} \rightarrow \text{HBrO}_4 \cdot 1723\text{H}_2\text{O} + (\infty - 1723)\text{H}_2\text{O}(l)$	$\Delta H_6 = 0.06 \pm 0.05 \text{ kcal mol}^{-1}{}^g$
7. $\text{H}_2\text{O}(l) \rightarrow \text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g})$	$\Delta H_7 = 68.32 \pm 0.02 \text{ kcal mol}^{-1}{}^h$
8. $0.5\text{Br}_2(l) + 0.5\text{F}_2(\text{g}) + 1.5\text{O}_2(\text{g}) \rightarrow \text{BrO}_3\text{F}(l)$	$\Delta H_f^\circ_{298.15}[\text{BrO}_3\text{F}(l)] = 26.78 \pm 0.25 \text{ kcal mol}^{-1}$

^a Species in this table are in the aqueous state, unless designated otherwise. ^b Uncertainties are twice the overall standard deviation. ^c Measured in present investigation. ^d Reference 8. ^e Reference 6. ^f D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Nat. Bur. Stand. (U. S.), Tech. Note*, No. 270-3 (1968). ^g Estimated value based on similarity to other perchlorates: V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," Report NSRDS-NBS-2, National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., 1965.

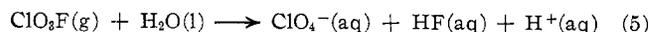
 TABLE IV
 THERMODYNAMIC PROPERTIES OF PERBROMYL FLUORIDE
 AT 298.15°K

	S° , cal deg ⁻¹ mol ⁻¹	ΔS_f° , ^a cal deg ⁻¹ mol ⁻¹	ΔH_f° , kcal mol ⁻¹	ΔG_f° , kcal mol ⁻¹
$\text{BrO}_3\text{F}(l)$	49.4 ± 3	-66.5 ± 3	26.78 ± 0.25	46.61 ± 0.92
$\text{BrO}_3\text{F}(g)$	71.4 ± 2	-44.5 ± 3	32.84 ± 0.26	46.11 ± 0.92

^a S°_{298} values for $\text{Br}_2(l)$, $\text{O}_2(g)$, and $\text{F}_2(g)$ were taken from the "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Mich., 1960-1965.

metry number was taken to be 3, in accordance with the tetrahedral C_{3v} symmetry deduced from the spectral studies.⁴ The ground-state quantum weight was assumed to be unity. $S^\circ_{298}(\text{BrO}_3\text{F}(l))$ was taken to be equal to $S^\circ_{298}(\text{BrO}_3\text{F}(g)) - \Delta H_{\text{vap}}^\circ/T_B$. From eq 3, T_B the normal boiling point, was calculated to be 275.5°K.

The hydrolyses of BrO_3F and ClO_3F may be written

$$\text{BrO}_3\text{F}(g) + \text{H}_2\text{O}(l) \longrightarrow \text{BrO}_4^-(\text{aq}) + \text{HF}(\text{aq}) + \text{H}^+(\text{aq}) \quad (4)$$


Based on the appropriate ΔG_f° values^{6,11,12} we find the Gibbs free energy of reaction 4 to be 4.3 kcal mol⁻¹ more negative than that of reaction 5. Hence, BrO_3F is slightly less stable with respect to perbromate ion than is ClO_3F with respect to perchlorate ion. This difference helps to explain the high reactivity of BrO_3F with such substances as water and glass, although purely kinetic effects are doubtless also involved.

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- (11) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Nat. Bur. Stand. (U. S.), Tech. Note*, No. 270-3 (1968).
 (12) P. A. G. O'Hare and A. C. Wahl, *J. Chem. Phys.*, **54**, 3770 (1971).

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Anomalous Reactions of Triphenylchlorosilane with Metal Carbonyl Anions

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Silyl halides react in an anomalous fashion with most metal carbonyl anions to give disiloxanes. The metal carbonyl anion may rearrange to polynuclear anions, abstract hydrogen from the solvent or other sources, be oxidized to the dimer or higher oligomers, or be halogenated by the silyl halide. Increasing the nucleophilicity of the metal carbonyl anion by phosphine substitution was thought to be a possible mechanism for suppressing the anomalous reaction, but only tricarbonyltriphenylphosphinecobaltate(1-) gives a normal substitution product. Germanium and tin halides give smooth substitution reactions except when bulky substituents on the anion cause severe steric hindrance.

Introduction

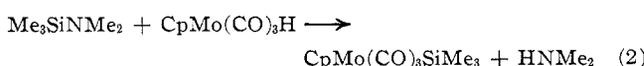
In connection with our research efforts aimed at stabilizing $p_\pi-p_\pi$ bonds¹ between carbon and its congeners, we desired a means of attaching silicon, bearing reactive functional groups, to a transition metal carbonyl moiety. In the past 10 years or so, a large number of compounds containing bonds between a transition metal and silicon, germanium, or tin have been reported. The methods used to prepare these compounds are rather varied, as the following examples illustrate:²

(A) reaction of a silyl metallic with a metal halide^{3,4}

- (1) M. D. Curtis, *J. Amer. Chem. Soc.*, **91**, 6011 (1969).
 (2) The following abbreviations will be used throughout the text: Cp, $\eta\text{-C}_5\text{H}_5$; Ph, C_6H_5 ; Me, CH_3 ; THF, tetrahydrofuran.

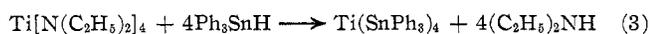


(B) reaction of a silylamine with a metal hydride³



(C) reaction of group IV hydrides with transition metal compounds^{5,6}

- (3) D. J. Cardin, S. A. Keppie, B. M. Kingston, and M. F. Lappert, *Chem. Commun.*, 1035 (1967).
 (4) E. Hengge and H. Zimmerman, *Angew. Chem.*, **80**, 153 (1968).
 (5) H. M. J. C. Creemers, F. Verbeek, and J. G. Noltes, *J. Organometal. Chem.*, **15**, 125 (1968).
 (6) W. Jetz, P. B. Simmons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966).



and (D) reaction of a transition metal carbonyl anion with a group IV halide⁷



The last reaction has proven to be most generally applied in the formation of transition metal bonds to germanium, tin, and lead. For instance, the following types of bonds have been formed from reactions analogous to (5): Sn-Co^{8,9} and Ge-Co;⁹ M-E¹⁰ where M = Cr, Mo, W and E = Ge, Sn, Pb; Mn-Sn and Mn-Pb.⁷ This list is by no means complete but is intended to show the scope of method D when applied to *germanium, tin, or lead*.

