Microanalyses (Table I) were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Bonn, Germany, and by the microanalytical laboratory of this department. Infrared spectra were measured with a Perkin-Elmer 337 grating spectrometer and recorded in expanded form on a Hewlett-Packard 7127A recorder using gaseous CO and DBr for calibration. Nmr measurements were made on a Varian A56/60A spectrometer and mass spectra were recorded using an AEI MS9 instrument.

Preparation of $C_5H_5CORh(H)Si(C_6H_5)_3$.—Cyclopentadienyldicarbonylrhodium (1.12 g, 5.0 mmol) was dissolved in benzene (30 ml) and triphenylsilane (1.30 g, 5.0 mmol) was added. The resulting solution was irradiated using a Hanovia Model 616A 100-W lamp for 5 days, keeping the quartz reaction vessel close to room temperature. After filtering through a very short column of Florisil and concentrating to about 2 ml, hexane (10 ml) was added to yield off-white crystals of product (0.26 g, 0.57 mmol, 11%).

The compound $C_5H_5CORh(H)Si(CH_2C_6H_5)_3$ was produced in analogous fashion using a reaction time of 1 week and recrystallizing the product twice from hexane. The yield of the greenish white derivative was 0.24 g (0.48 mmol, 10%) from 5 mmol of $C_5H_5Rh(CO)_2$.

Preparation of $C_5H_5CORh(SiCl_3)_2$.—Cyclopentadienyldicarbonylrhodium (0.89 g, 4.0 mmol) was added to trichlorosilane (1.37 g, 10.0 mmol). After a few seconds a vigorous reaction took place with evolution of much gas. The mixture was stirred for a further 2 hr and excess silane was then removed under high vacuum. The solid residue was recrystallized from hexane, sublimed under high vacuum, and recrystallized again from hexane. Colorless crystals of product (1.13 g, 2.43 mmol, 61%) were thus obtained.

In analogous fashion $C_5H_5CORh(SiCl_2CH_3)_2$ was prepared using methyldichlorosilane.

Preparation of $C_5H_5COClRhGeCl_3$.—Germanium tetrachloride (0.21 g, 1.0 mmol) was added to a stirred solution of cyclopentadienyldicarbonylrhodium (0.22 g, 1.0 mmol) in 20 ml of toluene and the mixture heated to 60° for 1 hr. After cooling and adding pentane (20 ml), the solid formed was recrystallized twice from dichloromethane–pentane to give the pure product (0.21 g, 0.51 mmol, 51%).

The above method without the use of heat was employed to obtain corresponding derivatives from the halides $GeBr_4$, $SnBr_4$, SnI_4, and CH_3SnI_3.

Preparation of $C_5H_5COIRhGeI_3$.—The compound $C_5H_5COClRhGeCl_3$ was prepared as above from $C_5H_5Rh(CO)_2$ (2.5 mmol) and $GeCl_4$ (2.6 mmol) and dissolved in 20 ml of dichloromethane. Sodium iodide (1.5 g, 10 mmol) was added and the mixture stirred for 2 days. After filtration, the filtrate was concentrated to 10 ml and pentane (10 ml) was added. Cooling to 0° afforded black crystals which were recrystallized from dichloromethane–pentane to yield 0.82 g of product (1.1 mmol, 42%).

Preparation of $C_5H_5COClRhSnCl_3$.—To a solution of $C_5H_5Rh(CO)_2$ (0.34 g, 1.5 mmol) in pentane (20 ml) was added $SnCl_4$ (0.18 ml, 1.5 mmol) also in pentane (20 ml). A highly air-sensitive orange-yellow precipitate was formed and collected. This was allowed to decompose completely in the laboratory atmosphere and the resulting viscous oil was extracted with dichloromethane (50 ml). Addition of pentane (50 ml), cooling to 0°, and subsequent recrystallization of the resulting solid from dichloromethane–pentane yielded orange-red crystals (0.24 g, 0.53 mmol, 35%) of the desired product.

Reactions with Tin(II) Chloride and Bromide.—Finely powdered tin(II) chloride (0.74 g, 4.0 mmol) was added to a solution of $C_5H_5Rh(CO)_2$ (0.89 g, 4.0 mmol) in 20 ml of 1,2-dichloroethane. This mixture was heated at 75° for 24 hr. After cooling, the precipitate was collected and dried under high vacuum to afford the orange polymeric product $[C_5H_5CORhSnCl_2]_n$, (1.26 g, 82%).

A little of this polymeric compound (0.30 g) was heated for 2 days at 75° in 1,2-dichloroethane (50 ml) with $C_5H_5Rh(CO)_2$ (0.22 g, 1 mmol). After the mixture had been cooled to room temperature and filtered, pentane (20 ml) was added to the filtrate and the resulting solution was cooled to −15°. Orange crystals of $[C_5H_5CORhSnCl_2 \cdot {}^1/_3C_2H_4Cl_2]_x$ (0.18 g, 58%) separated.

