to nearly free electrons moving in a periodic potential derived from the HOMO-LUMO excitations discussed above. The populating, therefore, of orbitals antibonding in nature would correspond to the "breaking" of an interatomic bond. If a bond energy of roughly 2 eV (46 kcal mol^{-1}) can be assigned to a normal As-As single bond,[29] then the value of the thermal energy gap at 1.2 eV corresponds well with the bond energy for the fractional-order As-As bonds whose bond order can be estimated from overlap calculations.[30,31] Since there are no other reported compounds possessing fractional As-As bonds, it is difficult to appraise the reliability of this assignment.

The first of this series of maxima at about 2.9 eV (~0.43 μm) corresponds well with the observed burgundy color of the crystals in thin sections and is considerably lower in energy than previously reported electronic transitions in polyarsines,[32] an effect of the spatially much more extensive opportunity for electron delocalization in polymer strands than in cyclic oligomers.[33] The second maxima at about 3.8 eV (0.32 μm) falls at the low-energy end of the band usually associated with As-As bonding and is therefore most likely localized in the 2.4-Å As-As bonds.

The polymers also exhibit a pronounced photoconductive effect as further indication of semiconductor behavior. When strongly illuminated by an ir source, a 10-100-fold dimunition in resistance is found, a factor typical of low-mobility semiconductors. A more detailed photoconductivity study is planned. Knowledge of the threshold excitation energy for photoconductivity will be important in further interpretation of the optical spectra.

If conductivity is achieved in these methylarsine polymers through excitation of valence electrons from HOMO levels to LUMO levels in the region of predominant intrinsic behavior, then this is primarily an n → d transition. It is this excitation that is suggested to explain the uv-vis band between 0.28 and 0.32 μm of polyphosphines and arsines;[32] nonbonding electrons are delocalized through excitation to d orbital networks. Total delocalization along the polymer ladder through d-orbital centers in a strictly aromatic sense is most probably not within reality.[34] This is corroborated by the low conductivity of the polymers—but nonetheless a conductivity several orders of magnitude greater than found in most molecular organic semiconductors whose only intermolecular association is through weak van der Waals bonds.[35] Comparisons of electronic spectra of solid polymers and essentially noninteracting monomers have obvious limitations for quantitative purposes, but the close similarity in optical properties of these ladder polymers and related monomeric compounds offers encouragement for more qualitative speculations.[36]

Registry No. $(CH_3As)_x$, 29402-29-7; CH_3AsH_2, 593-52-2; CH_3AsI_2, 7207-97-8; CH_3AsCl_2, 593-89-5; $(CH_3As)_5$, 20550-47-4.

(29) C. T. Mortimer and H. A. Skinner, *J. Chem. Soc.*, 4331 (1952): 38.3 kcal mol^{-1}, $As_2(CH_3)_4$. S. R. Gunn, *Inorg. Chem.*, 11, 796 (1972): 39.9 kcal mol^{-1}, As_2H_4.

(30) Approximative overlap integral calculations based upon Clementi orbitals[31] indicate that a reduction of about 50% in overlap occurs on lengthening the As-As bond from 2.4 to 2.9 Å. If orbital overlap and bond strength are roughly proportional, then a bond energy of about 20 kcal mol^{-1} can be estimated for the partial bond.

(31) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, 38, 996 (1963).

(32) B. G. Ramsey, "Electronic Transitions in Organometalloids," Academic Press, New York, N. Y., 1969, p 136, and references therein.

(33) F. Gutmann and L. E. Lyons, "Organic Semiconductors," Wiley, New York, N. Y., 1967, p 535; also, see ref 32.

(34) D. R. Eaton and W. R. McClellan, *Inorg. Chem.*, 6, 2134 (1967).

(35) Reference 33, p 448.

(36) Close similarity also exists between gas- and solid-phase electronic spectra of condensed-ring aromatics: ref 33, p 296. Also see R. C. Nelson in "Physical Methods of Chemistry," Part IIB, A. Weinberger and B. W. Rossiter, Ed., Interscience, New York, N. Y., 1971, p 214.

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Synthesis of Heteropolymetallic Silanes

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Convenient laboratory syntheses are described for the compounds $SiH_2ClCo(CO)_4$, $SiH_2[Co(CO)_4]_2$, $SiHCl_2Co(CO)_4$, $(CH_3)_2SiHCo(CO)_4$, $SiCl_2Co_2(CO)_7$, $SiH_2ClMn(CO)_5$, $SiH_2[Mn(CO)_5]_2$, and $SiCl_2[Mn(CO)_5]_2$. Of these compounds, only $SiH_2[Co(CO)_4]_2$ is previously reported. (Pentacarbonylmanganio)chlorosilane, $SiH_2ClMn(CO)_5$, reacts with dicobalt octacarbonyl, $Co_2(CO)_8$, to produce novel heteropolymetallic silanes, $SiHClMn(CO)_5Co(CO)_4$ and $SiClMn(CO)_5Co_2(CO)_7$. The general utility of this synthetic method is demonstrated by the reaction between $Fe_3(CO)_{12}$ and $SiHClMn(CO)_5Co(CO)_4$ to form $Fe(CO)_4[SiClMn(CO)_5]_2[Co_2(CO)_7]$.

Introduction

There has been, in recent years, a gratifying proliferation of knowledge in the area of transition metal chemistry. However, there remains a surprising paucity of molecular transition metal compounds combining different transition metals. Among the earliest reported examples of such "heteropolymetallic" compounds are those possessing metal to metal bonds formed, as shown in eq 1, by the reaction of

$$(CO)_nMX + NaM'(CO)_m \rightarrow NaX + (CO)_nM\text{-}M'(CO)_m \qquad (1)$$

a transition metal carbonyl halide with the sodium carbonyl metallate of a different transition metal.[2-4] Similar com-

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(1) The work herein reported in part satisfied requirements for the degree of Doctor of Philosophy for K. M. Abraham of Tufts University.

(2) E. W. Abel, A. Singh, and G. Wilkinson, *J. Chem. Soc.*, 1321 (1960).

(3) R. B. King, P. M. Treichel, and F. G. A. Stone, *Chem. Ind. (London)*, 747 (1961).

(4) K. K. Joshi and P. L. Pauson, *Z. Naturforsch., B*, 17, 565 (1962).

pounds can be prepared, as shown for one example in eq 2,

$$(\pi\text{-}C_5H_5)Co(CO)_2 + Fe_2(CO)_9 \rightarrow 2CO + (\pi\text{-}C_5H_5)CoFe_2(CO)_9 \quad (2)$$

by heating a judicious admixture of different carbonyl complexes or ions.[5-8]

This method of preparation relies upon a difference in reactivity of binuclear and trinuclear complexes. However, even the latter have been shown to be quite labile with respect to intermetallic exchange[8] as in eq 3. In any "hetero-

$$(\pi\text{-}C_5H_5)Rh(CO)_2 + (\pi\text{-}C_5H_5)CoFe_2(CO)_9 \rightarrow (\pi\text{-}C_5H_5)Co(CO)_2 + (\pi\text{-}C_5H_5)RhFe_2(CO)_9 \quad (3)$$

polymetallic" synthesis the cluster compound that results is thus preordained by which metal to metal bonds are preferred energetically. Possibly as a consequence of this, no "heterotrimetallic" cluster compounds of the transition metals have been reported to date.

More recently, the group IV metals tin and germanium have been used as catenating centers between two different transition metals.[9,10] The compounds formed are "trimetallic" in one sense but with respect to transition metals are "bimetallic." The use of a group IV element as a catenating center introduces a greater degree of flexibility to the synthesis of "heteropolymetallic" compounds since it can allow for compounds containing three or more different transition metals in contradistinction to the case of polymetallic cluster compounds previously discussed.

