crystallize). The products are, respectively, $C_5H_5RhBr(COCH_2CO_2C_2H_5)P(C_6H_5)_3$ (**12**), $C_5H_5RhCl(CH_2CH{=}CHC_6H_5)P(C_6H_5)_3$ (**14**), and $[C_5H_5RhBr(P(C_6H_5)_3)CH_2]_2C_6H_4$ (**13**). Analytical data are listed in Table I and the nmr spectrum of **12** is recorded in Table II.

(ii) $BrCH_2CO_2H$, ICH_2CO_2H, $ClCH_2COC_6H_5$, $BrCH_2COC_6H_5$, and $BrCH(CH_3)C_6H_5$ reacted readily but gave complex mixtures of products with many carbonyl stretching bands. The haloacetic acids reacted rapidly even at −78° and still gave complex mixtures.

(iii) IC_6H_5, p-$IC_6H_4NO_2$, propiolactone, $ICH_2CH_2CO_2H$, $BrCH_2C{\equiv}CH$, and $(CH_3)_4N^+Cl^-$ reacted, but the major products had no carbonyl stretching bands. The iodides in particular tended to give at least some of the dihalide $C_5H_5RhX_2P(C_6H_5)_3$.

(iv) p-$CH_3OSO_2C_6H_4CH_3$, propylene oxide, and $(CH_3CO)_2O$ showed no observable reaction in 1 week at room temperature.

Thus it appears that the reaction is applicable only to reactive halides which lack other complicating functional groups.

Conclusion

In part I of this series[1] we presented evidence (which we believe to be convincing) that the first step in the reactions of alkyl iodides with $C_5H_5Rh(CO)P(C_6H_5)_3$ and related compounds was a simple nucleophilic attack by the metal atom on the α carbon of the alkyl halide to displace halide ion. The reactions described in this paper support this conclusion. Since the first paper was submitted, evidence of inversion at carbon in a related reaction has been presented,[12] which again adds support to an SN2 mechanism.[13] Pearson and Muir, however, have shown[14] that in one case at least oxidative addition of alkyl halides can occur by a concerted three-center process. Thus it appears that two different mechanisms are possible. The actual pathway may be determined by the substrate.

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[13] A reviewer has suggested that we should mention the concerted and/or termolecular mechanism suggested by Douek and Wilkinson.[8] We find the arguments of these authors unconvincing and believe that a simple bimolecular displacment of halide ion operates in our system at least.

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Silyltricarbonyl-π-cyclopentadienylchromium, -molybdenum, and -tungsten[1,2]

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The new compounds $H_3SiCr(CO)_3(\pi\text{-}C_5H_5)$, $H_3SiMo(CO)_3(\pi\text{-}C_5H_5)$, and $H_3SiW(CO)_3(\pi\text{-}C_5H_5)$ were synthesized by the reaction of H_3SiBr with $KM'(CO)_3(\pi\text{-}C_5H_5)$ (where M′ = Cr, Mo, W). The thermal stability of the compounds was examined. The silicon–transition metal bond was cleaved at room temperature by water and hydrogen chloride and at slightly elevated temperatures by dimethylamine. Trimethylamine and dimethylamine formed adducts which were stable at room temperature.

The synthesis of $H_3CM'(CO)_3(\pi\text{-}C_5H_5)$ (where M′ = Cr, Mo, W) was reported in 1956 by Piper and Wilkinson.[3] Since that time, similar compounds containing the groups F_3C,[4] Cl_3Si,[5] and $(CH_3)_3Si$[6] have been characterized. The chief purpose of this present investigation, preliminary results of which have been reported previously,[7] was to study selected chemical properties of the parent molecules $H_3SiCr(CO)_3(\pi\text{-}C_5H_5)$, $H_3SiMo(CO)_3(\pi\text{-}C_5H_5)$, and $H_3SiW(CO)_3(\pi\text{-}C_5H_5)$, in order to obtain information concerning the nature of the silicon–transition metal linkage.