Attempts to prepare silicon-metal bonds by method D are generally unsuccessful. Cyclopentadienyliron dicarbonyl anion, CpFe(CO)₂⁻, reacts with *organo*¹¹ silicon halides to form CpFe(CO)₂SiR₃ in the normal fashion.¹² To this author's knowledge, the only other successful preparation of an R₃Si-metal bond was reported by Berry and MacDiarmid¹³ using *dry* NaMn(CO)₅ and trimethylchlorosilane. In THF, trimethylsilylmanganese pentacarbonyl does not form.

An inspection of methods A-C reveals that B and C are not suitable procedures if the silicon bears olefinic substituents (the metal hydrides add to the double bond), while method A is severely limited by the availability of silyllithium reagents. Therefore, we sought some modification of method D which would allow the formation of silicon-metal bonds under mild conditions. An examination of the reactions reported in the literature led to the conclusion that silicon-metal bonds should form provided the nucleophilicity of the metal carbonyl anion is greater than about 10⁶ on Dessy's scale (*k*₂).¹⁴ Substitution of carbonyl by triphenylphosphine should constitute a simple means of increasing the nucleophilicity of the anions¹⁵ inasmuch as the *pK* of HCo(CO)₃L increases from *ca.* 0 (L = CO) to *ca.* 7 (L = Ph₃P).¹⁶ Thus, large increases in nucleophilicities are possible if the trend in basicity is paralleled.

Experimental Section

All manipulations of metal carbonyl compounds were conducted on a vacuum line equipped with a dual manifold which allowed apparatus to be alternately evacuated and pressurized with dry N₂.¹⁷ Standard Schlenk tube techniques were employed.¹⁷ Melting points of carbonyl derivatives were obtained in evacuated capillaries and are uncorrected. The THF used in the Na-Hg reductions was distilled under vacuum from LiAlH₄ directly into the reaction vessel. The triphenylchlorosilane was freshly

(7) R. D. Gorsich, *J. Amer. Chem. Soc.*, **84**, 2486 (1962).

(8) A. D. Beveridge and H. C. Clark, *J. Organometal. Chem.*, **11**, 601 (1968).

(9) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967).

(10) H. R. H. Patil and W. A. G. Graham, *ibid.*, **5**, 1401 (1966).

(11) Silyl halides, H₃SiX, react more readily with metal anions: D. J. Russo and A. P. Hagen, *Inorg. Nucl. Chem. Lett.*, **5**, 885 (1969); B. J. Aylett, J. M. Campbell, and A. Walton, *ibid.*, **4**, 79 (1968); B. J. Aylett and J. M. Campbell, *ibid.*, **3**, 137 (1967).

(12) T. S. Piper, D. Lemal, and G. Wilkinson, *Naturwissenschaften*, **43**, 129 (1956).

(13) A. D. Berry and A. G. MacDiarmid, *Inorg. Nucl. Chem. Lett.*, **5**, 601 (1969).

(14) R. E. Dessy, R. L. Pohl, and R. B. King, *J. Amer. Chem. Soc.*, **88**, 5121 (1966).

(15) P. W. Jolly, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.*, 5830 (1965).

(16) W. Hieber and E. Lindner, *Z. Naturforsch. B*, **16**, 137 (1961); *Chem. Ber.*, **94**, 1417 (1961).

(17) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1968.

recrystallized from pentane and was free of disiloxane as shown by its ir spectrum. The technique used in the sodium amalgam reductions has been fully described elsewhere.¹ Routine ir spectra of air-stable solids were determined as KBr disks on a Beckman IR 5 except where noted otherwise. Crystal data were obtained on a Buerger precession instrument using Mo K α radiation. Mass spectra were obtained on an AEI MS902 spectrometer (ionizing energy 70 eV).

Cobalt Tetracarbonyl Anion and Triphenylchlorosilane.—NaCo(CO)₄ was prepared from 1.0 g (2.9 mmol) of Co₂(CO)₈ in THF. Triphenylchlorosilane (5.1 g, 17.4 mmol) was added in portions. After 1 week at room temperature, an off-white precipitate (A) was collected. Solid A was extracted with CH₂Cl₂ from which 1.8 g of pure hexaphenyldisiloxane and 0.5 g of a pale violet solid believed to be a mixture of NaCl and CoCl₂ were isolated. The disiloxane was identified by its melting point (227–228°) and by comparing its ir spectrum with authentic material. The violet solid was totally inorganic (no carbonyls), soluble in water, and tested strongly for Na⁺, Cl⁻, and Co²⁺. A further 0.8 g of disiloxane (total yield 2.6 g, 52%) was obtained from the THF. Complete removal of solvent gave a small amount of intractable red oil.

Ph₃ECo(CO)₃PPh₃ (E = Si, Ge, Sn).—A 1.0-g (1.2-mmol) sample of tricarbonyltriphenylphosphinecobalt dimer, [Co(CO)₃(CO)₃PPh₃]₂, was converted to tricarbonyltriphenylphosphinecobaltate(1-) anion, Co(CO)₃PPh₃⁻, by sodium amalgam reduction in THF. The reduced solution displayed absorptions of 1970 (m), 1930 (s), 1855 (vs), and 1810 (s) cm⁻¹. Triphenylchlorosilane (0.61 g, 2.4 mmol) was added and, after 1 week, only a single, broad band was present at 1960 cm⁻¹. The THF was stripped and the residue taken up in methylene chloride. After filtering, benzene was added to the filtrate and the CH₂Cl₂ pumped off, giving 0.1 g of [Co(CO)₃PPh₃]₂, identified by comparison with authentic material. From the benzene, 0.5 g (31%) of Ph₃SiCo(CO)₃PPh₃ was obtained. *Anal.* Calcd for C₃₉H₃₀CoO₃PSi: C, 70.97; H, 4.55. Found: C, 70.47; H, 4.48; dec pt 180°. ν_{CO} : 2020 (w), 1950 (vs) cm⁻¹.