One of the most compelling reasons for preparing such compounds is to furnish novel polynuclear catalysts for organic synthesis. There are several instances in the literature where "binuclear" complexes have been so used with interesting and novel consequences. Lemal's use of iron enneacarbonyl to dimerize norbornadiene to one of the cage dimers,[11] when compared with Schrauzer's dimerization of the same compound to a "head to head" syn dimer, called "Binor S," in the presence of zinc bis(tetracarbonylcobaltate) and similar binuclear catalysts,[12] illustrates the interesting possibilities of this class of compounds. A study of bimetallic binuclear catalysts apparently remains to be made. For this study stable structures incorporating different transition metals in predictable or known steric relation to one another are needed. In the present work we describe the use of silicon as a catenating center which allows a reasonably systematic and flexible approach to the general syntheses of "heteropolymetallic" transition metal complexes.

Results and Discussion

Silyl derivatives of the transition metals have been known since Piper, Lemal, and Wilkinson prepared (trimethylsilyl-π-cyclopentadienyldicarbonyl)iron in 1956.[13] More recently Aylett and Campbell[14] have described the preparation of the binuclear complex, bis(tetracarbonylcobaltio)silane,[15] $H_2Si[Co(CO)_4]_2$. The preparative reaction is shown in eq 4.

$$H_2SiI_2 + 2NaCo(CO)_4 \rightarrow 2NaI + H_2Si[Co(CO)_4]_2 \quad (4)$$

Another method which has proved useful in the preparation of silyl transition metal complexes is that described by Chalk and Harrod to prepare (tetracarbonylcobaltio)trichlorosilane, $Cl_3SiCo(CO)_4$, as shown in eq 5.[16]

$$2HSiCl_3 + Co_2(CO)_8 \rightarrow H_2 + 2Cl_3SiCo(CO)_4 \quad (5)$$

Yet another procedure that results in silyl transition metal compounds is that used by Jetz and Graham to prepare (pentacarbonylmanganio)triphenylsilane, $(C_6H_5)_3SiMn(CO)_5$, as in eq 6.[17]

$$(C_6H_5)_3SiH + HMn(CO)_5 \rightarrow H_2 + (C_6H_5)_3SiMn(CO)_5 \quad (6)$$

In the present investigation all three of these methods are used. Thus, in the reaction of dichlorosilane with sodium tetracarbonylcobaltate both (tetracarbonylcobaltio)chlorosilane, $H_2SiClCo(CO)_4$, and bis(tetracarbonylcobaltio)silane, $H_2Si[Co(CO)_4]_2$, are formed as described in eq 7 and 8. It is

$$H_2SiCl_2 + NaCo(CO)_4 \rightarrow NaCl + H_2SiClCo(CO)_4 \quad (7)$$

$$H_2SiCl_2 + 2NaCo(CO)_4 \rightarrow 2NaCl + H_2Si[Co(CO)_4]_2 \quad (8)$$

possible to separate the two products of this reaction since they differ in volatility. (Tetracarbonylcobaltio)chlorosilane is a pale yellow liquid with a melting point of −47° and the bis(tetracarbonylcobaltio)silane melts at 15° to a yellow liquid.

When dichlorosilane reacts with cobalt octacarbonyl, two products also are formed as in eq 9 and 10. Again it is

$$2H_2SiCl_2 + Co_2(CO)_8 \rightarrow H_2 + 2HSiCl_2Co(CO)_4 \quad (9)$$

$$H_2SiCl_2 + Co_2(CO)_8 \rightarrow H_2 + CO + Cl_2SiCo_2(CO)_7 \quad (10)$$

possible to separate the products since (tetracarbonylcobaltio)dichlorosilane is more volatile than the (heptacarbonyldicobaltio)dichlorosilane. The former is a volatile yellow liquid melting at −18° and the latter a crystalline blood red solid. The most reasonable structure for this new compound is one similar to that of cobalt octacarbonyl with one of the bridging carbonyls replaced by the $-SiCl_2-$ moiety. This is consistent with the presence of the bridging carbonyl absorption in the ir spectrum as well as with the mass spectral fragmentation pattern.

In an analogous fashion sodium pentacarbonylmanganate reacts with dichlorosilane to form (pentacarbonylmanganio)chlorosilane, $H_2SiClMn(CO)_5$, a colorless liquid melting at 14°, and bis(pentacarbonylmanganio)silane, $H_2Si[Mn(CO)_5]_2$, a white solid melting at 81-82°. Dichlorosilane reacts with manganese decacarbonyl to form a mixture of products which so far has resisted our efforts at separation. It is possible, however, to prepare bis(pentacarbonylmanganio)dichlorosilane as shown in eq 11.

$$H_2SiCl_2 + 2HMn(CO)_5 \rightarrow 2H_2 + Cl_2Si[Mn(CO)_5]_2 \quad (11)$$

It is interesting to note that in this case the reaction is

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(5) P. Chini, L. Colli, and M. Paraldo, *Gazz. Chim. Ital.*, 90, 1005 (1960).

(6) U. Anders and W. A. G. Graham, *Chem. Commun.*, 291 (1966).

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(12) G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *J. Amer. Chem. Soc.*, 88, 4890 (1966).

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

(14) B. J. Aylett and J. M. Campbell, *Chem. Commun.*, 217 (1965); *J. Chem. Soc. A*, 1910 (1969).

(15) There are several nomenclatures which could be used in naming these compounds. This compound could also be named tetracarbonylcobalt silyltetracarbonylcobaltate. We feel that the latter name erroneously implies a difference between the cobalt moieties and thus have decided to name this group of compounds as derivatives of silane. The silane nomenclature also fits heteropolymetallic compounds in a noncommittal fashion more consistent with our present state of knowledge.

(16) A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, 87, 1133 (1965); 89, 1640 (1967).

(17) W. Jetz, P. B. Simons, J. A. J. Thomson, and W. A. G. Graham, *Inorg. Chem.*, 5, 2217 (1966).

quantitative as written and the expected intermediate (pentacarbonylmanganio)dichlorosilane, $HSiCl_2Mn(CO)_5$, cannot be found.

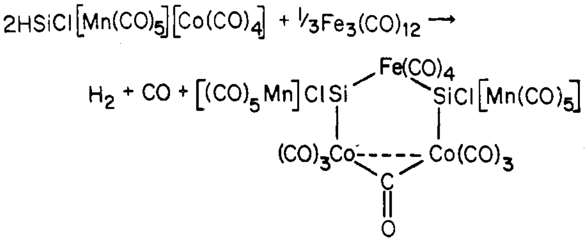
Two different "bimetallic" complexes result when (pentacarbonylmanganio)chlorosilane is treated with cobalt octacarbonyl. The formation reactions are shown in eq 12 and 13.

$$2H_2SiClMn(CO)_5 + Co_2(CO)_8 \rightarrow H_2 + 2HSiCl[Mn(CO)_5][Co(CO)_4] \qquad (12)$$

$$H_2SiClMn(CO)_5 + Co_2(CO)_8 \rightarrow H_2 + CO + ClSi[Mn(CO)_5][Co_2(CO)_7] \qquad (13)$$

(Pentacarbonylmanganio)(tetracarbonylcobaltio)chlorosilane, $HSiCl[Mn(CO)_5][Co(CO)_4]$, is a glassy red solid soluble in hexane while (pentacarbonylmanganio)(heptacarbonyldicobaltio)chlorosilane, $ClSi[Mn(CO)_5][Co_2(CO)_7]$, is a crystalline yellow solid, insoluble in hexane. This difference in solubility allows extraction of the former from the latter. It is probable that the heptacarbonyldicobalt derivative also has a structure similar to the bridged structure of cobalt octacarbonyl.