Results and Discussion

I. Synthesis of the Silicon–Transition Metal Bond.

—The synthesis of a number of compounds containing silicon linked to chromium, molybdenum, or tungsten has been reported by several workers. Jetz and Graham[5] reported the synthesis of $Cl_3SiMo(CO)_3(\pi\text{-}C_5H_5)$ from trichlorosilane and bis(tricarbonyl-π-cyclopentadienylmolybdenum) as the first compound containing a silicon–molybdenum linkage. In 1967 Cardin, Keppie, Kingston, and Lappert[6] reported the syntheses of $(H_3C)_3SiMo(CO)_3(\pi\text{-}C_5H_5)$ and of $(H_3C)_3SiW(CO)_3(\pi\text{-}C_5H_5)$ in tetrahydrofuran from the appropriate complex metal hydride and $(H_3C)_3SiN(CH_3)_2$, *viz.*, $HMo(CO)_3(\pi\text{-}C_5H_5) + (H_3C)_3SiN(CH_3)_2 \rightarrow (H_3C)_3SiMo(CO)_3(\pi\text{-}C_5H_5) + HN(CH_3)_2$. Patil and Graham,[8] in a very comprehensive paper in which they reported several germanium, tin, and lead compounds containing the $M'(CO)_3(\pi\text{-}C_5H_5)^-$ anion (where M′ = Cr, Mo, W), mentioned briefly that the interaction of the complex anion with a silicon halide did not lead to the desired

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product but that dimers of the starting material were recovered.

In the present study the new compounds $H_3SiCr(CO)_3(\pi\text{-}C_5H_5)$, $H_3SiMo(CO)_3(\pi\text{-}C_5H_5)$, and $H_3SiW(CO)_3(\pi\text{-}C_5H_5)$ were synthesized in 20–40% yields based upon the amount of anion employed by an exchange reaction between silyl bromide and the appropriate complex anion in the absence of a solvent at room temperature, *viz.*, $H_3SiBr + K[Mo(CO)_3(\pi\text{-}C_5H_5)] \rightarrow H_3SiMo(CO)_3(\pi\text{-}C_5H_5) + KBr$. These compounds are oxygen- and water-sensitive yellow solids which melt near or above 100° in a deoxygenated nitrogen atmosphere. The chromium compound partially decomposed upon melting; whereas the molybdenum and tungsten analogs were thermally stable when heated in excess of 160° for at least 45 min. However, when heated above 250°, a noncondensable gas, assumed to be a mixture of H_2 and CO, was evolved, and an uncharacterized black tar formed. In addition a trace of SiH_4 was identified as the only volatile substance which condensed at liquid nitrogen temperature.

The compounds $H_3CCr(CO)_3(\pi\text{-}C_5H_5)$, $H_3CMo(CO)_3(\pi\text{-}C_5H_5)$, and $H_3CW(CO)_3(\pi\text{-}C_5H_5)$ were prepared in an analogous manner to the silyl derivatives using diethyl ether as the solvent according to the established procedures of Piper and Wilkinson.[3] These compounds were of much less thermal stability than the silyl analogs. The methylmolybdenum species decomposed *in vacuo* when heated to 155° forming acetaldehyde, in addition to carbon monoxide and hydrogen. Methane, as would be expected by a comparison with the thermal decomposition of the silyl analog, was not observed. The thermal reaction forming $H_3CC(O)H$ can be postulated as taking place *via* the well-established initial insertion of CO into the methyl–molybdenum linkage followed by homolytic cleavage and hydrogen abstraction.

The apparent difference in thermal decomposition products when silicon replaces carbon may be justified in that no insertion of CO into a silicon–transition metal bond has been reported and that $H_3SiC(O)H$ may indeed form but then rapidly decomposes forming silane and carbon monoxide.