Cyclopentadienyldicarbonylrhodium (0.89 g, 4.0 mmol) was dissolved in toluene (20 ml), tin(II) chloride (1.5 g, 7.9 mmol) was added, and the mixture was stirred at 70° for 24 hr. After cooling to room temperature the mixture was filtered and the filtrate was cooled to −15°. Small bright orange crystals of $[C_5H_5CORhSnCl_2 \cdot {}^1/_3C_6H_5CH_3]_x$ (0.41 g, 25%) were formed.

An analogous reaction took place with stannous bromide to afford orange-red crystals of $[C_5H_5CORhSnBr_2 \cdot {}^1/_3C_6H_5CH_3]_x$ (0.28 g, 14%).

Acknowledgment.—We thank the National Research Council of Canada for financial support.

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

Silicon–Transition Metal Chemistry. I. Photochemical Preparation of Silyl(transition metal) Hydrides

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

Received June 16, 1970

Metal carbonyls and their derivatives react photochemically with silanes to form silyl-substituted transition metal hydrides according to the general reaction $M(CO)_n + R_3SiH \rightarrow R_3SiMH(CO)_{n-1} + CO$. Using trichlorosilane, *cis*-$Cl_3SiCrH(CO)_2C_6H_6$, *cis*-$Cl_3SiMnH(CO)_2C_5H_5$, $(Cl_3Si)_2FeH(CO)C_5H_5$, *cis*-$Cl_3SiFeH(CO)_4$, and $Cl_3SiCoH(CO)C_5H_5$ have been prepared. Using triphenylsilane, *cis*-$(C_6H_5)_3SiMnH(CO)_2C_5H_4CH_3$ and *cis*-$(C_6H_5)_3SiFeH(CO)_4$ have been prepared. The stereochemistry is inferred from intensities of infrared carbonyl stretching bands.

Introduction

Carbonyl hydrides of transition metals have been known for many years, but it is only recently that the stereochemical significance of the hydrogen ligand has been established.[1] Likewise, although the first silicon–transition metal bond was prepared some time ago,[2]

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* To whom correspondence should be addressed.

[1] S. J. La Placa, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, **8**, 1928 (1969), and references cited therein.

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

the field has attracted wide attention only in the past 3 or 4 years,[3] and many compounds having silicon–transition metal bonds are now known.

We are concerned here with a hybrid of these two fields, that of silyl-substituted carbonyl hydrides. The first compound to combine these two structural features was $Cl_3SiIrH(CO)Cl(P(C_6H_5)_3)_2$, prepared by the addition of trichlorosilane to $Ir(CO)Cl(P(C_6H_5)_3)_2$.[4] Oxidative addition or oxidative elimination reactions involving the silicon–hydrogen bond have afforded several other examples of silyl hydrides of rhodium,[5–7] iridium,[8] and platinum.[9] The reaction of $(C_6H_5)_3SiLi$ with *cis*-$PtCl_2(P(C_2H_5)_3)_2$ produces $(C_6H_5)_3SiPtH(P(C_2H_5)_3)_2$,[10] and, of more relevence to this work, a very low yield of $H_3SiFeH(CO)_4$ has been obtained from the reaction of H_3SiI with $Na_2Fe(CO)_4$.[11]

Our interest in the synthesis of silicon–transition metal bonds by the reaction of silanes with metal carbonyls at elevated temperatures[12–14] led us to postulate the formation of silyl hydrides as intermediates in these reactions. Studies of the photochemical initiation of silane–metal carbonyl reactions were undertaken with the object of preparing and isolating such intermediates under mild conditions. Our preliminary results have been outlined in a communication,[15] and the present paper presents full details. Future papers of this series will deal with the chemical reactions of the silyl hydrides and their derivatives, with the reactions of silanes and metal carbonyls at higher temperatures, and with developments in the chemistry of recently reported compounds believed to contain silicon–hydrogen–transition metal bridges.[16]

Results and Discussion

The ultraviolet irradiation of carbonyl–transition metal complexes, in the presence of a silane, leads to the formation of silyl(transition metal) hydrides with the loss of carbon monoxide. In these reactions, a carbon monoxide ligand is apparently ejected by a sufficiently energetic photon, producing the unsaturated intermediate (eq 1). In subsequent reaction steps, it may recombine with carbon monoxide to form starting material (eq 2) or add a silane to yield the observed product (eq 3). The reactions are carried out below 25° at atmospheric pressure in a saturated hydrocarbon solvent. The low solubility of carbon monoxide under these conditions, combined with the use of excess silane, ensures that reaction 3 is dominant.

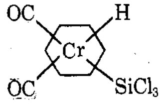
$$M(CO)_n \xrightarrow{h\nu} M(CO)_{n-1}^* + CO \qquad (1)$$

$$M(CO)_{n-1}^* + CO \longrightarrow M(CO)_n \qquad (2)$$

$$M(CO)_{n-1}^* + \text{Si-H} \longrightarrow SiHM(CO)_{n-1} \qquad (3)$$

Irradiation of benzenechromium tricarbonyl with trichlorosilane forms hydridotrichlorosilyl(π-benzene)dicarbonylchromium (**1**). The compound is insoluble in hexane and precipitates in microcrystalline form as the reaction proceeds. Probably as a result of this insolubility, near-quantitative conversion to the trichlorosilyl derivative may be obtained in oxygen-free hexane or heptane, under prolonged irradiation, in the presence of excess trichlorosilane.[17] In the crystalline state the hydride is moderately air stable, but in dichloromethane at room temperature decomposition occurs rapidly in the presence of trace amounts of air.