A novel "trimetallic" complex is the major product of the reaction of $HSiCl[Mn(CO)_5][Co(CO)_4]$ with iron dodecacarbonyl as shown in eq 14.



(14)

This "trimetallic" complex is a dark green crystalline solid soluble in hexane. The structure shown is a reasonable structure for this compound and is consistent with the presence of the bridging carbonyl as indicated by the ir spectrum and is also consistent with the available mass spectral information. It is also similar to the structure of a closely analogous germanium complex, $(C_5H_5CoCO)_2GeCl_2Fe(CO)_4$, reported recently.[10]

While a detailed study of the mass spectra of these new compounds is beyond the scope of this paper, it is possible to say that the metal-silicon bond enjoys moderate thermal stability. The intensities of fragments containing these bonds dominate all of the spectra observed.

Experimental Section

Apparatus and Methods. Unless otherwise stated, all reactions in this study were carried out in the absence of air and moisture. A standard vacuum apparatus and a polyethylene glove box were employed for this purpose. When the glove box was used, it was filled with nitrogen after several flushings and the nitrogen was allowed to stand in contact with P_2O_5 for approximately 30 min before the manipulation in question was begun. The lower manifold of the vacuum apparatus was equipped with stopcocks and standard O-ring joints. The stopcocks were lubricated with Apiezon-N vacuum grease. The upper manifold and the fractionating system were equipped with mercury float valves and constituted a grease-free system. The reaction section of the vacuum line was equipped with an O-ring joint and connected to the vacuum apparatus through mercury float valves.

Except for the techniques described below, all manipulations were carried out using typical vacuum techniques as reported in the literature.[18,19] ^1H nmr spectra were recorded on a Varian A-60A spectrometer. Infrared spectra were obtained on a Perkin-Elmer Model-621 grating infrared spectrometer. For vapor-phase ir spectra, the samples were placed in gas cells of 10-cm length, equipped with either cesium bromide or potassium bromide windows. The Hitachi Perkin-Elmer RMU-6L spectrometer was used to obtain the mass spectral data. Those elemental analyses not carried out in our laboratory were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Reagents. Trichlorosilane, $SiHCl_3$, purchased from Dow-Corning Corp., Midland, Mich., was purified by fractional condensation through low-temperature traps maintained at −78, −96, and −196°, respectively. The fraction retained at −96° had a vapor pressure of 218 mm at 0° (lit.[19] 218 mm at 0°).

Dichlorosilane, SiH_2Cl_2, was prepared by the catalytic redistribution of trichlorosilane by tetrabutylammonium chloride, $(C_4H_9)_4N^+Cl^-$, according to the method of Weyenberg, *et al.*, and modified by Joiner.[20] The reaction was effected under a nitrogen atmosphere and dichlorosilane was trapped in a −196° trap and then fractionated by distillation through a fractional condensation train, with traps maintained at −78, −116, and −196°. Pure dichlorosilane retained in the −116° trap exhibited a vapor tension of 548 mm at 0°. The ^1H nmr spectrum consisted of a singlet at τ 4.6 [$J(^{29}Si\text{-}H) = 288$ Hz (lit.[21] τ 4.6 ($J = 288$ Hz))].[21] Molecular weight by vapor density is 101 (calcd = 101).

Dimethylchlorosilane, $(CH_3)_2SiHCl$, was obtained from Peninsular Chemical Research, Fla., and further purified by fractional condensation through a series of U tubes kept at −78, −96, and −196°, respectively. The fraction retained at −96° exhibited a vapor tension of 190 mm at 0°. This vapor tension was independent of volume and the fraction thus was assumed to be pure. It was further identified by its ir and nmr spectra.

Methylene chloride, CH_2Cl_2, was used as obtained from Matheson Coleman and Bell, East Rutherford, N. J., after drying by distillation over phosphorus pentoxide.

***n*-Hexane,** C_6H_{14}, purchased from Fisher Scientific Co., Medford, Mass., was dried over lithium aluminum hydride before use.

Anhydrous diethyl ether, $(C_2H_5)_2O$, obtained from J. T. Baker Chemical Co., Phillipsburg, N. J., was used after distillation over sodium.

Manganese decacarbonyl, $Mn_2(CO)_{10}$, was used as obtained from Alfa Inorganics, Beverly, Mass.

Cobalt octacarbonyl, $Co_2(CO)_8$, was used as obtained from Alfa Inorganics, Beverly, Mass.

Sodium amalgam (1%) was prepared according to Vogel.[22]

Norbornadiene was used as obtained from Fisher Scientific Co., Medford, Mass.

Benzene was obtained from Fisher Scientific Co., Medford, Mass., and dried over $LiAlH_4$ before use.

Iron dodecacarbonyl, $Fe_3(CO)_{12}$, purchased from Strem Chemicals, Danvers, Mass., was dried *in vacuo* before use.

Pentacarbonylmanganese hydride, $HMn(CO)_5$, was prepared by the method of Hieber and Wagner[23] from $NaMn(CO)_5$ by acidification of the latter with phosphoric acid, H_3PO_4. It was identified by its vapor pressure and infrared spectrum.

Reaction of Dichlorosilane, SiH_2Cl_2, with Sodium Tetracarbonylcobaltate, $NaCo(CO)_4$. Syntheses of $SiH_2ClCo(CO)_4$ and $SiH_2[Co(CO)_4]_2$. The initial step in this synthesis is the preparation of a known quantity of $NaCo(CO)_4$, as shown in eq 15. In a typical

$$Co_2(CO)_8 + Na/Hg \xrightarrow{\text{ether}} 2NaCo(CO)_4 \qquad (15)$$

preparation 1.50 g (4.38 mmol) of $Co_2(CO)_8$ and about 30 g of 1% sodium amalgam were placed in a 200-ml round-bottom flask provided with an O-ring joint and breakoff seals equipped with a magnetic stirrer. After evacuating the flask, about 100 ml of anhydrous diethyl ether was introduced by vacuum distillation. The flask then was sealed off. The resulting solution (red-orange color) was stirred at ambient temperatures for a period of 3 hr. By this time the solution had changed to colorless. The ether solution of $NaCo(CO)_4$ thus obtained was vacuum filtered into another 200-ml reaction flask provided with breakoff seals. Into this solution 4.12 mmol of SiH_2Cl_2 was condensed at liquid nitrogen temperature. The reaction flask then was warmed to room temperature and allowed to stand at this temperature for about 45 min. The flask was occassionally

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(18) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," Wiley, New York, N. Y., 1949.