II. Spectral Properties.—The infrared spectra (Table I) in the carbonyl stretching region are consistent with the work of King and Houk,[9] who observed three carbonyl bands for $H_3CM'(CO)_3(\pi\text{-}C_5H_5)$ (M′ = Mo, W). It would be tempting to assume that the methyl and silyl compounds have the same structure; however with the apparent low symmetry such a conclusion may indeed be erroneous.

TABLE I
ABSORPTION SPECTRA

	Infrared,[a] cm^{-1}		Nmr,[b] τ	
	ν_{Si-H}	ν_{C-O}	$\pi\text{-}C_5H_5$	SiH_3
$H_3SiCr(CO)_3(\pi\text{-}C_5H_5)$	2102 m	1999 vs, 1943 vs, 1918 vs	5.11	5.88
$H_3SiMo(CO)_3(\pi\text{-}C_5H_5)$	2100 m	2005 vs, 1948 vs, 1925 vs	4.65	6.15
$H_3SiW(CO)_3(\pi\text{-}C_5H_5)$	2100 m	2005 vs, 1940 vs, 1931 vs	4.50	6.18

[a] Spectra recorded in Nujol. [b] Diethyl ether as solvent.

The observed silicon–hydrogen stretching frequencies are among the lowest in energy of any reported for a silyl group except for $H_3SiFe(CO)_2(\pi\text{-}C_5H_5)$ (2103 cm^{-1});[10] for example: –I, 2192 cm^{-1};[11] $-Ge(CH_3)_3$, 2154 cm^{-1};[12] $-Co(CO)_4$, 2150 cm^{-1};[13,14] $-Mn(CO)_5$, 2136 cm^{-1}.[15] The shift to lower energy of the Si–H stretching vibration has been interpreted by Aylett and Campbell[13,16] to be indicative of a multiple-bond character between the silyl grouping and cobalt in $H_3SiCo(CO)_4$. The multiple-bond character of the silicon–transition metal linkage has also been demonstrated[17] from X-ray studies, mass spectral data, and molecular orbital calculations.

In all cases, a sharp, single peak was observed for the five cyclopentadienyl ring protons and a sharp single peak for the silyl protons in the pmr signal. The trend in τ values for the $\pi\text{-}C_5H_5$ chemical shift indicates that the metal in $H_3SiCr(CO)_3(\pi\text{-}C_5H_5)$ has a greater negative charge than in the lower members of the series.[18] This correlation is also found in the relative values of τ for the $-SiH_3$ grouping. These correlations imply that when the group VI metals are a part of the $M'(CO)_3(\pi\text{-}C_5H_5)$ grouping they have the effective electronegativity order Cr > Mo = W. The closeness of chemical shift for the Mo and W compounds can be accounted for in terms of the so-called lanthanide contraction.[19]

The mass spectra of the analogous carbon and silicon compounds exhibited analogous fragments except for $H_3SiMo(CO)_3(\pi\text{-}C_5H_5)$. In a later communication a detailed discussion of the mass spectra of the individual compounds will be presented. For $H_3MM'(CO)_3(\pi\text{-}C_5H_5)$ (M = C, M′ = Cr, Mo, W; M = Si, M′ = Cr, W) peaks corresponding to the molecular ions $H_3MM'(CO)_3(\pi\text{-}C_5H_5)^+$, $H_3MM'(CO)_2(\pi\text{-}C_5H_5)^+$, $H_3MM'(CO)(\pi\text{-}C_5H_5)^+$, $H_3MM'(\pi\text{-}C_5H_5)^+$, $M'(CO)_3(\pi\text{-}C_5H_5)^+$, $M'(CO)_2(\pi\text{-}C_5H_5)^+$, $M'(CO)(\pi\text{-}C_5H_5)^+$, and $M'(\pi\text{-}C_5H_5)^+$ were observed. In each case the isotopic abundance of the transition metal was observed for the ions containing M′. For $H_3SiMo(CO)_3(\pi\text{-}C_5H_5)$ ions analogous to those for the other compounds were observed, except that the H_3Si grouping was not present. Peaks representing *m/e* values corresponding to ions such as $(\pi\text{-}C_5H_5)_2Mo_2^+$ or $(\pi\text{-}C_5H_5)_2Mo_2(CO)_2^+$, the most abundant species in the mass spectrum of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$,[20] were not observed.