There is a striking similarity in the physical properties of the manganese and iron compounds **2** and **3**,[18] prepared from π-cyclopentadienyltricarbonylmanganese and trichlorosilyl(π-cyclopentadienyl)dicarbonyliron,[13] respectively. The formation of both compounds is accompanied by substantial decomposition. Both crystallize from hexane as pale yellow, moderately air-stable needles. The methylcyclopentadienylmanganese analog of **2** is a liquid at room temperature and was not characterized, although some of its derivatives will be described in a subsequent paper. Triphenylsilane reacts with $CH_3C_5H_4Mn(CO)_3$ yielding crystalline $(C_6H_5)_3SiMnH(CO)_2CH_3C_5H_4$.



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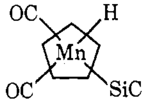

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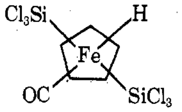

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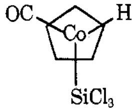

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The photochemical reaction between trichlorosilane and $C_5H_5Co(CO)_2$ does not proceed at 17–20°; however, raising the temperature to 45–50° during irradiation resulted in the formation of $Cl_3SiCoH(CO)C_5H_5$ (**4**) as well as a substantial quantity of $Cl_3SiCo(CO)_4$. It is not understood why, in this case, a higher temperature is required for the reaction to proceed. The cobalt derivative **4** is the least thermally stable and most air sensitive of the compounds mentioned thus far. Such a trend in stability is supported by our inability to isolate $(Cl_3Si)_2NiH(C_5H_5)$ from the reaction of trichlorosilane with $Cl_3SiNi(CO)C_5H_5$.[13]

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(17) When the reaction was repeated by W. J. Jacobs in this laboratory, employing a 450-W Hanovia lamp instead of the 100-W source, $(Cl_3Si)_2Cr(CO)_2C_6H_6$ was obtained. Further studies of this reaction will be reported.

(18) Compound **3** was first prepared by a thermal reaction between trichlorosilane and $[\pi\text{-}C_5H_5Fe(CO)_2]_2$.[14] Full details of this rather complex reaction and the nmr and infrared of **3** have been submitted for publication.

The hydride $Cl_3SiFeH(CO)_4$ is an extremely air-sensitive liquid at room temperature, but in its formation from $Fe(CO)_5$ and Cl_3SiH, very little decomposition is observed even under prolonged ultraviolet irradiation. For high yields of $Cl_3SiFeH(CO)_4$, cooling of the irradiated reaction mixture is essential. Above room temperature a substantial amount of $(Cl_3Si)_2Fe(CO)_4$ is formed as a side product. At $-78°$, $Cl_3SiFeH(CO)_4$ crystallizes from hexane as a white, coarse, crystalline material. Sublimation into a cold trap at $-78°$ yields white transparent needles. The triphenylsilyl analog, $(C_6H_5)_3SiFeH(CO)_4$, is a white crystalline product at room temperature and in its pure state may be handled in air for brief periods without appreciable oxidation.

When the colorless $(C_6H_5)_3SiFeH(CO)_4$ is heated in hexane, the solution turns rapidly dark green, forming $(C_6H_5)_3SiH$, $Fe(CO)_5$, and $Fe_3(CO)_{12}$, as identified by infrared spectroscopy. Bands at 2023 and 2000 cm^{-1} were assigned to $Fe(CO)_5$ and that at 2129 cm^{-1} (b) was assigned to the silicon–hydrogen stretching vibration of $(C_6H_5)_3SiH$. From the solution a dark, crystalline product, $Fe_3(CO)_{12}$, was isolated and identified by bands at 2046, 2023, and 1840 cm^{-1} (w, b).

It is suggested that under slight heating in solution, $(C_6H_5)_3SiFeH(CO)_4$ dissociates into $(C_6H_5)_3SiH$ and $Fe(CO)_4{}^*$. An electronically unsaturated species like $Fe(CO)_4{}^*$ would decompose or react rapidly with some other species in solution. In the absence of replacement ligands such as triphenylphosphine or carbon monoxide, successive insertion of $Fe(CO)_4{}^*$ into the iron–hydrogen or iron–silicon bonds of $(C_6H_5)_3SiFeH(CO)_4$, with the final elimination of $(C_6H_5)_3SiH$, is one possible explanation for the formation of $Fe_3(CO)_{12}$. Other processes may be occurring simultaneously. An infrared study of the reaction of triphenylphosphine with $(C_6H_5)_3SiFeH(CO)_4$ shows that $(C_6H_5)_3SiH$ is readily displaced with formation of $(C_6H_5)_3PFe(CO)_4$. On the other hand, heating of $Cl_3SiFeH(CO)_4$ in hexane under comparable conditions yields no detectable amounts of $Fe_3(CO)_{12}$ but mainly $(Cl_3Si)_2Fe(CO)_4$ and some gray insoluble residue.

