Volume 10
Number 1
January 1971

Inorganic Chemistry

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada

Organometallic Compounds with Metal–Metal Bonds. XVI.[1] The Preparation of Some Silicon, Germanium, and Tin Derivatives of Cyclopentadienyldicarbonylrhodium

By A. J. OLIVER and W. A. G. GRAHAM*

Received June 16, 1970

Triphenyl- and tribenzylsilane react with $C_5H_5Rh(CO)_2$ to yield $C_5H_5CORh(H)SiR_3$ whereas only a bis-silyl derivative, $C_5H_5CORh(SiCl_3)_2$, may be isolated from the reaction with trichlorosilane. Compounds of the type $C_5H_5COXRhMX_3$ (M = Ge, Sn; X = Cl, Br, I) are formed in the reaction of $C_5H_5Rh(CO)_2$ with the halides of germanium(IV) and tin(IV), while tin(II) chloride and bromide afford oligomeric and polymeric species.

Introduction

Many compounds containing metal–metal or metalloid–metal bonds have been prepared by oxidative addition reactions, *e.g.*

$$[(C_6H_5)_3P]_2Ir(CO)Cl + Cl_3SiH \longrightarrow [(C_6H_5)_3P]_2Ir(H)Cl(CO)SiCl_3{}^{2}$$

$$C_5H_5Co(CO)_2 + GeX_4 \longrightarrow C_5H_5COXCoGeX_3 + CO^{3}$$

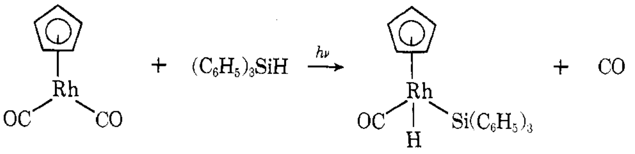
The more specific term, oxidative elimination, seems preferable for the latter reaction in order to express the loss of the neutral ligand carbon monoxide.

Few oxidative elimination reactions have been carried out on cyclopentadienyldicarbonylrhodium; those reported involve iodine[4] and perfluoroalkyl iodides.[5] Other oxidative reactions are known for phosphine-substituted cyclopentadienylrhodium carbonyls.[6,7]

Such methods could be expected to yield numerous group IV metal derivatives of cyclopentadienyldicarbonylrhodium and this has been verified by the findings reported here. We report here the first germanium–rhodium bonds, although silicon–rhodium bonds have been described recently,[8–10] and tin–rhodium bonds have been known for some years.[11–16]

Results and Discussion

Irradiation of $C_5H_5Rh(CO)_2$ in nonpolar solvents has been reported to yield $Cp_2Rh_2(CO)_3$[17] and $Cp_3Rh_3(CO)_3$,[18,19] probably *via* elimination of carbon monoxide and formation of the reactive intermediate "C_5H_5RhCO." The presence of silane, however, appears to inhibit the formation of oligomers as shown by the absence of bridging carbonyl bands in the infrared spectra of the reaction mixtures. The only isolable products were $C_5H_5CORh(H)SiR_3$ [R = C_6H_5 or $CH_2C_6H_5$). This is rationalized in terms of a preferential



reaction of "C_5H_5RhCO" with the silane rather than with another molecule of rhodium compound.

Although there was infrared evidence for the formation of similar products from trimethylsilane and triethylsilane, the compounds could not be isolated. This difficulty arises from the fact that the alkylsilane products did not crystallize readily or survive a lengthy

---

* To whom correspondence should be addressed.

[1] Part XV: D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **7**, 771 (1968).

[2] A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, **87**, 16 (1965).

[3] R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 523 (1968).

[4] R. B. King, *ibid.*, **5**, 82 (1966).

[5] J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 4200 (1964).

[6] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, **9**, 243 (1970).

[7] A. J. Hart-Davis and W. A. G. Graham, *idid.*, **9**, 2658 (1970).

[8] R. N. Haszeldine, R. V. Parish, and D. J. Parry, *J. Organometal. Chem.*, **9**, 13 (1967).

[9] R. N. Haszeldine, R. V. Parish, and D. J. Parry, *J. Chem. Soc. A*, 683 (1969).