III. Reaction with Amines.—The interaction between amines and silyl transition metal compounds has been studied for several molecules, including $H_3SiMn(CO)_5$,[21] $(H_3Si)_2Fe(CO)_4$,[22] $H_3SiFeH(CO)_4$,[22] $H_3SiCo(CO)_4$,[14,21] and $(CH_3)_3SiCo(CO)_4$.[23] It has been demonstrated using infrared spectroscopy that in the solid state the adducts are of the form $[H_3Si\cdot B_m]^+[M(CO)_n]^-$

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where B represents the base. Molecules having the same stoichiometry for carbon compounds, such as $H_3CMn(CO)_5$, have been shown actually to form an an acyl derivative, *e.g.*, $H_3CC(O)Mn(CO)_4(C_6H_{11}NH_2)$.[24,25]

In the present study, the compounds $H_3MM'(CO)_3(\pi\text{-}C_5H_5)$ (M = C, Si; M' = Cr, Mo, W) were combined with both dimethylamine and trimethylamine at room temperature. The carbon compounds were found not to react with $(H_3C)_3N$, but the formation of $H_3CC(O)Cr(CO)_2(\pi\text{-}C_5H_5)[HN(CH_3)_2]$ was observed with dimethylamine. With dimethylamine and $H_3CMo(CO)_3(\pi\text{-}C_5H_5)$ a small amount of interaction was noted; however, no reaction took place with $H_3CW(CO)_3(\pi\text{-}C_5H_5)$. Table II summarizes the data for the amine experiments.

TABLE II
COMPOSITION OF AMINE ADDUCTS

M	Amine	M:amine	Ir,[a] cm⁻¹
H_3SiCr	$N(CH_3)_3$	1.00:0.92	1900, 1775
H_3SiMo	$N(CH_3)_3$	1.00:1.09	1903, 1780
H_3SiW	$N(CH_3)_3$	No interaction	
H_3SiCr	$HN(CH_3)_2$	1.00:1.28	1900, 1775
H_3SiMo	$HN(CH_3)_2$	1.00:1.64	1900, 1770
H_3SiW	$HN(CH_3)_2$	1.00:2.06	1906, 1765
H_3CCr	$HN(CH_3)_2$	1.00:0.98	1887, 1760, 1615

[a] Spectra recorded in Nujol.

The positions of the carbonyl stretching vibrations of the silyl complexes indicate that a complex anion of the type $M'(CO)_3(\pi\text{-}C_5H_5)^-$ (M' = Cr, Mo, W) has formed and that the amine addition compound of $H_3CCr(CO)_3(\pi\text{-}C_5H_5)$ contains an acyl carbonyl group.[26,27] The reported bands in all cases are broad and represent the position of maximum absorption.

IV. Cleavage of the Silicon–Transition Metal Bond by Lewis Bases.—It has been reported that the silicon–transition metal linkage in $H_3SiCo(CO)_4$[14] and $(H_3Si)_2Fe(CO)_4$[22] is readily cleaved by water forming disiloxane and the anionic acid. However, when the silyl compounds reported in this paper were combined with water, the only volatile product observed was silane.

Baay and MacDiarmid[28] have reported that when the Si–Co linkage in $(H_3C)_3SiCo(CO)_4$ is cleaved by dimethylamine at room temperature, $(H_3C)_3SiN(CH_3)_2$ and $HCo(CO)_4$ are formed. Aylett and Campbell reported[21,29] that ammonia readily cleaves the Si–Mn bond in $H_3SiMn(CO)_5$ forming $(H_3Si)_2NH$ and $HMn(CO)_5$. In the present study, adduct formation was found to be the primary reaction at temperatures up to room temperature, with cleavage occurring at slightly elevated temperatures when $H_3SiM'(CO)_3(\pi\text{-}C_5H_5)$ and dimethylamine were mixed or the dimethylamine adduct heated.