Ph₃GeCo(CO)₃PPh₃ (1.5 g, 88%, mp 220° dec) was obtained in a similar fashion from 1.0 g of the cobalt dimer and 0.92 g of triphenylbromogermane. *Anal.* Calcd for C₃₉H₃₀CoGeO₃P: C, 66.05; H, 4.26. Found: C, 66.0; H, 4.29. ν_{CO} : 2010 (w), 1950 (vs) cm⁻¹. The triphenylstannyl derivative (mp 210–213°) was obtained in 83% yield. *Anal.* Calcd for C₃₈H₃₀CoO₃PSn: C, 62.02; H, 4.00. Found: C, 62.22; H, 3.98. ν_{CO} : 2000 (w), 1945 (vs) cm⁻¹.

Identical compounds were obtained by adding Ph₃ECo(CO)₄ (E = Si, Sn) to molten triphenylphosphine (~100% excess). The formation of Ph₃SiCo(CO)₃PPh₃ was complete in 5 min at 120° while the tin derivative required 1 hr at 150°. Yields of purified products were 77 and 69%, respectively.

Iodotricarbonyltriphenylphosphinecobalt(I).—A 2.0-g sample of [Co(CO)₃PPh₃]₂¹⁸ was suspended in 50 ml of carbon tetrachloride and 0.6 g of I₂ dissolved in 150 ml of CCl₄ was added slowly (~1 hr). The flocculent, brown solid was filtered, washed with CH₂Cl₂, and vacuum dried; yield 2.0 g. *Anal.* Calcd for C₂₀H₁₅CoIO₂P: I, 23.8; P, 5.83. Found: I, 24.0; P, 5.76.

Iodocarbonylbis(triphenylphosphine)cobalt(I).—ICo(CO)₂(PPh₃)₂ (1.0 g) was added to 3.0 g of triphenylphosphine at 120°. After 20 min, the mixture was allowed to cool and then treated with ether to remove excess phosphine. The ether-insoluble solid was recrystallized twice from CH₂Cl₂-ethanol to give 1.4 g (96%) of product. *Anal.* Calcd for C₃₈H₃₀CoIO₂P₂: C, 59.55; H, 3.95; I, 16.56. Found: C, 60.88; H, 3.96; I, 16.00.

Reactions of Na[Co(CO)₂(PPh₃)₂].—An 0.8-g (1-mmol) sample of ICo(CO)₂(PPh₃)₂ was reduced with sodium amalgam and 0.2 g of trimethylchlorostannane was added. After 3 hr the THF was removed, the residue was treated with CH₂Cl₂, and the mixture was filtered. Ethanol was added to the filtrate and the CH₂Cl₂ was pumped off giving Me₃SnCo(CO)₂(PPh₃)₂ (0.7 g, 87%) as yellow needles. *Anal.* Calcd for C₄₁H₃₀CoO₂P₂Sn: C, 61.30; H, 4.89; Co, 7.33; mol wt 803.3. Found: C, 60.51; H, 4.75; Co, 7.06. As determined by Mr. T. Giordano of this department, the crystals are triclinic; *a* = 14.49, *b* = 11.95, *c* = 11.22 Å, α = 81° 39', β = 80° 15', γ = 94° 14'; *d* = 1.41 g/cm³; *Z* = 2.

An equimolar amount of triphenylchlorostannane was added to Co(CO)₂(PPh₃)₂⁻. Work-up as above gave yellow crystals (A) with ν_{CO} at 1948 (mw) and 1894 (vs) cm⁻¹. From the mother

(18) A. R. Manning, *J. Chem. Soc. A*, 1135 (1968).

liquor a second crop of yellow crystals (B) was obtained with ν_{CO} at 2000 (w), 1945 (vs), and 1895 (w) cm^{-1} . *Anal.* Calcd for $\text{C}_{56}\text{H}_{48}\text{CoO}_7\text{P}_2\text{Sn}$: C, 68.0; H, 4.58. Found for A: C, 64.38; H, 4.26. Found for B: C, 63.00; H, 3.97.

With $\text{Co}(\text{CO})_2(\text{PPh}_3)_2^-$, triphenylchlorosilane or triphenylbromogermane gave products whose entire ir spectra were superpositions of the spectra of $\text{Ph}_3\text{ECo}(\text{CO})_3\text{PPh}_3$ (E = Si, Ge) and $\text{ICo}(\text{CO})_2(\text{PPh}_3)_2^-$.

Reactions of $\text{Na}[\text{Mn}(\text{CO})_4\text{PPh}_3]$.—The anion was prepared by sodium amalgam reduction of the dimer $[\text{Mn}(\text{CO})_4\text{PPh}_3]_2^{19}$ in THF. The reduced solution had absorption peaks at 1970 (w, sh), 1950 (m), 1860 (m), 1830 (s), and 1780 (ms) cm^{-1} . To a solution containing 1 mmol of anion was added 0.4 g (1 mmol) of triphenylbromogermane. Work-up as usual gave 0.5 g (68%) of $\text{Ph}_3\text{GeMn}(\text{CO})_4\text{PPh}_3$. ν_{CO} : 1997 (vw), 1956 (vs), 1920 (vw) cm^{-1} (determined in CH_2Cl_2 solution on a Beckman IR 12). *Anal.* Calcd for $\text{C}_{40}\text{H}_{30}\text{GeO}_4\text{MnP}$: C, 65.5; H, 4.12. Found: C, 65.30; H, 4.31.

Triphenylchlorosilane (0.6 g, 2 mmol) was added to a THF solution containing 2 mmol of $\text{NaMn}(\text{CO})_4\text{PPh}_3$. After 9 hr, the absorption spectrum consisted of peaks at 2020 (m), 1980 (s), 1955 (vs), 1920 (m, sh) cm^{-1} . The THF was stripped, the residue was dissolved in CH_2Cl_2 , and the solution was filtered. Dry benzene was added to the filtrate and the CH_2Cl_2 removed. After standing overnight, 0.3 g (55%) of hexaphenyldisiloxane separated. The filtrate from the disiloxane was concentrated and then diluted with petroleum ether (bp 30–60°). Standing gave a crop of yellow-orange crystals which were recrystallized from CH_2Cl_2 -ethanol (yield 0.2 g, 15%). ν_{CO} : 2020 (w), 1950 (vs), 1918 (s) cm^{-1} . *Anal.* Calcd for $\text{C}_{30}\text{H}_{30}\text{ClMnO}_3\text{P}_2$: C, 67.01; H, 4.32; Cl, 5.08; Mn, 7.85; P, 8.47. Found: C, 67.61; H, 4.78; Cl, 5.68; Mn, 7.37; P, 8.41. The benzene-petroleum ether mother liquor was taken nearly to dryness and the residue was dissolved in hexane. After 8 hr, orange crystals were obtained which after recrystallization melted at 214–215° dec. ν_{CO} : 1975 (sh), 1945 (vs), 1915 (sh) cm^{-1} . This compound was identified as the dimer $[\text{Mn}(\text{CO})_4\text{PPh}_3]_2$; yield 0.3 g, 35%. *Anal.* Calcd for $\text{C}_{44}\text{H}_{30}\text{Mn}_2\text{O}_3\text{P}_2$: C, 61.68; H, 3.53; Mn, 12.82; P, 7.03. Found: C, 60.86; H, 3.60; Mn, 12.80; P, 7.19.