(19) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

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Table I. Mass Spectra of Compounds at Inlet Temperatures

$SiH_2ClCo(CO)_4$, 80°		$SiHCl_2Co(CO)_4$, 80°		$SiCl_2Co_2(CO)_7$, 100°		$SiH_2ClMn(CO)_5$, 80°	
Ion	Rel peak height	Ion	Rel peak height	Ion	Rel peak height	Ion	Rel peak height
$H_2Si^{37}ClCo(CO)_4^+$	<1	$HSiCl_2Co(CO)_4^+$	2	$SiCl_2Co_2(CO)_7^+$	0.5	$SiH_2{}^{37}ClMn(CO)_5^+$	12
$H_2Si^{35}ClCo(CO)_4^+$	2	$HSiCl_2Co(CO)_3^+$	18	$SiCl_2Co_2(CO)_6^+$	0.6	$SiH_2{}^{35}ClMn(CO)_5^+$	34
$H_2SiClCo(CO)_4^+$	1	$HSiClCo(CO)_4^+$	2	$SiCl_2Co_2(CO)_5^+$	0.6	$SiH_2ClMn(CO)_4^+$	81
$SiClCo(CO)_4^+$	1	$HSiCl_2Co(CO)_2^+$	25	$SiCl_2Co_2(CO)_4^+$	0.5	$SiH_2ClMn(CO)_3^+$	25
$H_2SiClCo(CO)_3^+$	5	$HSiCl_2Co(CO)^+$	59	$SiCl_2Co_2(CO)_3^+$	0.8	$SiH_2ClMn(CO)_2^+$	57
$SiClCo(CO)_3^+$	25	$HSiCo(CO)_3^+$	2	$SiCl_2Co_2(CO)_2^+$	1	$SiH_2ClMn(CO)^+$	73
$SiH_2ClCo(CO)_2^+$	8	$Co(CO)_4^+$	2	$SiCl_2Co_2(CO)^+$	0.75	$Mn(CO)_3$, $Mn(CO)_2Si^+$	10
$SiClCo(CO)_2^+$	30	$HSiCl_2Co^+$	36	$SiCl_2Co_2^+$	2	$H_2SiClMn^+$	99
$Co(CO)_4^+$	4	$Co(CO)_3^+$	9	$SiCl_2Co^+$	2.5	$MnSiCl^+$	55
$SiH_2ClCo(CO)^+$	46	$SiClCo^+$	17	$Co(CO)_3^+$	1	$Mn(CO)_2$, $Mn(CO)Si^+$	27
$SiClCo(CO)^+$	11	$Co(CO)_2^+$	27	$Co(CO)_2^+$	3	$MnSiH_2^+$	9
$Co(CO)_3^+$	5	$HSiCl_2^+$	5	$SiCl_2^+$	0.7	$Mn(CO)^+$, $MnSi^+$	50
$H_2SiClCo^+$	30	$SiCl_2^+$	3	$Co(CO)^+$	6	H_2SiCl^+	5
$SiClCo^+$	31	$Co(CO)^+$	23	$SiCl^+$	7	$SiCl^+$	10
$Co(CO)_2^+$	31	$SiCl^+$	18	Co^+	8	Mn^+	100
$Co(CO)^+$	42	Co^+	17	Si^+, CO^+	100	Co^+, Si^+	63
$SiCl^+$	13	HCl^+	1				
Co^+	40	Cl^+	1				
Cl^+	2	CO^+, Si^+	100				
Si^+, CO^+	100						

$SiH_2Mn_2(CO)_{10}$, 100°		$SiHClMn(CO)_5Co(CO)_4$, 60°		$SiCl_2[Mn(CO)_5]_2$, 100°		$Fe(CO)_4[SiClMn(CO)_5]_2$-$[Co_2(CO)_7]$, 60°	
Ion	Rel peak height	Ion	Rel peak height	Ion	Rel peak height	Ion	Rel peak height
$SiH_2Mn_2(CO)_{10}^+$	8	$HSi^{37}ClMn(CO)_5Co(CO)_4^+$	<1				
$SiH_2Mn_2(CO)_9^+$	66	$HSi^{35}ClMn(CO)_5Co(CO)_4^+$	2	$SiCl_2Mn_2(CO)_{10}^+$	0.5	$Fe(SiCl)_2Co_2CO^+$	0.5
$SiH_2Mn_2(CO)_8^+$	20	$HSiClMnCo(CO)_8^+$	6	$SiCl_2Mn_2(CO)_9^+$	1	$Fe(SiCl)_2Co_2^+$	2
$SiH_2Mn_2(CO)_7^+$	2	$HSiClMnCo(CO)_7^+$	8	$SiCl_2Mn_2(CO)_8^+$	3	$Fe(CO)_4(SiCl)_2^+$	1
$SiH_2Mn_2(CO)_6^+$	4	$HSiClMnCo(CO)_6^+$	6	$SiCl_2Mn_2(CO)_7^+$	4	$Fe(CO)_3(SiCl)_2^+$	3
$SiH_2Mn_2(CO)_5^+$	75	$HSiClMnCo(CO)_5^+$	3	$SiCl_2Mn_2(CO)_6^+$	4	$Fe(CO)_2(SiCl)_2^+$	0.1
$SiH_2Mn_2(CO)_4^+$	100	$HSiClMnCo(CO)_4^+$	3	$SiCl_2Mn_2(CO)_5^+$	6	$Fe(CO)(SiCl_2)^+$	2
$SiH_2Mn_2(CO)_3^+$	39	$HSiClMnCo(CO)_3^+$	24	$SiCl_2Mn_2(CO)_4^+$	15	$Fe(SiCl)_2^+$	3.5
$SiH_2Mn_2(CO)_2^+$	20	$HSiClMnCo(CO)_2^+$	19	$SiCl_2Mn(CO)_5^+$	8	$Co(CO)_4^+$	0.2
$SiH_2Mn_2CO^+$	33	$HSiClMnCo(CO)^+$	20	$SiCl_2Mn_2(CO)_3^+$	18	$Fe(CO)_4^+$	0.2
$H_2SiMn_2^+$	40	$Mn(CO)_5^+$	24	$SiCl_2Mn(CO)_4^+$	21	$SiClMn^+$, Co_2^+	5
$HSiMn_2^+$	24	$HSiClMnCo^+$	27	$SiCl_2Mn_2(CO)_2^+$	7	$Co(CO)_2^+$	0.1
$SiMn_2^+$	50	$SiClMnCo^+$	4	$SiCl_2Mn(CO)_3^+$	8	$Fe(CO)_2^+$	1
$SiH_2Mn(CO)^+$	1.5	$Co(CO)_4^+$	3	$SiCl_2Mn_2(CO)^+$	7	$Mn(CO)_2^+$	5
$SiMn(CO)^+$, $Mn(CO)_2^+$	6	$HSiClCo^+$	1	$SiCl_2Mn(CO)_2^+$	22	$Co(CO)^+$	2
$Mn(CO)^+$, $MnSi^+$	33	$SiClCo^+$	3	$SiCl_2Mn_2^+$	10	$Fe(CO)^+$	2
Mn^+	57	$SiClMn^+$	6	$Mn(CO)_5^+$	20	$Mn(CO)^+$	8
CO^+, Si^+	70	$Co(CO)_2^+$	3	$SiCl_2Mn(CO)$	23	$SiCl^+$	9
		$Mn(CO)_2^+$	20	$SiCl_2Mn^+$	12	Co^+	30
		$Co(CO)^+$	12	$SiClMn^+$	25	Fe^+	3
		$Mn(CO)^+$	26	$Mn(CO)_2^+$	17	Mn^+	31
		$SiCl^+$	12	$SiCl^{2+}$	5	Si^+, CO^+	100
		Co^+	3	$Mn(CO)^+$	35		
		Mn^+	68	$SiCl^+$	70		
		SiH^+	11	Mn^+	100		
		Si^+, CO^+	100	Si^+, CO^+	75		

shaken to effect thorough mixing of the reactants. During this treatment the solution became yellow.

The reaction flask then was attached to the vacuum system and the materials volatile at room temperature were removed and fractionated by passing through U tubes maintained at −45 and −196°, respectively. After about 12 hr of extensive repeated fractionation a yellow liquid was collected into the −45° U tube. The −196° trap contained ether and some unreacted dichlorosilane (0.812 mmol); the latter was separated from the ether by vacuum distilling the dichlorosilane from the solution maintained at −78° into a trap cooled to −196°. The ether remained at −78°.

The yellow liquid collected in the −45° U tube was further fractionated by passing the vapor through traps maintained at 12 and −45°, respectively. The 12° trap retained $SiH_2[Co(CO)_4]_2$. The −45° fraction was $SiH_2ClCo(CO)_4$.