V. Cleavage of the Silicon–Transition Metal Linkage by Covalent Halides.—The silicon–transition metal linkage was readily cleaved by HCl at room temperature, *viz.*, $H_3SiM'(CO)_3(\pi\text{-}C_5H_5) + HCl \rightarrow H_3SiCl + HM'(CO)_3(\pi\text{-}C_5H_5)$. When the analogous carbon compound was treated with an excess of HCl, the volatile products were methane and $ClM'(CO)_3(\pi\text{-}C_5H_5)$. This reaction could have taken place *via* a two-step process, *viz.*

$$H_3CM'(CO)_3(\pi\text{-}C_5H_5) + HCl \longrightarrow H_3CCl + HM'(CO)_3(\pi\text{-}C_5H_5)$$

$$H_3CCl + HM'(CO)_3(\pi\text{-}C_5H_5) \longrightarrow CH_4 + ClM'(CO)_3(\pi\text{-}C_5H_5)$$

However, the products of the former reaction were never isolated.

The initial interaction with the methyl compound may be the formation of a hydridic cation[30] which then decomposes, forming methane, *viz.*,

$$H_3CW(CO)_3(\pi\text{-}C_5H_5) + HCl \longrightarrow [H_3CWH(CO)_3(\pi\text{-}C_5H_5)]Cl$$

$$[H_3CWH(CO)_3(\pi\text{-}C_5H_5)]Cl \longrightarrow ClW(CO)_3(\pi\text{-}C_5H_5) + CH_4$$

It would be expected that if the silyl grouping removes electron density from the transition metal, perhaps *via* a $(d \rightarrow d)\pi$ interaction, then the base strength of the $M'(CO)_3(\pi\text{-}C_5H_5)$ grouping would be smaller than for the methyl compound. The proton from the HCl would therefore not be able to have as strong an interaction with $H_3SiMo(CO)_3(\pi\text{-}C_5H_5)$ as with $H_3CMo(CO)_3(\pi\text{-}C_5H_5)$, reducing the probability of forming a hydridic cation.

When the silyl compounds were combined with PF_5, a complex mixture resulted which included $HSiF_3$, PF_3, and OPF_3, indicating that the silicon–transition metal linkage had been cleaved.

Experimental Section

Apparatus.—All work was carried out in a borosilicate glass vacuum system constructed with Teflon stopcocks (Fisher & Porter Co., Warminster, Pa., No. 795-005-0004). Reactions were carried out in pressure reactors which were constructed from thick-walled borosilicate tubing to which one of the above stopcocks was attached.[31]

Materials.—The following commercial reagents were used without further purification: HCl (mol wt: calcd, 36.5; found, 36.5; confirmed by infrared spectrum),[32] $(CH_3)_2NH$ (anhydrous; mol wt: calcd, 45.1; found, 45.0; confirmed by infrared spectrum), PF_5 (mol wt: calcd, 126.0; found, 125.1; confirmed by infrared spectrum),[33] $(H_3C)_3N$ (mol wt: calcd, 59.1; found, 58.8; confirmed by infrared spectrum),[32] $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, and carbon monoxide. Silyl bromide was prepared from $C_6H_5SiH_3$ and HBr[34] (mol wt: calcd, 111.0; found, 110.5; confirmed by infrared spectrum).[11] $KM'(CO)_3(\pi\text{-}C_5H_5)$ (where M' = Cr, Mo, W) was prepared following literature methods.[35]

Infrared Absorption Spectra.—Spectra were recorded with a Beckman Model IR-8 double-beam, grating spectrophotometer. Volatile materials were confined in a 10-cm cell fitted with KBr windows cemented with Glyptal resin. Nonvolatile materials were recorded as mineral oil (Nujol) mulls between KBr disks; bands due to the mulling agent are not reported. Peak positions were calibrated with respect to polystyrene film. Absorptions assigned to carbon–oxygen and silicon–hydrogen stretching vibrations are listed in Table I; other vibrations are listed in the text (vs = very strong, s = strong, m = medium, w = weak as compared to the strongest absorption peak, excluding the mulling agent where used).