Manganese Pentacarbonyl Anion and Triphenylchlorosilane.—A 2.0-g (5.0-mmol) sample of $\text{Mn}_2(\text{CO})_{10}$ was reduced to $\text{NaMn}(\text{CO})_5$ in THF. A 3.0-g (10-mmol) amount of triphenylchlorosilane was added and the solution was stirred for 4 days. The THF was then removed and the residue was extracted with toluene. The toluene solution yielded 1.4 g (52%) of hexaphenyldisiloxane. The solid remaining after the extraction was taken up in ether and filtered. The ether was removed from the red filtrate, and the resulting red solid was dissolved in ethanol. A solution of 1.0 g of tetraethylammonium chloride was added to the alcoholic solution causing an orange solid to precipitate. The precipitate was collected and dried and then extracted with acetone, leaving a residue of sodium chloride. Alcohol was added to the red solution, and the acetone was slowly pumped off. In this manner, large, red crystals, soluble in acetone, slightly soluble in alcohol, and insoluble in nonpolar solvents were obtained. The solid is air stable but solutions are rapidly decomposed by air. The ν_{CO} bands listed in the Results and Discussion were obtained in acetone solution on a Beckman IR 12. An nmr spectrum in acetone- d_6 gave only peaks due to the $(\text{C}_2\text{H}_5)_4\text{N}^+$ ion. The crystals are monoclinic; $a = 11.7$, $b = 14.9$, $c = 8.06$ Å; $\beta = 96^\circ 45'$; $d = 1.60$ g/cm³. Systematic extinctions were observed for $h + k \neq 2n$ giving C_2 , Cm , or $C_{2/m}$ as the possible space groups. The maximum molecular weight for the compound is 672 ($Z = 2$).

Identical samples of this compound were sent to two laboratories ("C" and "G") for analyses. Their results are given in Table I. The elemental composition calculated for $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Mn}_3(\text{CO})_{14}]$ ($\text{C}_{22}\text{H}_{20}\text{Mn}_3\text{NO}_{14}$) is as follows: C, 38.45; H,

2.91; Mn, 23.98; N, 2.04; mol wt 687.2. The starred values agree reasonably well with the calculated values.

Rhenium Pentacarbonyl Anion and Triphenylchlorosilane.— $\text{NaRe}(\text{CO})_5$ was produced from 1.0 g (1.5 mmol) of $\text{Re}_2(\text{CO})_{10}$. To the anion solution was added 0.9 g (3 mmol) of triphenylchlorosilane, and the mixture was allowed to stir for 2 days. The THF was then pumped off and the residue was extracted with benzene. This solution was transferred to a Florisil column under a N_2 atmosphere and eluted using deoxygenated solvents. The products were identified by mass spectrometry and high-resolution ir (Beckman IR 12) and are described in the Results and Discussion.

The benzene-insoluble material was then treated with CH_2Cl_2 and filtered. Benzene was added and the CH_2Cl_2 was removed, giving 0.8 g of hexaphenyldisiloxane (~100%).

Cyclopentadienyldicarbonyltriphenylphosphinemolybdenum Dimer, $[\text{CpMo}(\text{CO})_2\text{PPh}_3]_2$.—This air-sensitive compound was prepared by adding 1.5 g (3.1 mmol) of finely ground $[\text{CpMo}(\text{CO})_3]_2$ to 3.0 g of triphenylphosphine at 130°. Evolution of carbon monoxide ceased after 5 min. After cooling, ether was added and the mixture was filtered to remove unreacted triphenylphosphine. The insoluble material was then treated with CH_2Cl_2 and filtered, giving a red filtrate and leaving a trace of purple solid.^{20,21} Ethanol was added to the CH_2Cl_2 solution and the CH_2Cl_2 was pumped off giving brilliant yellow crystals, dec pt 180°; yield 2.8 g (95%). ν_{CO} : 1900 (s), 1770 (s) cm^{-1} (CH_2Cl_2 solution). *Anal.* Calcd for $\text{C}_{30}\text{H}_{40}\text{Mo}_2\text{O}_4\text{P}_2$: C, 62.63; H, 4.20; P, 6.46. Found: C, 61.21; H, 4.04; P, 6.31.

Reactions of Cyclopentadienyldicarbonyltriphenylphosphinemolybdenum Anion.—Trimethylchlorostannane (0.6 g, 3 mmol) was added to a solution of $[\text{CpMo}(\text{CO})_2\text{PPh}_3]$ prepared by sodium amalgam reduction of 1.4 g (1.5 mmol) of the dimer $[\text{CpMo}(\text{CO})_2\text{PPh}_3]_2$. After stirring for 2 hr, the THF was removed and the residue was taken up in CH_2Cl_2 and filtered. Ethanol was added to the filtrate and the CH_2Cl_2 was boiled off giving pale yellow crystals. Following recrystallization, 0.6 g (47%) of product, mp 206–207°, was obtained. *Anal.* Calcd for $\text{C}_{28}\text{H}_{20}\text{MoO}_2\text{PSn}$: C, 52.28; H, 4.54; P, 4.82. Found: C, 52.33; H, 4.43; P, 4.88.

An identical procedure yielded 0.4 g (17%) of $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{GePh}_3$, dec pt 280°. *Anal.* Calcd for $\text{C}_{43}\text{H}_{35}\text{GeMoO}_2\text{P}$: C, 65.93; H, 4.51; P, 3.96. Found: C, 65.43; H, 4.51; P, 4.45.