$SiH_2[Co(CO)_4]_2$ was identified by its melting point which agreed well with the previously reported value of 15°. The ^1H nmr spectrum of $SiH_2[Co(CO)_4]_2$, not reported previously, showed a singlet at τ 5.42 with respect to external TMS [$J(^{29}Si–H) = 203$ Hz]. The yield of $SiH_2[Co(CO)_4]_2$ from the reaction was 0.65 g (1.75 mmol).

$SiH_2ClCo(CO)_4$ was identified by its ir, nmr, and mass spectra. The ^1H nmr spectrum of the neat liquid consisted of a singlet at τ 4.89 (TMS external standard) [$J(^{29}Si–H) = 239$ Hz]. The vapor-phase infrared spectrum of $SiH_2ClCo(CO)_4$ (CsBr gas cell) displayed the following absorptions: 2160 (s), 2100 (s), 2060–2000 (s), 1990 (w), 1100–1050 (w), 930 (s), 825 (s), 700 (m), 565 (sh), 550 (s), 470 (w), 400 (m), 310 cm^{-1} (w). The mass spectrum of $SiH_2ClCo(CO)_4$ was observed at an ionizing voltage of 80 eV and an inlet temperature of 80°. It is summarized in Table I.

$SiH_2ClCo(CO)_4$ had a vapor pressure of 6 mm at 24.8° and melted between −47 and −46°. The yield of $SiH_2ClCo(CO)_4$ was 0.22 g (0.93 mmol). It is possible to obtain $SiH_2ClCo(CO)_4$ in higher yields by treating SiH_2Cl_2 and $NaCo(CO)_4$ in a 1:1 molar ratio.

Reaction of Dichlorosilane, SiH_2Cl_2, with Cobalt Octacarbonyl, $Co_2(CO)_8$. Syntheses of $SiHCl_2Co(CO)_4$ and $SiCl_2Co_2(CO)_7$. In a typical experiment a mixture of 1.17 g (3.44 mmol) of $Co_2(CO)_8$ and 7.54 mmol of SiH_2Cl_2 was placed in a reaction flask (50 ml) provided with breakoff seals. The contents of the flask were degassed, frozen, and then sealed off. The flask then was allowed to warm to room temperature at which temperature a rapid reaction ensued, as evidenced by the evolution of a gas. A liquid and a dark red solid remained in the reaction flask at this point. The reaction vessel then was allowed to stand at room temperature for a period of about 18 hr. The mixture appeared dark red at the end of this period. The vessel then was attached to the vacuum apparatus and cooled to −196° and opened. Some material which was noncondensable at −196° was observed. This was collected using a Toepler pump. The total amount of this gas was 5.20 mmol. The gas was identified as a mixture of hydrogen and carbon monoxide by mass spectrometry. The gas mixture was circulated over copper oxide (CuO), preheated to 300°, for a period of about 2 hr. During this time the pressure in the manometer disappeared and the carbon monoxide and water produced were collected in a U tube maintained at −196°. The CO_2 was separated from the water by warming the U tube to −78° and collecting the CO_2 in another U tube cooled to −196°. The CO_2 was measured to be 1.76 mmol which corresponded to 1.76 mmol of carbon monoxide produced in the reaction. The hydrogen produced in the reaction therefore was (5.20 − 1.76) 3.44 mmol.

The reaction flask then was warmed to room temperature and materials volatile at this temperature separated by passing through U tubes maintained at −78 and −196° All of the unreacted dichlorosilane was collected in a −196° trap and measured to be 2.34 mmol. Thus the amount of SiH_2Cl_2 consumed in the reaction was 7.54 − 2.34 = 5.20 mmol. The −78° trap contained a yellow solid which melted to a yellow liquid at −18°. This liquid was identified as (tetracarbonylcobaltio)dichlorosilane [$SiHCl_2Co(CO)_4$] from its ir, nmr, and mass spectra as well as elemental analysis. Since $SiHCl_2Co(CO)_4$ had only a very low vapor pressure (2 mm at 25.1°), complete separation of $SiHCl_2Co(CO)_4$ from the reaction mixture required a long period of fractionation with constant pumping. When all the $SiHCl_2Co(CO)_4$ was removed, a dark red solid was left in the reaction flask.

The ^1H nmr spectrum of $SiHCl_2Co(CO)_4$ (neat liquid) exhibited a singlet at τ 3.90 with respect to external TMS [$J(^{29}Si\text{-}H) = 280$ Hz]. The vapor-phase infrared spectrum of $SiHCl_2Co(CO)_4$ (CsBr cell) displayed the following absorptions: 2180 (m), 2115 (s), 2060 (s), 2020 (s), 1995 (w), 795 (s), 700 (w), doublet (m) at 565 and 550, 520 (m), 400 (w), 305 cm^{-1} (w). The mass spectrum of $SiHCl_2Co(CO)_4$ was recorded with an inlet temperature of 80° and an ionizing voltage of 80 eV. It is given in Table I. *Anal.* Calcd for $SiHCl_2Co(CO)_4$: Si, 10.37; Cl, 25.9; Co, 21.85. Found: Si, 10.78; Cl, 25.0; Co, 20.74.

The total amount of $SiHCl_2Co(CO)_4$ obtained from the reaction was 0.95 g (3.5 mmol). Of the total amount of SiH_2Cl_2 used, 65% had been converted to $SiHCl_2Co(CO)_4$.

The solid left behind in the reaction flask was heated *in vacuo* (10^{-4} mm) at 40°. No materials were sublimed to a cold finger at this temperature. If there was any unreacted $Co_2(CO)_8$ present, it should have sublimed. The solid was thus presumed to be free from $Co_2(CO)_8$. It was soluble in hexane but could not be crystallized from it. However, it is possible to obtain a red crystalline solid from CH_2Cl_2 solution. Stoichiometry of the reaction proved the composition $Si_{1.06}Cl_{2.12}Co_2(CO)_{6.99}$ for this compound.

The elemental analysis and ir and mass spectra data also agreed with the formula $SiCl_2Co_2(CO)_7$. *Anal.* Calcd for $SiCl_2Co_2(CO)_7$: Si, 6.8; Co, 28.64; Cl, 16.9. Found: Si, 7.7; Co, 28.65; Cl, 14.8.

The infrared spectrum in Nujol mull showed absorptions at 2100 (m), 2080 (s), 2020 (sh), 1990-1970 (s), 1835 (m), 780 (w), 560 (s), 500 (s), 400 (m), and 380 cm^{-1} (m).

The mass spectrum of the compound was recorded at an ionization voltage of 80 eV and an inlet temperature of 100°. The major ion fragments are shown in Table I. The yield of $SiCl_2Co_2(CO)_7$ from this reaction was 0.68 g which corresponded to the conversion of 35% of SiH_2Cl_2 consumed in the reaction to $SiCl_2Co_2(CO)_7$.

Reaction of Trichlorosilane, $SiHCl_3$, with Sodium Tetracarbonylcobaltate, $NaCo(CO)_4$. Synthesis of $HSiCl_2Co(CO)_4$. In a typical preparation, 2.18 mmol of $SiHCl_3$ was mixed with $NaCo(CO)_4$ (6.8 mmol dissolved in diethyl ether) in a 200-ml round-bottom flask provided with breakoff seals. The flask with the contents was now kept at room temperature for a period of 1.5 hr. The flask was shaken occasionally to ensure efficient mixing of the reactants. During this period, the solution gradually turned yellow and then pink. The materials volatile at room temperature were removed from the reaction flask and fractionally condensed by passing through low-temperature traps maintained at −45 and −196°. At the completion of the fractionation, *i.e.*, when no more pressure was observed in the manometer, $SiHCl_2Co(CO)_4$ was retained in the −45° trap as a yellow solid. The −196° trap retained diethyl ether which was tensimetrically pure. A red low-volatile material remained in the reaction flask along with the precipitate of NaCl.