It is clear from the last observation that $(C_6H_5)_3SiH$ is eliminated much more readily than Cl_3SiH. A similar trend has been observed in this laboratory for $(C_6H_5)_3SiMnH(CO)_2C_5H_5$ and $Cl_3SiMnH(CO)_2C_5H_5$.[19] It has previously been noted in the case of silyl hydrides of iridium that electronegative substituents such as chlorine or ethoxy groups on the silane result in a more stable product.[4,8]

In an attempt to prepare a more tractable derivative of $Cl_3SiFeH(CO)_4$, the latter was treated with tetrafluoroethylene in the expectation that the tetrafluoroethyl compound would be formed. An extremely rapid reaction occurred at room temperature to form not the expected product, but yellow, crystalline $[Cl_3SiFe(CO)_4]_2$. In the solid state at room temperature, the compound is stable; at 120° under vacuum, it decomposes with the formation of $[Cl_2SiFe(CO)_4]_2$,[13] $Fe(CO)_5$, and $SiCl_4$. The infrared spectrum of a solution in hexane shows some seven carbonyl stretching bands, in addition to bands of $Fe(CO)_5$, which increase rapidly with time. Silylruthenium compounds of the same composition have recently been prepared by a different route.[20] These compounds, specifically $[Cl_3SiRu(CO)_4]_2$, are more stable thermally and in solution than the iron compound. On the basis of their simple three-band carbonyl stretching band pattern, a linear Si–Ru–Ru–Si framework was inferred.[20] The complex band pattern of the iron compound excludes the linear structure as the only isomer present. The iron compound may exist as a radial–radial or radial–axial isomer, or as a mixture of one or both of these with a linear form. The mechanism by which $[Cl_3SiFe(CO)_4]_2$ is formed in this unusual reaction has now been elucidated by Dr. W. Jacobs in this laboratory, and the findings will be submitted shortly.

A reaction long considered characteristic of transition metal hydrides is that with carbon tetrachloride to form the metal chloride and chloroform;[21] in the case of $C_5H_5W(CO)_3H$, this reaction is rapid and exothermic. Although we have not investigated this reaction generally with the silyl(transition metal) hydrides reported here, it is slow with the silylmanganese hydride **2**. Thus, carbon tetrachloride serves as a solvent for infrared study of more concentrated solutions of **2** and its triphenylsilyl analog. The nmr spectrum of $Cl_3SiHMn(CO)_2C_5H_5$ in carbon tetrachloride immediately after preparation shows the cyclopentadienyl and manganese protons at τ 5.1 and 19.8, respectively, but the signals are very broad, showing signs of deterioration. After several hours at room temperature the sample had decomposed completely forming a black residue. The solvent distilled from the decomposed sample showed only one signal at τ 2.80 corresponding to chloroform. The anticipated counter product, $Cl_3SiMnCl(CO)_2C_5H_5$, which would resemble $Cl_3SnCoCl(CO)C_5H_5$,[22] has thus far not been isolated. It has also been observed that $(C_6H_5)_2SiH_2Re_2(CO)_8$ reacts very slowly if at all with carbon tetrachloride.[16]

Infrared Spectra and Structures.—The chromium and manganese compounds **1** and **2** are regarded as distorted square-pyramidal structures, with the benzene or cyclopentadienyl ring in the apical position. This resembles the idealized structure of $C_5H_5M(CO)_2XL$ (where M = Cr, Mo, W; X = H or halogen; L = a phosphine or phosphite), and a similar possibility of cis–trans isomerism results. Previous workers have suggested that the relative intensity of the two carbonyl stretching bands observed in these molecules can be used to distinguish between the two possibilities,[23] although the distinction cannot be regarded as certain in view of the underlying assumptions. In both **1** and **2**, the higher frequency (symmetric) stretching band is slightly

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TABLE I

ANALYTICAL DATA, COLOR, AND MELTING POINTS OF SILYL(TRANSITION METAL) HYDRIDES

Compound	Mp, °C	Color	% calcd C	% calcd H	% calcd Cl	% found C	% found H	% found Cl
$Cl_3SiCrH(CO)_2C_6H_6$[a]	114–115	Yellow	29.88	2.20	...	29.87	2.22	...
$Cl_3SiMnH(CO)_2C_5H_5$	82–83	Pale yellow	26.99	1.94	34.14	26.55	1.81	34.81
$Cl_3SiMnD(CO)_2C_5H_5$	82–83	Pale yellow	26.90	2.25	...	27.56	2.06	...
$(Cl_3Si)_2FeH(CO)C_5H_5$	130–131	Pale yellow	17.21	1.44	50.78	17.27	1.78	50.28
$Cl_3SiCoH(CO)C_5H_5$	31–33	Yellow	25.07	2.10	36.99	26.67	2.03	37.06
$(C_6H_5)_3SiFeH(CO)_4$	85–87	White	61.69	3.77	...	61.69	3.75	...
$(C_6H_5)_3SiMnH(CO)_2C_5H_4CH_3$	95–96	Pale yellow	69.32	5.14	...	69.66	5.15	...