Triphenylchlorosilane (0.9 g, 3.0 mmol) was added to a THF solution prepared by reducing 1.3 g (1.4 mmol) of $[\text{CpMo}(\text{CO})_2\text{PPh}_3]_2$. After 5 min, the THF was pumped off and the residue was stirred with benzene and then filtered. From the filtrate 0.5 g of orange platelets, identified as $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{H}$, was obtained. *Anal.* Calcd for $\text{C}_{20}\text{H}_{21}\text{MoO}_2\text{P}$: C, 62.50; H, 4.41; P, 6.45. Found: C, 62.48; H, 4.35; P, 6.43.

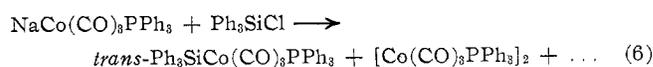
The benzene-insoluble material was extracted with CH_2Cl_2 , giving a solution containing no carbonyls (ir). Addition of benzene, followed by removal of the CH_2Cl_2 , gave 0.5 g (62%) of hexaphenyldisiloxane.

The residue remaining after the extraction with CH_2Cl_2 was extracted with acetone. To this acetone solution was added tetraethylammonium chloride in ethanol. The off-white solid which precipitated was recrystallized from acetone-ethanol to give glittering yellow platelets. ν_{CO} : 1885 (s), 1775 (s), and 1740 (s) cm^{-1} .

The ir spectrum of the solid is identical in all respects with that of $[(\text{C}_2\text{H}_5)_4\text{N}][\text{CpMo}(\text{CO})_3]$, prepared by reduction of $[\text{CpMo}(\text{CO})_3]_2$.

Results and Discussion

Sodium tetracarbonylcobaltate(1-) reacts very slowly with triphenylchlorosilane in THF to produce cobalt chloride and hexaphenyldisiloxane as principal products. A small amount of intractable oil is also formed. In contrast, $\text{NaCo}(\text{CO})_3\text{PPh}_3$ reacts over a period of several days with triphenylchlorosilane to give the products shown in the reaction



(20) This purple solid is probably $\text{Cp}_2\text{Mo}_2(\text{CO})_6\text{PPh}_3$.²¹

(21) K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, **6**, 294 (1967).

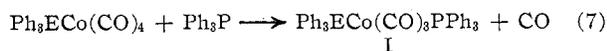
TABLE I

Lab.	% Mn	% N	% C	% H
"C"	23.02	2.39	38.68*	3.08*
		2.35		
"G"	22.84	2.37		
	23.63*	2.17*		
Av	23.18	Av 2.37		

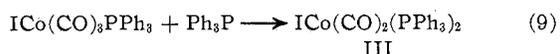
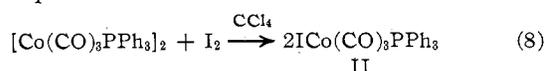
(19) A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc. A*, (1964).

The silyl derivative is obtained in 31% yield along with a trace of the dimer. Both Ph_3SnCl and Ph_3GeBr react rapidly with $\text{NaCo}(\text{CO})_3\text{PPh}_3$ to give the corresponding *trans*- $\text{Ph}_3\text{ECo}(\text{CO})_3\text{PPh}_3$ (E = Ge, Sn).

The stereochemistry was inferred from the ir spectra which exhibit bands at ~ 2000 (w) and 1950 (vs) cm^{-1} assigned, respectively, to the A_1 and E stretching modes of the CO groups in C_{3v} symmetry. The geometry of the germanium derivative has been confirmed by an X-ray structure determination.²² Identical *trans*-substituted compounds are obtained by allowing $\text{Ph}_3\text{ECo}(\text{CO})_4$ (E = Si, Sn) to react with molten triphenylphosphine at 120 – 150°



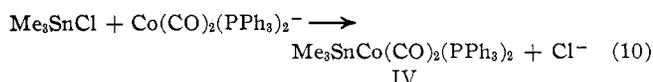
In order to increase the basicity of the metal carbonyl anion further, two carbonyl groups were replaced by triphenylphosphine *via*



The addition of I_2 to tricarbonyltriphenylphosphinecobalt dimer gives the previously unreported iodo complex II, dec pt $\sim 170^\circ$ *in vacuo*. ν_{CO} : 2020 (w), 1950 (vs) cm^{-1} .

The E-mode stretch is curiously insensitive to the nature of the axial substituent in these *trans* phosphine complexes. The CO absorbances of III occur at 1985 (m) and 1920 (vs) cm^{-1} .

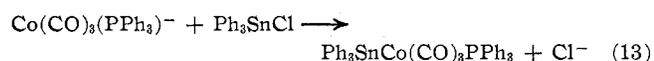
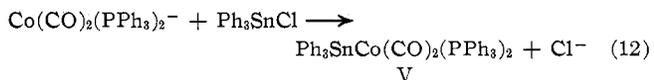
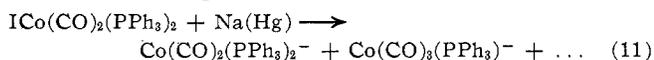
Reduction of $\text{ICo}(\text{CO})_2(\text{PPh}_3)_2$ with sodium amalgam in THF gives $\text{NaCo}(\text{CO})_2(\text{PPh}_3)_2$.²³ When allowed to react with trimethylchlorostannane, an 87% yield of $\text{Me}_3\text{SnCo}(\text{CO})_2(\text{PPh}_3)_2$ is obtained



The ν_{CO} bands of IV occur at 1940 (m) and 1882 (vs) cm^{-1} . The nmr spectrum consists of a broad, unresolved multiplet at τ 3.4 and a sharp singlet at τ 9.95.²⁴

The reaction of triphenyltin chloride and $\text{NaCo}(\text{CO})_2(\text{PPh}_3)_2$ gave two products which could not be completely separated because of their similar solubilities and the small amounts of material available. The ir spectra and chemical analyses leave little doubt, however, that the two compounds are V (ν_{CO} : 1948 (m), 1894 (vs) cm^{-1}) and I (E = Sn; ν_{CO} : 2000 (w), 1945 cm^{-1}).

The $\text{Ph}_3\text{SnCo}(\text{CO})_3\text{PPh}_3$ is undoubtedly formed from $\text{Co}(\text{CO})_3\text{PPh}_3^-$ produced by ligand exchange during the reduction step²⁵



(22) J. K. Stalick and J. A. Ibers, *J. Organometal. Chem.*, **22**, 213 (1970).

(23) W. Hieber and H. Duchatsch, *Chem. Ber.*, **98**, 2530, 2933 (1965).