Nuclear Magnetic Resonance Spectra.—Proton magnetic resonance spectra were recorded by means of an A-60 Varian Associates spectrometer at 60 MHz at the ambient temperature of the probe. The spectra were determined using diethyl ether as the solvent with tetramethylsilane as an internal standard (τ 10).

Mass Spectra.—Mass spectra were taken at 75-eV electron energies on a Hitachi Perkin-Elmer RMU-6E mass spectrometer at ambient temperature.

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Synthetic Procedure.—Reactions were carried out in the vacuum system or in a deoxygenated nitrogen or carbon monoxide atmosphere. Whenever possible, initial reagents as well as materials from a reaction vessel were identified and then confirmed by two independent methods chosen from the following list of properties: melting point, vapor pressure, infrared spectrum, mass spectrum, and/or proton magnetic resonance spectrum.

Synthesis of $H_3SiCr(CO)_3(\pi\text{-}C_5H_5)$.—$K[Cr(CO)_3(\pi\text{-}C_5H_5)]$ (926.2 mg, 3.856 mmol) and H_3SiBr (648.1 mg, 5.839 mmol) were held at room temperature in a 20-ml glass reactor for 30 min. The reaction mixture turned orange with the formation of a brown residue, and heat was evolved. The mixture was held at −196° for 5 min before removing a small amount (~4 mg) of noncondensable material assumed to be carbon monoxide. Upon warming the reactor to −78°, unreacted H_3SiBr was recovered (235.9 mg, 2.125 mmol).[11] The resulting solid material was sublimed *in vacuo* at room temperature resulting in the recovery of $Cr(CO)_6$ (33.4 mg, 0.151 mmol),[36] and upon further sublimation at 75°, yellow crystals were collected on the sublimer cold finger which had been cooled to −196°. The resulting pure material (341.2 mg, 1.469 mmol) which melted at 129–130° with decolorization in a nitrogen atmosphere was obtained in 40% yield based on the amount of $K[Cr(CO)_3(\pi\text{-}C_5H_5)]$ initially employed. *Anal.*[37] Calcd for $H_3SiCr(CO)_3(\pi\text{-}C_5H_5)$ ($C_8H_8CrO_3Si$): C, 41.38; H, 3.47; Si, 12.09. Found: C, 40.60; H, 3.49; Si, 11.50. Infrared bands in addition to those listed in Table I are 945 (w), 900 (s), 835 (w), 600 (w), and 628 cm^{-1} (w).

Synthesis of $H_3SiMo(CO)_3(\pi\text{-}C_5H_5)$.—The above procedure formed this compound in 41% yield as a yellow solid which melted at 96–97°. *Anal.*[37] Calcd for $H_3SiMo(CO)_3(\pi\text{-}C_5H_5)$ ($C_8H_8MoO_3Si$): C, 34.79; H, 2.91; Si, 10.17. Found: C, 34.02; H, 3.23; Si, 10.25. Infrared bands in addition to those listed in Table I are 1005 (w), 935 (m), 890 (s), and 805 cm^{-1} (m).

Synthesis of $H_3SiW(CO)_3(\pi\text{-}C_5H_5)$.—The above procedure formed this compound in 21% yield as a yellow solid which melted at 112–113°. *Anal.*[37] Calcd for $H_3SiW(CO)_3(\pi\text{-}C_5H_5)$ ($C_8H_8O_3SiW$): C, 26.39; H, 2.15; Si, 7.71. Found: C, 26.69; H, 2.28; Si, 7.91. Infrared bands in addition to those listed in Table I are 935 (w), 895 (m), 815 cm^{-1} (w).