$SiHCl_2Co(CO)_4$ melted to a yellow liquid at −18°. It exhibited a vapor pressure of 2 mm at 24°. Complete identification of $SiHCl_2Co(CO)_4$ was done from its melting point and nmr and ir spectra. The melting point of −18° was identical with that of the $SiHCl_2Co(CO)_4$ prepared from $Co_2(CO)_8$ and SiH_2Cl_2. The ^1H nmr spectrum and the vapor-phase ir spectrum of the pure were identical with those of the $SiHCl_2Co(CO)_4$ prepared from SiH_2Cl_2 and $Co_2(CO)_8$. The yield of product using this method was 53% (0.312 g) based on the trichlorosilane used.

About 10 ml of *n*-hexane was condensed onto the residue in the flask maintained at −196°. When the flask and its contents were allowed to warm to room temperature, all of the red material was soluble in the hexane. It was filtered. When the solvent was distilled off, a red viscous residue which could not be crystallized was left behind. The nmr spectrum of this material in hexane did not show any peaks corresponding to a Si-H even at high gain. It is thus unlikely that either $SiHCl[Co(CO)_4]_2$ or $HSi[Co(CO)_4]_3$ is present. This material was not characterized further in the present work.

The yield of $SiHCl_2Co(CO)_4$ from the reaction probably can be improved by using a large excess of $HSiCl_3$ over $NaCo(CO)_4$. The latter reagent was in excess for the reaction described above.

Reaction of Dimethylchlorosilane, $(CH_3)_2SiHCl$, with Sodium Tetracarbonylcobaltate, $NaCo(CO)_4$. Synthesis of $(CH_3)_2SiHCo(CO)_4$. In a typical experiment 13 mmol of $(CH_3)_2SiHCl$ was condensed into about 10 mmol of $NaCo(CO)_4$ in 100 ml of diethyl ether contained in a 200-ml reaction flask provided with a breakoff seals. The flask was sealed off and kept at room temperature for about 1 hr. During this period, the colorless solution gradually turned yellow and finally pink. The flask then was attached to the vacuum system and the materials volatile at room temperature were fractionally condensed by passing through traps maintained at −45, −96, and −196°, respectively. The −96° fraction was found to be tensimetrically pure diethyl ether. Unreacted $HSi(CH_3)_2Cl$, collected in the −196° trap, was identified by its vapor pressure of 198 mm at 0°. The quantity of this fraction was determined as 3.2 mmol by measurement in the vapor phase.

The −45° trap retained a colorless solid which melted to a colorless liquid at room temperature. This liquid had a vapor pressure of 5 mm at 20.9°. It was identified as $(CH_3)_2SiHCo(CO)_4$ from its elemental analysis and nmr and ir spectra. *Anal.* Calcd for $(CH_3)_2SiHCo(CO)_4$: C, 31.30; Si, 12.17; H, 3.00. Found: C, 31.38; Si, 12.10; H, 3.38.

The ^1H nmr spectrum of the neat liquid consisted of a septet centered at τ 5.57 and a doublet at τ 9.62 and 9.77. The vapor-phase ir spectrum of $(CH_3)_2SiHCo(CO)_4$ in a CsBr cell showed absorptions at 2985 (m), 2920 (w), 2135 (s), 2100 (s), 2035 (s), 2010 (s), 1990 (m), 1255 (s), 875 (s), 840 (s), 760 (m), 700 (m), 650 (m), 550 (s), 511 (m), 405 (w), 375 (w), and 290 cm^{-1} (w). The amount of $(CH_3)_2SiHCo(CO)_4$ obtained was 1.95 g which corresponded to a yield of 86% based on the dimethylchlorosilane consumed in the reaction.

Reaction of Dichlorosilane, SiH_2Cl_2, with Sodium Pentacarbonylmanganate, $NaMn(CO)_5$. Syntheses of $SiH_2ClMn(CO)_5$ and $SiH_2[Mn(CO)_5]_2$. The preparation of a known quantity of the reactant sodium pentacarbonylmanganate, from manganese decacarbonyl [$Mn_2(CO)_{10}$] and 1% sodium amalgam in tetrahydrofuran (THF) according to the method of Hieber, *et al.*,[23] as shown in eq 16, is the

$$Mn_2(CO)_{10} + Na/Hg \xrightarrow{THF} 2NaMn(CO)_5 \qquad (16)$$

initial step in this synthesis.

In a typical experiment 1.2 g (3.08 mmol) of $Mn_2(CO)_{10}$ and about 70 g of 1% Na/Hg were placed in a 100-ml round-bottom flask fitted with a magnetic stirrer and breakoff seals. The flask then was attached to the vacuum system and evacuated. Freshly distilled THF (25 ml) was condensed into the flask maintained at −78° and sealed off from the vacuum system. The flask then was allowed to warm to room temperature and the contents were vigorously stirred for a period of 2 hr. During this time, the solution which was initially yellow turned to greenish yellow. The solution of $NaMn(CO)_5$ thus obtained was filtered to remove mercury and excess sodium. The solvent then was removed *in vacuo* (10^{-4} mm) to obtain white solid $NaMn(CO)_5$.

Now 10 ml of *n*-hexane was added to the $NaMn(CO)_5$ in a reaction flask (100 ml) fitted with breakoff seals. $NaMn(CO)_5$ is insoluble in *n*-hexane. The mixture thus obtained was cooled to −196° and 4.23 mmol of SiH_2Cl_2 introduced from the vacuum system. The reaction flask and its contents were warmed to 0° and kept at that temperature for 0.5 hr. During this period the flask was occasionally shaken to effect efficient mixing of the reactants. The progress of the reaction was observed by the disappearance of the solid chunks of $NaMn(CO)_5$ and the formation of a fine white precipitate of NaCl. At the end of the reaction the initially colorless solution had turned slightly yellow. The flask was now warmed to room temperature (24°) and kept at that temperature for another 15 min or until all of the solid $NaMn(CO)_5$ had disappeared.

After the completion of the reaction, the materials volatile at room temperature were fractionally condensed by passing them through low-temperature traps maintained at −30, −96, and −196°. The −96° fraction was identified as the solvent *n*-hexane from its vapor pressure. The −196° trap contained unreacted dichlorosilane (vp 45° = 58 mm) (0.62 mmol). Therefore, the amount of dichlorosilane consumed in the reaction was found to be 3.61 mmol (4.23 − 0.62).

The −30° trap contained $SiH_2ClMn(CO)_5$, a solid which melted at 14° to a colorless liquid. Complete removal of this material from the reaction vessel into the −30° trap required continuous pumping for a period of 12 hr.

The ^1H nmr spectrum of neat liquid $SiH_2ClMn(CO)_5$ displayed a singlet at τ 4.91 relative to external TMS [$J(^{29}Si\text{–}H) = 210$ Hz]. The infrared spectrum of the neat liquid in a CsBr cell (liquid film) showed absorptions at 2140 (w), 2060 (m), 2000 (sh), 1985 (s), 950 (m), 900 (w), 840 (m), 790 (mw), 660 (s), 638 (vw), 500 (w), 480 (vw), and 405 cm^{-1} (w).

The mass spectrum of $SiH_2ClMn(CO)_5$ was recorded at an ionization potential of 75 eV and an inlet temperature of 80°. The spectrum is described in Table I.