[a] A satisfactory chlorine analysis was not obtained for this compound. The molecular ion was observed mass spectrometrically.

more intense than the lower as expected for a cis isomer. In derivatives of **1** and **2** in which the hydride ligand is replaced by substituents such as Cl_3Si– and Cl_3Sn–, the high-frequency band is weaker, consistent with a trans placement of the bulky ligands.[17,24]

The structure of **3** in the solid state has recently been reported,[25] although the iron-bonded hydrogen was not observed. It was considered that space existed between the two Cl_3Si groups for the hydrogen ligand, and our nmr data on the compound (to be reported later in connection with its preparation by a thermal reaction[14]) support the trans arrangement shown in **3** in solution.

The tetracarbonyl iron derivatives $Cl_3SiFeH(CO)_4$ and $(C_6H_5)_3SiFeH(CO)_4$ show the four-band spectrum (Table II) characteristic of cis-octahedral geometry.[26] When the hydrogen of $Cl_3SiFeH(CO)_4$ is replaced with a trichlorosilyl group, a cis geometry is maintained,[13] in contrast to the chromium and manganese square-pyramidal compounds mentioned above. It is not surprising that $(Cl_3Si)_2Fe(CO)_4$ retains the cis configuration, since a study of $(X_3Ge)_2Fe(CO)_4$ compounds[27] (X = Cl, Br, I) has shown that the cis isomer is the preferred form for X = Cl but that the trans isomer only was obtained for the bulkier X = Br, I ligands.[28] A compound assumed to be *trans*-$(Cl_3Si)_2Fe(CO)_4$ was reported recently by Kahn and Bigorgne as a product (in addition to the cis isomer) from the reaction of $Fe_3(CO)_{12}$ with excess Cl_3SiH at 70°.[29] Carbonyl stretching bands at 2058.0 and 2054.5 cm^{-1} were attributed by these workers to the assumed trans isomer; the appearance of two bands, rather than the single band expected for D_{4h} symmetry, was attributed to an unspecified splitting. On the basis of the spectrum of $Cl_3SiFeH(CO)_4$, which shows bands at 2124 (m), 2069 (m), 2058 (s), and 2053 cm^{-1} (s), it appears to us more likely that the bands earlier attributed to *trans*-$(Cl_3Si)_2Fe(CO)_4$ are in fact the two lower bands of the hydride; the two higher frequency bands of the hydride would be masked by bands of *cis*-$(Cl_3Si)_2Fe(CO)_4$ at 2125 and 2071 cm^{-1}.[13,29] We have observed formation of $Cl_3SiFeH(CO)_4$ in the reaction of Cl_3SiH with $Fe_3(CO)_{12}$ under these mild conditions, but the yield becomes very low at temperatures near 140°.

At higher concentrations (carbon tetrachloride solution, *ca.* 15 mg ml^{-1} in 0.5-mm cells) a band at 1889 cm^{-1} is observed in the infrared spectrum of **2**; the assignment as ν(Mn–H) is confirmed by the shift of this band to 1360 cm^{-1} in the Mn–D analog (prepared from Cl_3SiD). A broad, weak band at 1960 cm^{-1} in **3** is assigned to ν(Fe–H), and this has been confirmed by deuteration.[18]

One interesting phenomenon observed among these compounds is that the carbonyl stretching bands (in hexane solution) of trichlorosilyl derivatives are slightly sharper than those of corresponding triphenylsilyl derivatives. A similar trend is observed among various other compounds such as $Cl_3SiFe(CO)_2C_5H_5$ and $(C_6H_5)_3SiFe(CO)_2C_5H_5$. The origin of this effect is not understood, but it seems possible that it may result from the various conformations possible about the phenyl–silicon bond, in conjunction with conformations about the Fe–Si bond.[13]

Experimental Section

All reactions were carried out in a fume hood, with the reaction mixture at atmospheric pressure. The reaction mixture was open to an oil-filled bubbler. Large-scale reactions (200–250 ml) were carried out in a Pyrex vessel equipped with a water-cooled quartz finger joined to the outer jacket by a 60/50 standard taper joint. A 450-W uv source (Hanovia high-pressure mercury, No. 679A) was placed inside the quartz finger. Reactions on a smaller scale (40–60 ml) were carried out in a quartz vessel equipped with a water-cooled finger and a reflux condenser. This system was irradiated externally with a 100-W uv light source (Hanovia utility lamp, No. 616A) at a distance of approximately 6–8 in. The water cooling in both large and small reactors maintained reaction temperatures below 25°.

Nitrogen was passed through the reaction vessel prior to the addition of the starting materials and the solvent. An inert atmosphere was maintained during the reaction and recovery of products.

Physical properties and analytical results are given in Table I. Melting points were taken on a Kofler hot-stage apparatus. Microanalyses were performed in the microanalytical laboratory of this department.