Reaction of $H_3SiCr(CO)_3(\pi\text{-}C_5H_5)$ with H_2O.—In a preliminary experiment $H_3SiCr(CO)_3(\pi\text{-}C_5H_5)$ (35.9 mg, 0.155 mmol) was combined with H_2O (0.5 ml) in a 10-ml glass pressure reactor. Upon identification of the volatile products only water and silane[38] were observed.

Reaction of $H_3SiMo(CO)_3(\pi\text{-}C_5H_5)$ with PF_5.—$H_3SiMo(CO)_3(\pi\text{-}C_5H_5)$ (121.3 mg, 0.4392 mmol) and PF_5 (237.2 mg, 1.883 mmol) were held in a 20-ml reactor for 6 days at room temperature. After this time the reaction vessel was cooled to −196° for 5 min before removing a small quantity of noncondensable material. After removing the volatile materials, a dark red-purple solid (170.9 mg) remained in the vessel. The volatile material was passed through traps cooled to −130 and −160° into a trap cooled to −196°. The material stopping at −130° consisted of OPF_3 (54.5 mg, 0.524 mmol).[39] A mixture of SiF_4 and PF_5 (66.4 mg)[33,40] condensed in the −160° trap and PF_3 (44.8 mg, 0.509 mmol)[39] stopped at −196°.

Reaction of $H_3SiM'(CO)_3(\pi\text{-}C_5H_5)$ with HCl.—$H_3SiCr(CO)_3(\pi\text{-}C_5H_5)$ (51.9 mg, 0.223 mmol) and HCl (50.9 mg, 1.40 mmol) were held in a 20-ml reaction vessel for 6 hr at room temperature. The reactor was cooled to −196° and opened to a manometer. No noncondensable material was observed. The volatile materials which distilled from the reaction vessel at −78° contained HCl (40.2 mg, 1.11 mmol)[32] and H_3SiCl (10.8 mg, 0.162 mmol).[11] The latter material was obtained as condensate on distillation of the volatile material recovered from the reactor through a trap held at −126° in which the former compound did not condense. The bright yellow residue remaining was pure $HCr(CO)_3(\pi\text{-}C_5H_5)$ (44.5 mg, 0.220 mmol; 99% yield based on the quantity of $H_3SiCr(CO)_3(\pi\text{-}C_5H_5)$ employed).[41]

When M′ = Mo or W, the formation of H_3SiCl and $HM'(CO)_3(\pi\text{-}C_5H_5)$ in nearly quantitative yields was observed.[41]

Reaction of $H_3CM'(CO)_3(\pi\text{-}C_5H_5)$ with HCl.—$H_3CW(CO)_3(\pi\text{-}C_5H_5)$ (111.9 mg, 0.3073 mmol) and HCl (179.7 mg, 4.929 mmol) were held at room temperature for 3 days in a 20-ml reactor. The reactor was cooled to −196° and opened to a manometer. A large quantity of noncondensable gas (assumed to be CH_4) was observed. The material which volatilized at room temperature was passed through a trap cooled to −130° and identified as HCl (171.2 mg, 4.696 mmol).[32] The reactor contained a bright orange solid (111.1 mg, 0.3021 mmol) identified as $ClW(CO)_3(\pi\text{-}C_5H_5)$. *Anal.* Calcd for $ClW(CO)_3(\pi\text{-}C_5H_5)$ ($C_8H_5ClO_3W$): C, 23.56; H, 1.51; Cl, 9.94. Found: C, 24.32; H, 1.26; Cl, 9.70. Infrared bands (Nujol mull) are 3102 (w), 2036 (vs), 1986 (vs), 1915 (s), 1063 (w), 1012 (w), 1002 (w), 875 (w), 840 (s), 825 cm^{-1} (s).

With $H_3CMo(CO)_3(\pi\text{-}C_5H_5)$, an essentially quantitative yield of $ClMo(CO)_3(\pi\text{-}C_5H_5)$[42] was obtained.