[10] F. de Charentenay, J. A. Osborn, and G. Wilkinson, *ibid.*, *A*, 787 (1968).

[11] A. G. Davies, G. Wilkinson, and J. F. Young, *J. Amer. Chem. Soc.*, **85**, 1642 (1963).

[12] J. F. Young, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 5176 (1964).

[13] D. M. Adams and P. J. Chandler, *Chem. Ind.* (*London*), 269 (1965).

[14] J. P. Collman, F. D. Vastine, and W. R. Roper, *J. Amer. Chem. Soc.*, **88**, 5035 (1966).

[15] D. F. Shriver and M. P. Johnson, *Inorg. Chem.*, **6**, 1265 (1967).

[16] J. V. Kingston, *Inorg. Nucl. Chem. Lett.*, **4**, 65 (1968).

[17] O. S. Mills and J. P. Nice, *J. Organometal. Chem.*, **10**, 337 (1967).

[18] O. S. Mills and E. F. Paulus, *Chem. Commun.*, 815 (1966).

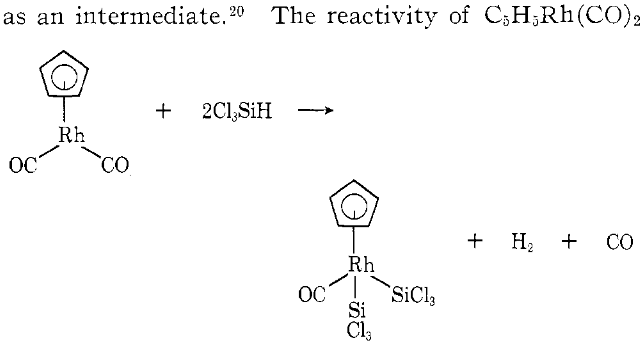
[19] E. F. Paulus, E. O. Fischer, H. P. Fritz, and H. Schuster-Woldan, *J. Organometal. Chem.*, **10**, 3 (1967).

work-up. Owing to decomposition both in the reaction mixture and during the work-up, only low yields (*ca.* 10%) of the triphenylsilyl and tribenzylsilyl derivatives could be obtained. As solids, these compounds showed signs of decomposition over a period of a few days at room temperature although they seem stable at $-15°$. In solution they are considerably less stable, particularly if polar solvents are used. Silyl hydrides of a number of metals have been prepared from various metal carbonyl derivatives by similar irradiation procedures.[20,21]

An ^1H nmr spectrum of $C_5H_5CORh(H)Si(C_6H_5)_3$ was measured in carbon tetrachloride solution; this solvent was chosen in preference to chloroform, dichloromethane, or acetone since the compound appears to decompose more rapidly in the latter solvents. The use of carbon tetrachloride as solvent emphasizes the contrast in properties with more common hydrides, which react rapidly to form chloroform and the metal chloride. Typical resonances were observed for phenyl and cyclopentadienyl protons; the most intense peak of the phenyl system was observed at τ 2.72 while the cyclopentadienyl resonance was observed as a triplet ($J = 0.5$ cps) at τ 4.77. The cyclopentadienyl protons might be expected to couple to ^{103}Rh (100% abundance, spin $^1/_2$) and to the unique proton.[22,23] Since a triplet is observed it must be concluded that the couplings to these two nuclei of spin $^1/_2$ are equal in magnitude.

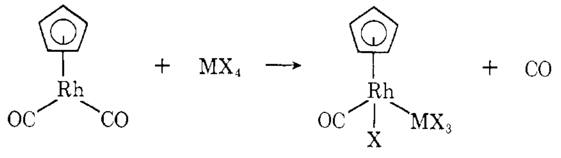
The hydrogen directly bonded to rhodium can be anticipated to couple to the metal,[22,24] and thus a doublet ($J = 31.8$ cps) was observed at τ 21.1. The peaks were broad (width 3 cps), presumably because of coupling to the five cyclopentadienyl protons, mentioned above. It is of interest that this high-field resonance is found at a chemical shift close to those observed for the hydridic protons in $C_5H_5Mn(CO)_2(H)Si(C_6H_5)_3$ (τ 21.7)[21] and $C_5H_5Re(CO)_2(H)Si(C_6H_5)_3$ (τ 19.1).[21]