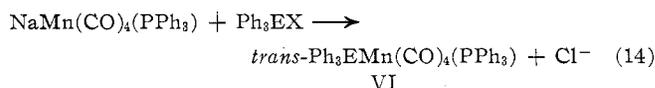
(24) Chemical shifts are referenced to internal TMS.

(25) W. Hieber, M. Höfler, and J. Muschi, *Chem. Ber.*, **98**, 311 (1965).

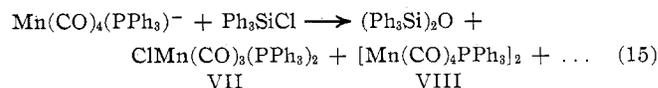
Mixtures are also obtained when the solution resulting from the reduction of $\text{ICo}(\text{CO})_2(\text{PPh}_3)_2$ is allowed to react with Ph_3SiCl or Ph_3GeBr . In these instances, the ir spectra indicate that the products are I (E = Si, Ge) and III. Again, I probably forms from the $\text{Co}(\text{CO})_3(\text{PPh}_3)_2^-$ anion produced during the reduction step, but the $\text{ICo}(\text{CO})_2(\text{PPh}_3)_2$ appears to be formed during the reaction. After the reduction step, the bands characteristic of III are absent, but after addition of Ph_3SiCl or Ph_3GeBr , bands appear at 1985 (m), 1950 (vs), and 1920 (s) cm^{-1} over a 10-hr period. The source of the iodine must be the sodium iodide produced in the initial reduction of III.

The above observations indicate that the triphenylphosphine ligands in $\text{Co}(\text{CO})_2(\text{PPh}_3)_2^-$ effectively block access to the cobalt atom and that steric factors are of overriding importance. The "availability" of the central atom to nucleophiles increases in the order $\text{Me}_3\text{SnX} > \text{Ph}_3\text{SnX} > \text{Ph}_3\text{GeX} > \text{Ph}_3\text{SiX}$. The trimethyltin moiety undergoes facile substitution with $\text{Co}(\text{CO})_2(\text{PPh}_3)_2^-$, triphenyltin chloride gives mixtures and lower yields, and there is no evidence for substitution on germanium or silicon.

Gorsich⁷ has reported that $\text{NaMn}(\text{CO})_4(\text{PPh}_3)$ reacts with triphenylchlorostannane to give VI (E = Sn). It was found that $\text{NaMn}(\text{CO})_4(\text{PPh}_3)$ also reacts readily with triphenylbromogermane to give the corresponding germanium compound, VI (E = Ge)



In contrast, neither trimethylchlorosilane nor triphenylchlorosilane forms the silyl analog of VI. In the reaction with triphenylchlorosilane, a complex mixture is produced which had to be separated by fractional crystallization. The carbonyl components appeared to decompose on attempted column chromatography even when the column was prepared under completely anaerobic conditions. From the mixture, pure hexaphenyldisiloxane (55%), $\text{ClMn}(\text{CO})_3(\text{PPh}_3)_2$ (15%), and $[\text{Mn}(\text{CO})_4(\text{PPh}_3)]_2$ (35%) were isolated

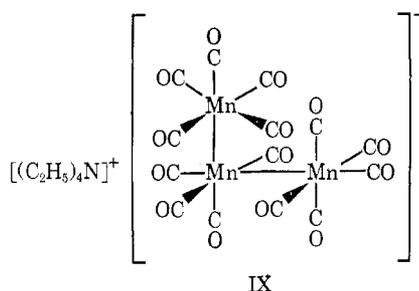


There are no bands attributable to VIII in the solution of $\text{Mn}(\text{CO})_4(\text{PPh}_3)^-$ after reduction is complete; hence, the dimer VIII forms during the reaction with the chlorosilane. The only source of chlorine for the formation of VII is the chlorosilane. Since ligand exchange must occur in the formation of VII, it was thought that an insight into the mechanism might be easier to obtain by investigating the reaction of the unsubstituted manganese pentacarbonyl anion.

Gorsich⁷ erroneously reported that triphenylsilylmanganese pentacarbonyl is produced in the reaction of Ph_3SiCl with $\text{NaMn}(\text{CO})_5$. The compound was described as a red, unstable solid, properties inconsistent with authentic $\text{Ph}_3\text{SiMn}(\text{CO})_5$ prepared by method C.⁶ In this work, it was found that $\text{Mn}(\text{CO})_5^-$ reacts slowly with triphenylchlorosilane to produce hexaphenyldisiloxane (52%) and a red anionic compound of manganese which contains no silicon and may be isolated as the sodium or tetraethylammonium salt.

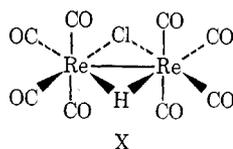
Solutions of the red compound in acetone give bands at 2049 (w), 2039 (w), 2014 (m), 1980 (vs), 1946–1943 (m, doublet), and 1869 (m) cm^{-1} . A KBr pellet of the tetraethylammonium salt of the material shows no other absorbances above 600 cm^{-1} except those of the tetraethylammonium cation.

Elemental analyses, performed on different portions of the same batch of purified crystals, were variable. The average values of the per cent nitrogen (2.37%) and manganese (23.18%) give a nitrogen:manganese ratio of 1:2.50. This led to the formulation of this compound as $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Mn}_5(\text{CO})_{24}]$, mol wt 1187.²⁶ However, the maximum molecular weight, derived from the volume of the unit cell and the density, is 672, clearly inconsistent with any reasonable $\text{Mn}_5(\text{CO})_n^{2-}$ formulation. With the crystal data in hand, one can deduce a chemically reasonable structure which is consistent with the elemental analyses, unit cell data, and ir spectrum



The assumed C_s structure of the anion of IX allows all 14 CO stretching modes in the ir spectrum (nine observed). A linear (D_{4h}) arrangement of Mn atoms has only four ir-active stretching modes. The C_s structure is consistent with the imposed symmetry of one of the possible space groups (Cm), is very similar to the protonated forms $\text{HMnRe}_2(\text{CO})_{14}$ and $\text{HRe}_3(\text{CO})_{14}$,^{27,28} and is isoelectronic with the known compounds $\text{Na}_2[\text{Cr}_3(\text{CO})_{14}]$ and $\text{Na}_2[\text{Mo}_3(\text{CO})_{14}]$.²⁹