Reaction of $H_3SiM'(CO)_3(\pi\text{-}C_5H_5)$ with $N(CH_3)_3$.—$H_3SiCr(CO)_3(\pi\text{-}C_5H_5)$ (112.4 mg, 0.4841 mmol) and $N(CH_3)_3$ (414.2 mg, 7.007 mmol) were held in a 20-ml reaction vessel for 6 days at room temperature. The reactor was cooled to −196° and opened to a manometer. No noncondensable material was observed. The volatile materials which distilled from the reactor were distilled through a trap cooled to −126°. The trap contained $N(CH_3)_3$ (373.4 mg, 6.317 mmol).[32] The reaction vessel contained a bright yellow solid (138.7 mg), which represents a material having the gross composition indicated by a 1.00:0.92 $H_3SiCr(CO)_3(\pi\text{-}C_5H_5):N(CH_3)_3$ ratio.

The same procedure was followed when M′ = Mo or W. The formation of a yellow solid was observed having the stoichiometry as given in Table II.

Reaction of $H_3CM'(CO)_3(\pi\text{-}C_5H_5)$ with $N(CH_3)_3$.—$H_3CMo(CO)_3(\pi\text{-}C_5H_5)$ (201.8 mg, 0.7755 mmol) and $N(CH_3)_3$ (1867.0 mg, 31.585 mmol) were held at room temperature for 6 days in a 20-ml reactor. The reactor was cooled to −196° and opened to a manometer; no noncondensable material was observed. The volatile materials which distilled from the reactor at room temperature were passed through a trap cooled to −130°. The trap contained $N(CH_3)_3$ (1866.4 mg, 31.575 mmol; identified by infrared spectrum),[32] and the solid remaining in the reactor was unchanged. Similar results were obtained when M′ = Cr or W.

Reaction of $H_3SiM'(CO)_3(\pi\text{-}C_5H_5)$ with $HN(CH_3)_2$.—$H_3SiCr(CO)_3(\pi\text{-}C_5H_5)$ (96.8 mg, 0.419 mmol) and $HN(CH_3)_2$ (507.1 mg, 11.25 mmol) were held in a 20-ml glass reaction vessel for 6 days at room temperature. The reactor was cooled to −196° and opened to a manometer; a small amount of noncondensable material was observed. The volatile material which distilled from the reaction vessel at room temperature was identified as $HN(CH_3)_2$ (483.4 mg, 10.72 mmol).[32] The reactor contained a yellow solid (120.9 mg) which represents a substance having the gross composition indicated by a 1.00:1.28 $H_3SiCr(CO)_3(\pi\text{-}C_5H_5):HN(CH_3)_2$ ratio.

The same procedure was followed when M′ = Mo or W. The formation of a yellow solid was observed having the stoichiometry as given in Table II.

When a sample of the $H_3SiMo(CO)_3(\pi\text{-}C_5H_5)$ adduct was heated at 70° in addition to dimethylamine, $H_3SiN(CH_3)_2$[43] and $HMo(CO)_3(\pi\text{-}C_5H_5)$ were recovered.

Reaction of $H_3CM'(CO)_3(\pi\text{-}C_5H_5)$ with $HN(CH_3)_2$.—$H_3CCr(CO)_3(\pi\text{-}C_5H_5)$ (26.7 mg, 0.123 mmol) and $HN(CH_3)_2$ (1091.4 mg, 24.210 mmol) were held in a 20-ml glass reaction vessel for 30 min forming a bright orange solution. The reactor was cooled to −196° and opened to a manometer; no noncondensable material was observed. The material which distilled from the vessel at room temperature was identified as $HN(CH_3)_2$ (1085.9 mg, 24.088 mmol).[32] The reactor contained an orange-red solid (32.2 mg) which represents a substance having the gross composition indicated by a 1.00:0.98 $H_3CCr(CO)_3(\pi\text{-}C_5H_5):HN(CH_3)_2$ ratio.

The same procedure was followed where M′ = Mo or W; however, no appreciable interaction was observed.

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