This new compound, $SiH_2ClMn(CO)_5$, has a vapor pressure of 1 mm at 24°. The yield of $SiH_2ClMn(CO)_5$ from the reaction was 0.532 g.

When all the volatile materials were separated, an off-white solid was left behind in the reaction flask. About 10 ml of methylene chloride was added to this solid and the solution was filtered. Removal of the solvent from the filtrate gave white solid crystals of $SiH_2[Mn(CO)_5]_2$ which melted at 81°. This solid was identified as $SiH_2[Mn(CO)_5]_2$ from its nmr, ir, and mass spectra. The ^1H nmr spectrum of $SiH_2[Mn(CO)_5]_2$ in methylene chloride exhibited a singlet at τ 6.2. The infrared spectrum of $SiH_2[Mn(CO)_5]_2$ in a CsBr cell (Nujol mull) displayed the absorptions at 2120 (m), 2095 (w), 2000 (s), 1980 (s), 945 (w), 810 (w), 730 (m), 670 (m), 660 (s), and 480 cm^{-1} (vw). The mass spectrum was recorded at an inlet temperature of 100° and an ionization voltage of 75 eV; the sample was held at 40°. The spectrum is recorded in Table I. The amount of $SiH_2[Mn(CO)_5]_2$ obtained was 0.235 g.

Reaction of (Pentacarbonylmanganio)chlorosilane, $SiH_2ClMn(CO)_5$, with Cobalt Octacarbonyl, $Co_2(CO)_8$. Preparation of $SiHClMn(CO)_5Co(CO)_4$ and $SiClMn(CO)_5Co_2(CO)_7$. In a typical preparation 0.44 g (1.70 mmol) of $SiH_2ClMn(CO)_5$ and 0.401 g (1.18 mmol) of $Co_2(CO)_8$ were mixed under vacuum in the presence of 2 ml of *n*-hexane in a reaction tube provided with breakoff seals. After sealing from the vacuum system, the apparatus with the contents was cooled to 0° and kept at that temperature for about 6 hr. A sudden reaction was observed upon mixing the two reactants as evidenced by bubbling of the reaction mixture. At the end of the reaction, *i.e.*, when no more bubbling was observed, a yellow solid and a dark red solution remained. The tube with the contents now was attached to the vacuum system and cooled to −196°. The mixture of hydrogen and carbon monoxide produced in the reaction was collected using a Toepler pump and measured to be 1.72 mmol. The H_2 and CO were separated as described previously, after converting them to H_2O and CO_2 by passing over copper oxide (CuO) heated to 300°. Carbon dioxide was calculated to be 0.58 mmol which correspond to 0.58 mmol of carbon monoxide produced in the reaction. The amount of hydrogen produced therefore was 1.14 mmol (1.72 − 0.58).

The yellow solid, $SiClMn(CO)_5Co_2(CO)_7$, is insoluble in hexane and could be separated from the dark red hexane solution of $SiHClMn(CO)_5Co(CO)_4$ by vacuum filtration.

The ^1H nmr spectrum of $SiHClMn(CO)_5Co(CO)_4$ in hexane exhibited a singlet at τ 4.00 with respect to external TMS. When the solvent was removed this compound was obtained as a red solid. The mass spectrum of $SiHClMn(CO)_5Co(CO)_4$, recorded at an ionization voltage of 75 eV and an inlet temperature 60°, is given in Table I.

This material was free from both $SiH_2ClMn(CO)_5$ and $Co_2(CO)_8$, since no ionic fragments corresponding to them are observed in the mass spectrum. Under the experimental conditions they are usually easily detected. The total amount of $HSiClMn(CO)_5Co(CO)_4$ produced in the reaction was 0.48 g.

$SiClMn(CO)_5Co_2(CO)_7$ is insoluble in hexane but soluble in chloroform and methylene chloride and can be recrystallized as yellow crystals from the latter solvent. Slight decomposition of the above compound in these solvents was noted if the solution was kept at room temperature for long periods of time. *Anal.* Calcd for $SiClMn(CO)_5Co_2(CO)_7$: Si, 4.89; Cl, 6.12; Mn, 9.61; Co, 20.62; C, 25.18. Found: Si, 5.25; Cl, 7.00; Mn, 9.32; Co, 19.83; C, 23.07. Since $SiClMn(CO)_5Co_2(CO)_7$ is not volatile at temperatures below which it is stable, it was not possible to obtain a mass spectrum. The infrared spectrum (Nujol mull) displayed absorptions at 2106 (s), 2100 (s), 2070 (m, s), 2045 (vs), 2040 (sh), 2015 (vs), 1955 (m), 1850 (m), 685 (m), 660 (m), 650 (w), 550 (w), and 520 cm^{-1} (w).

The amount of $SiClMn(CO)_5Co_2(CO)_7$ obtained from this reaction was 0.33 g. This new compound melted with decomposition at 124–125°.

Reaction of Dichlorosilane, SiH_2Cl_2, with Pentacarbonylmanganese Hydride, $HMn(CO)_5$. Synthesis of $SiCl_2[Mn(CO)_5]_2$. In a typical experiment a mixture of 0.459 g (2.35 mmol) of $HMn(CO)_5$ and 1.15 mmol of dichlorosilane was prepared in an evacuated reaction tube provided with breakoff seals. The vessel was sealed and its contents were heated at 85° for a period of 10 hr. During this time colorless crystals of $SiCl_2[Mn(CO)_5]_2$ formed in the reaction tube. The mixture of hydrogen and carbon monoxide produced in the reaction was collected in the vacuum system using the Toepler pump and measured to be 2.07 mmol. Carbon monoxide and hydrogen were separated and measured as described elsewhere after converting them to CO_2 and H_2O. The total amount of hydrogen produced in the reaction was 2.04 mmol. The carbon monoxide was found to be 0.03 mmol.

The materials in the reaction tube volatile at room temperature were now separated by passing them through low-temperature traps maintained at −78 and −196°, respectively. The −196° trap contained 0.54 mmol of unreacted SiH_2Cl_2 which was identified by its vapor pressure of 58 mm at −45°. The −78° trap contained 0.0441 g (0.23 mmol) of unreacted $HMn(CO)_5$.

When all the volatile materials were removed, the colorless crystalline solid, $SiCl_2[Mn(CO)_5]_2$, remained in the reaction tube. It was soluble in methylene chloride and a ^1H nmr spectrum of this solution did not show any Si–H absorption, thus ruling out the presence of $HSiCl_2Mn(CO)_5$ in the reaction product. The $SiCl_2[Mn(CO)_5]_2$ was characterized by its elemental analysis and mass spectrum. *Anal.* Calcd for $SiCl_2[Mn(CO)_5]_2$: Mn, 22.49; Si, 5.72; Cl, 14.51. Found: Mn, 22.38; Si, 5.70; Cl, 14.60.

The mass spectrum, recorded at an ionization voltage of 60 eV and an inlet temperature of 100°, gave a parent peak at *m/e* 488, calculated for $Si^{35}Cl_2[Mn(CO)_5]_2$ 488. The mass spectrum is shown in Table I.