Trichlorosilane and methyldichlorosilane undergo very facile reactions with $C_5H_5Rh(CO)_2$ to afford bissilyl derivatives, presumably *via* a silyl hydride species as an intermediate.[20] The reactivity of $C_5H_5Rh(CO)_2$ is appreciably greater than that of $C_5H_5Co(CO)_2$; the cobalt derivative reacts with trichlorosilane only with the assistance of ultraviolet light to give $C_5H_5COCo(H)SiCl_3$[20] or upon heating to 100° to give $C_5H_5COCo(SiCl_3)_2$.[25] This appears to be another example of the enhanced reactivity of metal carbonyl derivatives of the second transition series, analogous to the fairly well-known reactivity of $Mo(CO)_6$ relative to $Cr(CO)_6$.



The compound $C_5H_5CORh(SiCl_2CH_3)_2$ exhibited an ^1H nmr spectrum in $CDCl_3$ solution consistent with the proposed structure. One resonance which appeared as a sharp doublet at τ 4.33 can be assigned to the cyclopentadienyl ring. A second doublet at τ 8.73 could be attributed to two methyl groups attached to silicon, particularly as this resonance integrated with the cyclopentadienyl resonance in the ratio of 6:5. The doublet structures can be ascribed to coupling with rhodium, and for both doublets J(Rh–H) = 0.8 cps. The compounds $C_5H_5CORh(SiCl_3)_2$ and $C_5H_5COIRhSnI_3$ (see below) show cyclopentadienyl resonances at τ 4.21 and 4.00, respectively, although the expected doublet structures could not be resolved.

Products of the type $C_5H_5COXRhMX_3$ (M = Ge or Sn and X = Cl, Br, or I) are formed under moderate conditions by the treatment of $C_5H_5Rh(CO)_2$ with the tetrahalides of germanium and tin. This is to be expected by analogy with the reactions of $C_5H_5Co(CO)_2$.[3] However, although compounds of the type $C_5H_5COCo(MX_3)_2$ could be isolated when an excess of halide and temperatures up to 110° were employed, only the compounds $C_5H_5COXRhMX_3$ formed under similar reaction conditions. The inability to form $C_5H_5CORh(MX_3)_2$ is rather surprising, not only because the cobalt analogs can be prepared but because of the existence of the isoelectronic compounds $C_5H_5CORh(SiCl_3)_2$ and $C_6H_6CORu(GeCl_3)_2$.[26] It seems reasonable that this is a kinetic rather than a thermodynamic effect, possibly attributable to a strong Rh–X bond which might inhibit the insertion of MX_2.[3]



In preparing the derivatives $C_5H_5COXRhMX_3$, difficulty was experienced in two cases. Germanium tetraiodide gives a moderate yield of $C_5H_5CORhI_2$ which cannot easily be separated from the required product. This problem was overcome by using the method of halogen exchange on $C_5H_5COClRhGeCl_3$. Tin tetrachloride in toluene or pentane reacts with $C_5H_5Rh(CO)_2$ to form a highly air-sensitive, orange-yellow powder which decomposes in air to give the required product. A similar intermediate is obtained with tin tetrabromide when pentane is used as solvent. Presumably these intermediates are adducts between the Lewis base, $C_5H_5Rh(CO)_2$, and the Lewis acids, SnX_4, similar to adducts such as $C_5H_5Rh(CO)_2 \cdot HgCl_2$.[27]

---

(20) W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 3375 (1969); *Inorg. Chem.*, **10**, 4 (1971).

(21) J. K. Hoyano and W. A. G. Graham, *J. Amer. Chem. Soc.*, in press.

(22) M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, **7**, 115 (1965).

(23) E. O. Fischer and M. W. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **6**, 93 (1967).

(24) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(25) W. Jetz, Ph.D. Thesis, University of Alberta, 1970.

(26) R. K. Pomeroy and W. A. G. Graham, to be submitted for publication.

(27) J. L. Dawes and R. D. W. Kemmitt, *J. Chem. Soc. A*, 1072 (1968).