Infrared spectra were obtained using a Perkin-Elmer 337 spectrometer with scale expansion and calibration as previously described,[12] except for the substitution of a Hewlett-Packard Model 7127A recorder. Varian A-60, 56-60A, or HA-100 instruments were used to record nmr spectra. Infrared and nmr data are given in Table II. Mass spectra were measured using an Associated Electrical Industries MS-9 spectrometer, 70-eV ionizing energy, with direct introduction of solid sample.

Starting materials such as $C_6H_6Cr(CO)_3$, $C_5H_5Mn(CO)_3$, C_5H_5-

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TABLE II

INFRARED CARBONYL STRETCHING BANDS AND PROTON NMR DATA

Compound	Ir bands,[a] ν(CO), cm^{-1}	Nmr data[h]	
		τ(M–H)	τ(C_5H_5)
$Cl_3SiFeH(CO)_4$[b]	2124 m, 2069 m, 2058 s, 2053 s	19.00	
$Cl_3SiCrH(CO)_2C_6H_6$[c]	1982 vs, 1922 s	20.53	4.00
$Cl_3SiMnH(CO)_2C_5H_5$[d]	2028 vs, 1972 s	19.70[i]	4.89
$Cl_3SiMnD(CO)_2C_5H_5$[e,f]	2026 vs, 1973 s	...	...
$(Cl_3Si)_2FeH(CO)C_5H_5$[g]	2025	21.64	4.57
$Cl_3SiCoH(CO)C_5H_5$	2045	23.33[j]	4.87
$(C_6H_5)_3SiFeH(CO)_4$[b]	2097 m, 2036 m, 2026 s, 2018 s	...	...
$(C_6H_5)_3SiMnH(CO)_2C_5H_4CH_3$	1983 vs, 1926 s	21.50[i]	5.70[i,k]

[a] In hexane solution. [b] Shows additional bands due to $Fe(CO)_5$. [c] In dichloromethane. [d] ν(Mn–H) 1889 cm^{-1}. In carbon tetrachloride, ν(Mn–H) is 1887 cm^{-1} and ν(CO) is 2026 (vs) and 1975 cm^{-1} (s). [e] In carbon tetrachloride. [f] ν(Mn–D) in carbon tetrachloride is at 1360 cm^{-1}. [g] ν(Fe–H) 1960 cm^{-1}. [h] In acetonitrile. [i] Broad. [j] In cyclohexane, very broad. [k] Refers to ring protons of $CH_3C_5H_4$ group.

$Co(CO)_2$, and $Fe(CO)_5$ were purchased from Strem Chemicals Inc. or Alfa Inorganics. A sample of $CH_3C_5H_4Mn(CO)_3$ was obtained from the Ethyl Corp., New York, N. Y. Tetrafluoroethylene was purchased from Peninsular ChemResearch Inc., Gainesville, Fla., but is no longer available from this source due to the hazards of compressed tetrafluoroethylene. Deuterated trichlorosilane was synthesized for us by Merck Sharp and Dohme of Canada Ltd., Montreal. Silanes were purchased from Pierce Chemical Co., Rockford, Ill.

Hydridotrichlorosilyl(π-benzene)dicarbonylchromium, $Cl_3SiCrH(CO)_2C_6H_6$.—A sample of 1.04 g of $C_6H_6Cr(CO)_3$ (4.85 mmol) in 10 ml of Cl_3SiH (excess) and 40 ml of hexane was irradiated with a 100-W lamp for 28 hr. The yellow, crystalline product precipitated during irradiation and showed no noticeable decomposition. The solvent and excess Cl_3SiH were decanted and unreacted $C_6H_6Cr(CO)_3$ was sublimed off at 65° (0.01 mm). The residue of lower volatility was dissolved in a minimum amount of dichloromethane and filtered under nitrogen. Hexane was slowly added to the clear, yellow filtrate until the solution became turbid. This was slowly cooled to $-78°$, precipitating a fine yellow crystalline product. An additional recrystallization afforded the analytically pure sample in high yield (*ca.* 90%). A weak set of peaks due to the molecular ion was observed in the mass spectrum at source temperatures above 90°.

Hydridotrichlorosilyl(π-cyclopentadienyl)dicarbonylmanganese, $Cl_3SiMnH(CO)_2C_5H_5$.—A mixture of 1.01 g of $C_5H_5Mn(CO)_3$ (4.95 mmol) and 70 ml of Cl_3SiH (excess) in 50 ml of hexane was irradiated for 9 hr. Considerable decomposition was noted. The volume of the reaction mixture was reduced to 20 ml under vacuum. The remaining solution was filtered hot and the clear yellow filtrate was cooled to $-78°$, precipitating a yellow, microcrystalline material. This was isolated and unreacted $C_5H_5Mn(CO)_3$ was sublimed off at 25° (0.01 mm). The temperature was then raised to 60° and the sublimation continued, depositing pale yellow, crystalline product (0.324 g, 1.05 mmol, 21% based on $C_5H_5Mn(CO)_3$ employed). This was recrystallized from a minimum amount of hot hexane. For the synthesis of the deuteride **$Cl_3SiMnD(CO)_2C_5H_5$** a similar procedure was employed.