Rhenium pentacarbonyl anion has a high nucleophilicity ($k_2' = 2.5 \times 10^4$) on Dessy's scale.¹⁴ Hence, silicon-rhenium bonds might be expected to form in the reaction of $\text{NaRe}(\text{CO})_5$ with Ph_3SiCl . It was found, however, that no triphenylsilylrhenium compounds were formed; instead a quantitative yield of hexaphenyldisiloxane and a mixture of rhenium carbonyls were obtained. The mixture of carbonyls was dissolved in benzene and chromatographed from Florisil. The first material collected (pentane eluent) had an ir spectrum identical with that of $\text{Re}_2(\text{CO})_{10}$. The second band was pale yellow and had ir bands at 2106 (mw), 2074 (vw), 2050 (vw, sh), 2031 (vs), 2013 (s), and 1971 (vs) cm^{-1} . The mass spectrum of this material is consistent with structure X, in which each rhenium



achieves 18 electrons. In the mass spectrum of X, loss of hydrogen is not observed until two carbonyls

(26) M. D. Curtis, *Inorg. Nucl. Chem. Lett.*, **6**, 859 (1970).

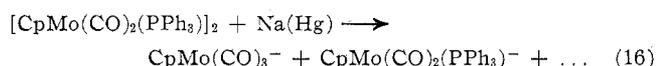
(27) W. Fellman and H. D. Kaesz, *ibid.*, **2**, 63 (1966).

(28) M. R. Churchill and R. Bau, *Inorg. Chem.*, **6**, 2086 (1967).

(29) H. Behrens and W. Haag, *Chem. Ber.*, **94**, 320 (1961).

are cleaved, and the hydrogen loss is not appreciable until four carbonyls are lost. Similarly, chlorine is held tenaciously and the ions HRe_2Cl^+ and Re_2Cl^+ are observed, the latter being the most intense peak in the spectrum. Mass spectra with these features are characteristic of carbonyls with bridging groups.³⁰ The C_{2v} symmetry of X allows for seven ir-active carbonyl stretching modes (six are observed). A third band (yellow) eluted from the column with hexane-benzene and was identified by its ir and mass spectra as $\text{HRe}_3(\text{CO})_{14}$.^{27,31,32}

Upon reduction of $[\text{CpMo}(\text{CO})_2(\text{PPh}_3)]_2$ with sodium amalgam, the ir bands of the dimer are replaced by bands at 1970 (mw), 1905 (vs), 1800 (vs), 1745 (s), and 1695 (ms) cm^{-1} . $\text{CpMo}(\text{CO})_3^-$ is responsible for the bands at 1905, 1800, and 1745 cm^{-1} as shown by isolating the anion as the tetraethylammonium salt. Thus, phosphine exchange occurs upon reduction



The addition of triphenylbromogermane or trimethylchlorostannane to the mixture of anions causes the rapid disappearance of all anion ir bands. A 47% yield of *trans*- $\text{CpMo}(\text{CO})_2(\text{PPh}_3)(\text{SnMe}_3)$ was obtained. The compound has CO stretching frequencies at 1900 and 1830 cm^{-1} , and the nmr spectrum consists of a multiplet at $\tau \sim 2.7$, a doublet at $\tau 4.67$ (C_5H_5 , $J_{\text{P-H}} = 1.0$ Hz), and a singlet at $\tau 9.66$ (CH_3 , $J_{\text{Sn-H}} = 48$ Hz). The coupling of cyclopentadienyl and phosphorus is characteristic of *trans* isomers of $\text{CpMo}(\text{CO})_2(\text{PR}_3)\text{X}$.³³

Triphenylbromogermane gave only a 17% yield of *trans*- $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{GePh}_3$ (ν_{CO} : 1910, 1836 cm^{-1}). The nmr spectrum displays $\tau(\text{Ph}) \sim 2.5$ and $\tau(\text{Cp}) 5.17$ with $J_{\text{P-H}} = 1.1$ Hz.

Trimethylchlorosilane reacts rapidly with $\text{CpMo}(\text{CO})_2(\text{PPh}_3)^-$ as shown by the disappearance of the ir bands of the anion within 5 min of mixing, leaving unchanged the absorptions of the $\text{CpMo}(\text{CO})_3^-$ ion.³⁴ Work-up of the mixture gave a 62% yield of hexaphenyldisiloxane and $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{H}$. The latter compound was identified by elemental composition and mass spectrometry (see Appendix). When the hydride is crystallized from benzene-petroleum ether, orange platelets are formed having ir bands at 1965 (sh), 1932 (vs), and 1850 (vs) cm^{-1} . When crystallized from CH_2Cl_2 -ethanol, yellow needles are formed in addition to the orange platelets. The yellow needles have ir bands at 1922 (s) and 1845 (vs) cm^{-1} . Both forms have the same melting point, identical mass spectra, and the same nmr spectra ($\tau(\text{Cp}) 5.25$, singlet). It is concluded that the orange and yellow forms are *cis* and *trans* isomers of $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{H}$ which interconvert rapidly in solution. Faller³³ has reported an averaged spectrum at room temperature for the

(30) J. Lewis and B. F. G. Johnson, *Accounts Chem. Res.*, **1**, 245 (1968).

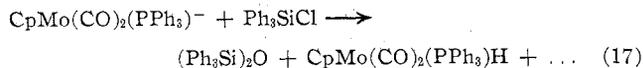
(31) J. M. Smith, K. Mehner, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **89**, 1759 (1967).

(32) In an early experiment, very weak peaks corresponding to $\text{Re}(\text{CO})_n^+$ ions were observed in the mass spectrum of $\text{HRe}_2(\text{CO})_9\text{Cl}$.²⁶ These peaks may have arisen from thermal decomposition in the spectrometer source of a trace of $\text{HRe}_3(\text{CO})_{14}$ contaminant in the sample.

(33) J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **91**, 1550 (1969).

(34) Separate experiments revealed that 10 hr is required for appreciable diminution of the ir bands of $\text{CpMo}(\text{CO})_3^-$. Triphenylchlorosilane reacts with the tricarbonyl anion to give the dimer $[\text{CpMo}(\text{CO})_3]_2$ ¹⁰ and hexaphenyldisiloxane (this work).

isomers of $\text{CpMo}(\text{CO})_2(\text{P}(\text{OR})_3)\text{H}$. The 1965-cm^{-1} band in the orange form is assigned to the Mo-H stretch. The reaction between triphenylchlorosilane and $\text{CpMo}(\text{CO})_2(\text{PPh}_3)^-$ is summarized as



The initial goal of this research, *viz.*, to develop a facile path to silyl(transition metal) derivatives, was realized in a very limited manner: only $\text{Co}(\text{CO})_3\text{PPh}_3^-$ reacts smoothly with Ph_3SiCl to form $\text{Ph}_3\text{SiCo}(\text{CO})_3(\text{PPh}_3)$. All other reactions investigated were characterized by the formation of hexaphenyldisiloxane. The products which have been isolated shed little information on the nature of the intermediates in these anomalous reactions. However, some generalizations are possible.