TABLE I

ANALYTICAL DATA

	% calcd				% found			
	C	H	O	X	C	H	O	X
$C_5H_5CORh(H)Si(C_6H_5)_3$[a]	63.19	4.64	. . .	. . .	63.44	4.47	. . .	. . .
$C_5H_5CORh(H)Si(CH_2C_6H_5)_3$[b]	65.05	5.49	. . .	. . .	65.28	5.39	. . .	. . .
$C_5H_5CORh(SiCl_3)_2$	15.50	1.08	. . .	45.76	15.64	0.92	. . .	45.54
$C_5H_5CORh(SiCl_2CH_3)_2$	22.66	2.62	. . .	. . .	22.81	2.66	. . .	. . .
$C_5H_5COClRhGeCl_3$	17.56	1.23	3.90	34.55	17.70	1.23	4.02	34.38
$C_5H_5COBrRhGeBr_3$	12.25	0.86	2.72	54.33	12.30	0.89	2.55	54.45
$C_5H_5COIRhGeI_3$	9.28	0.65	2.10	65.35	9.28	0.65	2.06	65.39
$C_5H_5COClRhSnCl_3$	15.79	1.10	. . .	31.06	15.92	1.61	. . .	31.32
$C_5H_5COBrRhSnBr_3$	11.36	0.79	2.52	50.39	11.54	0.83	2.62	50.38
$C_5H_5COIRhSnI_3$	8.76	0.61	1.95	61.73	8.91	0.58	2.08	61.68
$C_5H_5COIRhSnI_2CH_3$	11.83	1.14	2.25	53.39	11.99	1.47	2.42	53.59
$[C_5H_5CORhSnCl_2 \cdot {}^1/_3C_2H_4Cl_2]_x$[c]	19.13	1.55	. . .	22.59	19.17	1.11	. . .	22.78
$[C_5H_5CORhSnCl_2 \cdot {}^1/_3C_6H_5CH_3]_x$[c]	24.04	1.86	3.84	17.03	23.93	1.72	4.76	16.44
$[C_5H_5CORhSnBr_2 \cdot {}^1/_3C_6H_5CH_3]_x$[c]	19.81	1.53	3.17	31.61	19.78	1.61	3.95	30.61
$[C_5H_5CORhSnCl_2]_n$	18.69	1.31	4.15	18.39	18.51	1.76	4.23	18.35

[a] Confirmed by exact mass measurement on the ion $C_5H_5Rh(H)Si(C_6H_5)_3^+$: calcd, 428.0467; found, 428.0469. Parent ion was of very low intensity. [b] Confirmed by exact mass measurement on the parent ion $C_5H_5CORh(H)Si(CH_2C_6H_5)_3^+$: calcd, 498.0885; found, 498.0885. [c] Compounds assumed to be trimers ($x = 3$); see Discussion.

Oligomeric compounds formed on reaction of $C_5H_5Rh(CO)_2$ with stannous halides but were difficult to characterize fully. Owing to their high mass and relative insolubility they are unsuitable for molecular weight determination, nmr, or mass spectrometry. From the elemental analyses the derivatives were assigned the formula $(C_5H_5CORhSnX_2 \cdot {}^1/_3(\text{solvent}))_x$ (see Table I); however, the value of x is uncertain. A value of x equal to 3 seems most reasonable, for in the compound $(C_5H_5COCoSnCl_2 \cdot {}^1/_3C_6H_6)_x$, x was again considered to be 3[28] and the compound $(C_5H_5CORhSnCl_2)_3$ could be expected to result from stannous chloride insertion into the known trimer $(C_5H_5RhCO)_3$.[18,19] We consider it likely that these compounds contain six-membered rings with alternating tin and rhodium atoms.

Infrared Spectra.—Most of the compounds show one carbonyl stretching vibration (Table II) as expected for monocarbonyl molecules. However, the compounds $C_5H_5CORh(H)Si(CH_2C_6H_5)_3$, $C_5H_5CORh(SiCl_2CH_3)_2$, and $C_5H_5COIRhSnI_2CH_3$ show extra bands in cyclohexane solution. Such effects, which may be attributed to the asymmetry of the substituents on rhodium, have already been well documented and explained as due to conformers.[3,29] The tribenzylsilane derivative is worthy of particular note, since the silicon carries three chemically identical substituents. These substituents will in general assume conformations such that threefold symmetry about the silicon is lacking. Rotation about the silicon–rhodium bond will then produce different conformations, as in previously known cases.