Hydridotriphenylsilyl(π-methylcyclopentadienyl)dicarbonylmanganese, $(C_6H_5)_3SiMnH(CO)_2C_5H_4CH_3$.—A mixture of 20 ml of $CH_3C_5H_4Mn(CO)_3$ (0.128 mol) and 21 g of $(C_6H_5)_3SiH$ (0.081 mol) in 180 ml of heptane was irradiated for 10 hr. The progress of the reaction was followed by the carbon monoxide evolution, which had virtually stopped at the end of the reaction. The reaction mixture was filtered under nitrogen and the clear yellow filtrate was allowed to cool slowly in the refrigerator. Pale yellow crystals precipitated in good yield. A small fraction was recrystallized from hexane as the analytical sample.

Hydridobis(trichlorosilyl)π-cyclopentadienylcarbonyliron, $(Cl_3Si)_2FeH(CO)C_5H_5$.—A sample of 0.65 g of $Cl_3SiFe(CO)_2C_5H_5$[13] (2.09 mmol) in a solution of 6.0 ml of Cl_3SiH (excess) and 45 ml of hexane was irradiated for 4 hr. Dark deposits on the wall of the reaction vessel indicated substantial decomposition. At reduced pressure, the volume of the reaction mixture was reduced to 30 ml. The remaining solution was filtered warm and the clear yellow filtrate was cooled to $-78°$, precipitating a yellow microcrystalline material. This was isolated and sublimed at 25° (0.01 mm) to remove unreacted $Cl_3SiFe(CO)_2C_5H_5$. The temperature was then raised to 65° and sublimation continued. The yield (0.32 g, 0.76 mmol) was 37% based on $Cl_3SiFe(CO)_2C_5H_5$ employed. This complex was recrystallized from hexane.

Hydridotrichlorosilyl-π-cyclopentadienylcarbonylcobalt, $Cl_3SiCoH(CO)C_5H_5$.—A mixture of 2.0 ml of $C_5H_5Co(CO)_2$ (2.8 g, 15.5 mmol) and 7.0 ml of Cl_3SiH (excess) in 50 ml of hexane was irradiated without cooling so that the temperature of the reaction mixture rose to 40–50°. After 3 hr, all of the $C_5H_5Co(CO)_2$ was consumed. The infrared spectrum showed bands at 2117, 2062, 2045, and 2037 cm^{-1}. (Reported values for $Cl_3SiCo(CO)_4$ are at 2117, 2062, and 2037 cm^{-1}.[30]) The reaction mixture was filtered and the clear, yellow filtrate was cooled to $-78°$, which crystallized a yellow material of crude, oily appearance. The cold solution was decanted. The yellow, oily material was sublimed at 25° (0.01 mm) depositing the coarse, yellow, crystalline product in low yield (*ca.* 10%). The complex was resublimed twice. In the impure state it was extremely air sensitive.

Hydridotrichlorosilyltetracarbonyliron, $Cl_3SiFeH(CO)_4$.—A solution of 15 ml of $Fe(CO)_5$ (22 g, 0.11 mol), 20 ml of Cl_3SiH (27 g, 0.20 mol), and 180 ml of heptane was irradiated for 24 hr. The mixture was then transferred to a 500-ml flask and reduced in volume to 120–150 ml at reduced pressure, eliminating almost all unreacted Cl_3SiH. The remaining solution was filtered under nitrogen pressure through a 10–20-μ glass sinter. The clear yellow filtrate was cooled to $-78°$, resulting in the crystallization of a white product. The cold solvent was decanted and the vessel was refilled with 100 ml of pentane. The clear solution was again cooled to $-78°$, to crystallize a white material. This recrystallization process in pentane was repeated three or four times. The cold solution was decanted and the remaining pentane was removed at reduced pressure, leaving a viscous, pale yellow, oily product, $Cl_3SiFeH(CO)_4$, at room temperature. The product (26.0 g, 0.086 mol, 78% based on $Fe(CO)_5$ employed) at this stage was sufficiently pure for further reactions. For higher purity, slow sublimation into a $-78°$ trap under high vacuum yielded white, needle-shaped crystals. The compound was extremely air sensitive and was not analyzed. Moderately air-stable derivatives of this hydride have since been synthesized and characterized.[24]

Hydridotriphenylsilyltetracarbonyliron, $(C_6H_5)_3SiFeH(CO)_4$.—A mixture of 15 ml of $Fe(CO)_5$ (22 g, 0.11 mol) and 25.5 g of $(C_6H_5)_3SiH$ (0.098 mol) in 180 ml of heptane was irradiated for 22 hr. Initially the carbon monoxide evolution was rapid (*i.e.*, one bubble/sec) but at the end of the reaction time it had virtually stopped. A small amount of decomposition was observed. The reaction mixture was filtered and the clear, pale yellow solution was slowly cooled in the refrigerator. A massive amount of white coarse crystalline material formed in good yield (>70%).

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The analytical sample was recrystallized from pentane. When this hydride was heated in solution, it decomposed rapidly and the solution turned dark green.