Halogen transfer from silicon to the transition metal is observed for both first- and third-row transition elements, *e.g.*, in the formation of CoCl_2 , $\text{ClMn}(\text{CO})_3(\text{PPh}_3)_2$, and $\text{HRe}_2(\text{CO})_8\text{Cl}$. The first-row elements appear to form dimers, *e.g.*, $[\text{Co}(\text{CO})_3\text{PPh}_3]_2$, $[\text{CpMo}(\text{CO})_3]_2$, $[\text{Mn}(\text{CO})_4\text{PPh}_3]_2$, etc. Manganese pentacarbonyl anion forms a new trimeric anion, $\text{Mn}_3(\text{CO})_{14}^-$.^{34a} The heavier elements Re and Mo form hydrides, *e.g.*, $\text{HRe}_2(\text{CO})_8$, $\text{HRe}_3(\text{CO})_{14}$, and $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{H}$. Both dimers and hydrides could arise from reactive "free-radical" precursors. The "free radicals" of the heavier elements are perhaps more reactive than those of the first-row elements and abstract hydrogen atoms from solvent or reactant.

The oxygen found in the disiloxane almost certainly comes from the carbonyl groups. Schrieke and West³⁵ have observed disiloxane formation upon treating $\text{Ph}_3\text{SiMn}(\text{CO})_5$ with triphenylphosphine in oxygen-free benzene, and thermal decomposition silylmetal carbonyls also leads to disiloxanes.^{36,37} $\text{Ph}_3\text{SiMn}(\text{CO})_5$ and $\text{Ph}_3\text{SiCo}(\text{CO})_4$ are stable at room temperature, however, so it is highly unlikely that these silylmetallics form and then decompose to the disiloxane in the reactions described in this work. An alternate path, in which the oxygen atom of the carbonyl anion acts as the nucleophile to give an unstable metal-carbene type complex, may be operative. The variety of metal carbonyl products formed in these reactions suggests the likelihood of more than one mechanism.

Acknowledgment.—The author thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The author is also grateful to the Rackham School of Graduate Studies, The University of Michigan, for a Faculty Research Grant and a Faculty Research Fellowship.

(34a) NOTE ADDED IN PROOF.— $\text{Mn}_3(\text{CO})_{14}^-$ is formed by a slow reaction between $\text{Mn}_2(\text{CO})_{10}$ and $\text{Mn}(\text{CO})_5^-$. Thus, the dimer is probably a primary product in the reaction between $\text{Mn}(\text{CO})_5^-$ and Ph_3SiCl .

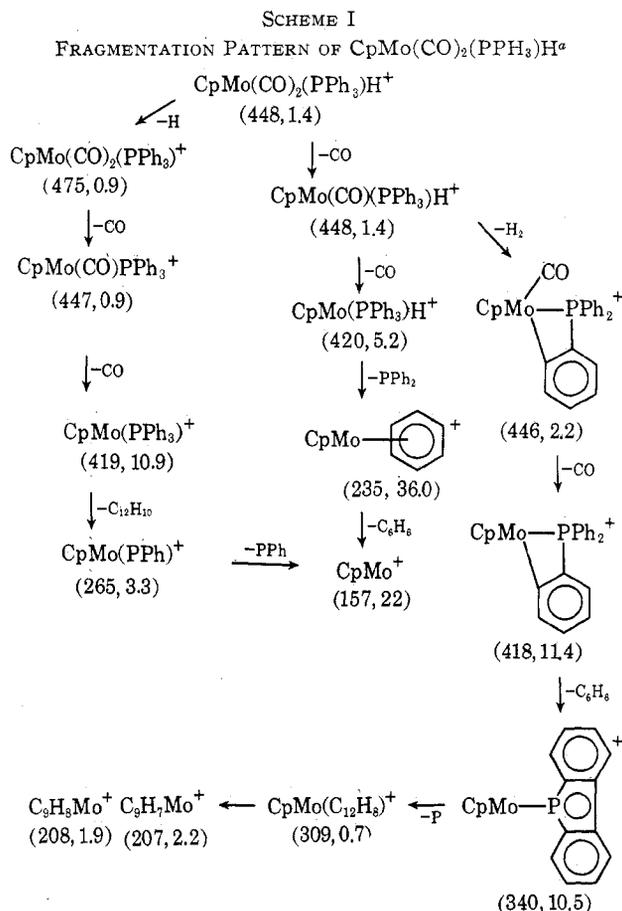
(35) R. R. Schrieke and B. O. West, *Aust. J. Chem.*, **22**, 49 (1969).

(36) A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, **89**, 1640 (1967).

(37) Y. L. Baay and A. G. MacDiarmid, *Inorg. Nucl. Chem. Lett.*, **3**, 159 (1967).

Appendix

Mass Spectrum of $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{H}$.—The mass numbers and relative intensities of the molybdenum-containing ions observed in the spectrum of $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{H}$ are shown in Scheme I. The fragmentation pathways in Scheme I are not to be taken literally, but this method of presenting the data does show a relation between fragment masses and the structure of the complex and, in this sense, is useful.



One striking feature of the fragmentation process shown in Scheme I is the loss of two hydrogen atoms from the parent ion. The second hydrogen undoubtedly is lost from the ortho position of one of the phenyl groups on phosphorus and represents a previously unobserved fragmentation route for phosphine complexes. Several structures are now known in which the metal atom bonds to the ortho carbon of the ring.^{38,39} Another interesting feature of this spectrum is apparent upon comparing it with the spectrum of triphenylphosphine.⁴⁰ The fragmentation pattern involving the phosphine group is hardly changed at all by coordination to the molybdenum.

(38) G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).

(39) J. Halpern, *ibid.*, **3**, 386 (1970).

(40) D. H. Williams, R. S. Ward, and R. G. Cooks, *J. Amer. Chem. Soc.*, **90**, 966 (1968).