The proposed trimeric species each exhibit two carbonyl stretching bands which are at almost the same frequencies in each case. The appearance of two bands is most probably due to coupling of the vibrations of the single carbonyl groups on each rhodium, although a splitting of conformational origin cannot be excluded.

TABLE II

PHYSICAL PROPERTIES AND CARBONYL STRETCHING FREQUENCIES

Compound[a]	Color	% yield	ν_{CO},[b] cm^{-1}
$C_5H_5CORh(H)Si(C_6H_5)_3$[c]	Off-white	11	2024[d]
$C_5H_5CORh(H)Si(CH_2C_6H_5)_3$[e]	Off-white	10	2023 m, 2020 w, sh, 2008 s[d]
$C_5H_5CORh(SiCl_3)_2$[f]	Colorless	61	2073[d]
$C_5H_5CORh(SiCl_2CH_3)_2$[g]	Colorless	55	2050 s, 2037 m[d]
$C_5H_5COClRhGeCl_3$	Orange	51	2098
$C_5H_5COBrRhGeBr_3$	Red	82	2092
$C_5H_5COIRhGeI_3$	Black	42	2080
$C_5H_5COClRhSnCl_3$	Orange-red	35	2093
$C_5H_5COBrRhSnBr_3$	Red	89	2087
$C_5H_5COIRhSnI_3$	Black	71	2074
$C_5H_5COIRhSnI_2CH_3$	Black	77	2060 2067 m, 2061 s[d]
$[C_5H_5CORhSnCl_2 \cdot {}^1/_3C_2H_4Cl_2]_x$	Orange	58	2050 s, 2034 m
$[C_5H_5CORhSnCl_2 \cdot {}^1/_3C_6H_5CH_3]_x$	Orange	25	2052 s, 2035 m
$[C_5H_5CORhSnBr_2 \cdot {}^1/_3C_6H_5CH_3]_x$	Orange-red	14	2051 s, 2033 m
$[C_5H_5CORhSnCl_2]_n$	Orange	82	2058 m, 2034 s[h]

[a] Decomposition temperatures around 200° and poorly defined (over 10–40° range) except as noted. [b] Dichloromethane solution except as noted. [c] Dec pt 95–100°. [d] Cyclohexane solution. [e] Dec pt 64–66°. [f] Dec pt 120–125°. [g] Dec pt 110–115°. [h] Nujol mull.

Reactions of dichloromethane solutions of $(C_5H_5CORhSnCl_2 \cdot {}^1/_3C_2H_4Cl_2)_x$ or $(C_5H_5CORhSnCl_2 \cdot {}^1/_3C_6H_5CH_3)_x$ or a suspension of $(C_5H_5CORhSnCl_2)_n$ in dichloromethane with chlorine gas give solutions which show only one carbonyl stretching vibration at 2093 cm^{-1}. Thus the product in each case may be assumed to be $C_5H_5COClRhSnCl_3$ (ν_{CO} 2093 cm^{-1}) and this verifies the similarity of the starting materials.

Experimental Section

All reactions were carried out under a nitrogen atmosphere, mainly by the use of Schlenk-tube techniques. Pentane, hexane, benzene, and toluene were dried over sodium or 9.5% sodium–lead alloy. Published procedures were used for the preparation of GeI_4,[30] $SnBr_4$,[30] SnI_4,[30] CH_3SnI_3,[31] and $C_5H_5Rh(CO)_2$.[6,32] Other reagents and solvents were available commercially and were used without further purification.

---

(28) R. Kummer and W. A. G. Graham, unpublished work; see also M. J. Bennett, W. Brooks, M. Elder, W. A. G. Graham, D. Hall, and R. Kummer, *J. Amer. Chem. Soc.*, **92**, 208 (1970).

(29) W. Jetz and W. A. G. Graham, *ibid.*, **89**, 2773 (1967).

(30) G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry," Vol. 1, 2nd ed, Academic Press, New York, N. Y., 1963.

(31) P. Pfeiffer and R. Lehnardt, *Chem. Ber.*, **36**, 1054 (1903).

(32) E. O. Fischer and K. Bittler, *Z. Naturforsch. B*, **16**, 225, 835 (1961).

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]

---

* 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).