Bis(trichlorosilylirontetracarbonyl), $[Cl_3SiFe(CO)_4]_2$.—A sample of 2–3 g of $Cl_3SiFeH(CO)_4$ was slowly sublimed under high vacuum into a 60–70 ml Carius tube equipped with a Teflon valve. Pentane (5.0 ml) and tetrafluoroethylene (1.2 l. at STP) were introduced at liquid nitrogen temperature. The reaction mixture was then warmed slowly to room temperature. Gentle agitation of the tube immediately precipitated a coarse, bright yellow, crystalline material. (During this process the Carius tube was kept behind a protective shield. Tetrafluoroethylene under pressure is potentially dangerous.) The excess tetrafluoroethylene and pentane were removed at reduced pressure. The remaining product, $[Cl_3SiFe(CO)_4]_2$, is pure as formed and decomposes above 90°. The infrared spectrum was complicated by the rapid decomposition of the complex in solution. The bands observed immediately after preparing a hexane solution were 2114 (w), 2079 (w), 2070 (m), 2061 (m), 2053 (s), 2049 (vs), 2037 (w), and 2011 cm^{-1} (w); additional weak bands of $Fe(CO)_5$ at 2023 and 2000 cm^{-1} were observed even in the fresh sample and increased rapidly with time.

Thermal Decomposition of $[Cl_3SiFe(CO)_4]_2$.—A sample of 0.20 g of $[Cl_3SiFe(CO)_4]_2$ (0.33 mmol) was placed in a 25-ml Carius tube equipped with a Teflon valve. The tube was evacuated and then slowly heated. At 120–130°, the compound melted to an orange-brown semisolid, which resolidified at this temperature, in approximately 10 min, to a powdery yellow solid, $[Cl_2SiFe(CO)_4]_2$, which was identified by infrared spectroscopy;[13] this reaction proceeded in high yield. The mass spectrum of the gaseous reaction products contained the ions $SiCl_4^+$ and $Fe(CO)_5^+$ as well as their fragments.

Acknowledgment.—We thank the National Research Council of Canada for financial support and for a bursary to W. J.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY 08540

Raman Spectra and Metal–Metal Bonds. Force Constants and Bond Polarizability Derivatives for Hexamethyldisilicon, -germanium, -tin, and -lead[1]

BY BERNARDO FONTAL AND THOMAS G. SPIRO*

Received July 20, 1970

Raman and infrared frequencies below 700 cm^{-1} are assigned to the various skeleton modes of the hexamethyldimetal derivatives of silicon, germanium, tin, and lead. A staggered, D_{3d}, configuration is clearly indicated for $(CH_3)_6Ge_2$, while for the remaining molecules the evidence with regard to selection rules is not clear-cut. Approximate normal-coordinate analyses were carried out to obtain a consistent set of skeletal force constants for the molecules. The eigenvectors from the analyses were used to calculate bond polarizability derivatives from the absolute Raman intensities of the A_1 skeletal modes. These in turn were used to calculate bond orders, $n/2$, *via* Long and Plane's δ function model equation. While lower by a factor of 3 than the expected value of unity, the $n/2$ values for the metal–metal bonds are fairly constant despite substantial changes in the force constants. Furthermore the previously determined $n/2$ values for Hg_2^{2+} and $Re_2(CO)_{10}$ fall in the same range, with only $Mn_2(CO)_{10}$ having an exceptional (high) value. It appears that a value of $n/2 = 0.3$–0.4 may be characteristic of single homonuclear metal–metal bonds

Introduction

A recent paper[2] from this laboratory reported absolute Raman intensities and metal–metal bond polarizability derivatives for the molecules $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ and for the aquo Hg_2^{2+} ion, as well as for the bridged complexes $Bi_6(OH)_{12}^{6+}$, $Pb_4(OH)_4^{4+}$, and $Tl_4(OC_2H_5)_4$. The major conclusion was that weak metal–metal interaction in the bridged species could be readily distinguished from the genuine bonds present in the nonbridged species. For this purpose Raman intensities, interpreted with the aid of Long and Plane's semiempirical equation connecting bond polarizability derivatives with bond orders,[3] are much more useful than are vibrational frequencies and the force constants determined from them. These considerations were confirmed and extended in a study of the bridged species $[(CH_3)_3PtX]_4$, where X = OH, Cl, and I.[4] On the other hand the situation with regard to the three reference unbridged molecules was not quantitatively satisfactory, with $Mn_2(CO)_{10}$ giving, inexplicably, a substantially higher estimated metal–metal bond order than either $Re_2(CO)_{10}$ or Hg_2^{2+}, though still lower than the expected value of unity.

It seemed worthwhile examining a broader range of metal–metal bonds, and we report here a Raman and infrared study of the molecules $(CH_3)_6M_2$, where M = Si, Ge, Sn, and Pb. While spectra for all of these species have been reported before[5] and some simple valence force constant calculations have been carried

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* To whom correspondence should be addressed.

(1) This investigation was supported by Public Health Service Grant GM-13498 from the National Institute of General Medical Sciences and by National Science Foundation Grant GP-10122.

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