Dimerization of Norbornadiene, C_7H_8, in the Presence of $SiCl_2Co_2(CO)_7$. In a typical experiment 15 ml of benzene and 0.45 g (1.09 mmol) of $SiCl_2Co_2(CO)_7$ were placed in a three-necked flask fitted with a dropping funnel, reflux condenser, and a thermometer, and containing a magnetic stirrer. Norbornadiene (4.5 g, 49.5 mmol) was taken in the dropping funnel. The entire system was flushed with dry nitrogen for about 0.5 hr. The norbornadiene then was added in one lot to the vigorously stirred solution of $SiCl_2Co_2(CO)_7$. The temperature of the flask was raised to 75° and kept at that temperature for 5 hr with the solution being stirred during the entire period. The initially red solution now turned dark red. It then was cooled to normal room temperature and kept at that temperature for about 11 hr. The mixture was washed first with 15 ml of 5% hydrochloric acid and then with 10 ml of 5% Na_2CO_3 solution. The benzene layer was collected in a separatory funnel. The benzene was stripped from this solution at reduced pressure (10^{-5} mm) to obtain an oily liquid. On adding 5 ml of 95% ethanol a white solid was formed out of the oily liquid. It was dissolved in benzene and recrystallized to obtain the white solid dimer: mp 150–155°; mol wt calcd 184, found 184 (mass spectrum); yield 45 mg after purification and recrystallization.

Reaction of Triiron Dodecacarbonyl, $Fe_3(CO)_{12}$, with $SiHClMn(CO)_5Co(CO)_4$. Synthesis of $Fe(CO)_4[SiClMn(CO)_5]_2[Co_2(CO)_7]$. In a typical experiment 0.210 g (0.396 mmol) of $Fe_3(CO)_{12}$ was mixed with 0.611 g (1.42 mmol) of $SiHClMn(CO)_5Co(CO)_4$ dissolved in 4 ml of hexane and sealed in an evacuated reaction vessel. A sudden reaction was observed at room temperature as evidenced by the change in color from an initial red to a dark green. The vessel with the contents was allowed to stand at room temperature for 12 hr. It was then attached to the vacuum system and cooled to −196°. The mixture of hydrogen and carbon monoxide was collected by using a Toepler pump and analyzed as described elsewhere. The reaction produced 0.64 mmol of carbon monoxide and 0.680 mmol of hydrogen. The solid remaining in the reaction vessel was extracted with *n*-hexane and filtered. On removal of the solvent, $Fe(CO)_4[SiClMn(CO)_5]_2[Co_2(CO)_7]$ was obtained as a dark green solid. The infrared spectrum of that solid (hexane solution) displayed the absorptions at

2140 (m), 2115 (s), 2035 (sh), 2000–1980 (s), 1845 (m), 1160–1070 (m), 660 (sh), 650 (m), 635 (w), 540 (m), 500–470 (m), 420 (w), and 340 cm^{-1} (w).

The mass spectrum of the solid was recorded at an ionizing voltage of 80 eV and an instrument temperature of 105°. The inlet was kept at 60°. Prominent ion peaks in the mass spectrum are shown in Table I. No parent peak was observed in this case. Again, the compound apparently decomposes before reaching temperatures at which it is volatile. The amount of $Fe(CO)_4[SiClMn(CO)_5]_2[Co_2(CO)_7]$ obtained was 0.698 g (0.699 mmol). This corresponds to 98.45% yield of $Fe(CO)_4[SiClMn(CO)_5]_2[Co_2(CO)_7]$ based on the amount of $SiHClMn(CO)_5Co(CO)_4$ consumed in the reaction shown in eq 17.

$$\begin{aligned} &Fe_3(CO)_{12}\ (0.396\ \text{mmol}) + 6SiHClMn(CO)_5Co(CO)_4 \\ &\quad (1.42\ \text{mmol}) \rightarrow 3Fe(CO)_4[SiClMn(CO)_5]_2[Co_2(CO)_7] \\ &\quad (0.699\ \text{mmol}) + 3CO\ (0.64\ \text{mmol}) + 3H_2\ (0.68\ \text{mmol}) \qquad (17) \end{aligned}$$

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Registry No. SiH_2Cl_2, 4109-96-0; $NaCo(CO)_4$, 14878-28-5; $SiH_2ClCo(CO)_4$, 41913-72-8; $SiH_2[Co(CO)_4]_2$, 23591-62-0; $Co_2(CO)_8$, 10210-68-1; $SiHCl_2Co(CO)_4$, 41913-73-9; $SiCl_2Co_2(CO)_7$, 41913-74-0; $SiHCl_3$, 10025-78-2; $(CH_3)_2SiHCl$, 1066-35-9; $(CH_3)_2SiHCo(CO)_4$, 41913-75-1; $NaMn(CO)_5$, 13859-41-1; $SiH_2ClMn(CO)_5$, 20347-37-9; $SiH_2[Mn(CO)_5]_2$, 4193-68-2; $SiHClMn(CO)_5Co(CO)_4$, 41913-77-3; $SiClMn(CO)_5Co_2(CO)_7$, 41913-78-4; $HMn(CO)_5$, 16972-33-1; $SiCl_2[Mn(CO)_5]_2$, 41913-79-5; C_7H_8, 121-46-0; $(C_7H_8)_2$, 16422-76-7; $Fe_3(CO)_{12}$, 18497-45-5; $Fe(CO)_4[SiClMn(CO)_5]_2[Co_2(CO)_7]$, 41948-82-7.

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Scrambling of Substituents between Dimethylsilicon and Various Methylphosphorus Moieties

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Equilibrium constants have been measured for the scrambling of pairs of substituents between the $(CH_3)_2Si<$ and either the $CH_3P<$, $CH_3P(O)<$, or $CH_3P(S)<$ moiety. It is found that, for exchange of chlorine with bromine, the chlorine preferentially bonded to the silicon no matter which phosphorus-containing group is involved. For exchange of chlorine with either a phenoxyl or dimethylamino group, the chlorine is preferentially bonded to the silicon in the case of the $CH_3P(O)<$ and $CH_3P(S)<$ moieties; but the reverse situation is found for the $CH_3P<$ moiety. The quantitative equilibrium data are discussed, as are the kinetics of exchange of chlorine and bromine between the dimethylsilicon and the methylthiophosphonyl moieties.

Introduction

Studies of competition equilibria have shown that pairs of exchangeable monofunctional substituents when scrambled between two kinds of polyfunctional central moieties at equilibrium display a pronounced preference of attachment for one kind of central moiety. This has been exemplified earlier for pairs of central moieties based on silicon and germanium[1-4] and for pairs of variously methyl-substituted silicon moieties[5-8] or germanium moieties.[9] Also reported were scrambling equilibria between methylgermanium and various methylphosphorus moieties.[10,11] The present paper reports additional studies of this general type, with the exchange of substituents being between dimethylsilicon and various methylphosphorus groups: $CH_3P<$, $CH_3P(O)<$, and $CH_3P(S)<$.

Experimental Section

Reagents. Dimethyldichlorosilane and dimethyldimethoxysilane were obtained from the Anderson Chemical Co., Weston, Mich., and were fractionated before use. Dimethyldibromosilane,[12] dimethylbis(methylthio)silane,[13] and dimethylbis(dimethylamino)silane[14] were made according to the literature. Dimethyldiphenoxysilane, bp 95° (0.8 mm), was prepared from dimethyldichlorosilane, phenol, and triethylamine in petroleum ether as solvent. Diphenyl methylphosphonate was obtained in a similar manner, bp 130–133° (0.5 mm). Methyldichlorophosphine,[15] methylphosphonic dichloride,[16] and methylphosphonothioic dichloride[17] were prepared according to the literature.

Procedures. Sample preparation, equilibration, proton nuclear magnetic resonance (nmr) measurements, and the calculation of weighted-average equilibrium constants were performed as previously reported.[1,3] The proton nmr chemical shifts of the methyl groups directly attached to both the silicon and the phosphorus atoms as well as of SCH_3 and $N(CH_3)_2$ groups in the compounds at equilibrium are listed in Table I. Only the relative areas of the various CH_3Si and CH_3P peaks were used for the quantitative determination of the molecular species. The experimental error of the relative area of each peak

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