TABLE III

INTERATOMIC DISTANCES AND BOND ANGLES IN $2AgNO_3 \cdot C_7H_8$

	Distance, A	s^a, A		Angle, Deg	s, Deg
$Ag–C_4$	2.41	0.04	$O_2–Ag–C_4$	122.4	1.3
$Ag–C_5$	2.31	0.05	$C_4–Ag–C_5$	34.1	0.6
$Ag–O_2$	2.27	0.04	$C_6–Ag–O_3$	122.1	2.4
$Ag–O_3$	2.34	0.04	$O_3–Ag–O_2$	84.6	0.6
$Ag–O_3'$	2.70	0.04	$O_1–N–O_2$	122.9	3.1
$C_1–C_2$	1.52	0.17	$O_2–N–O_3$	125.8	2.2
$C_1–C_3$	1.57	0.22	$O_3–N–O_1$	109.2	2.8
$C_2–C_5$	1.47	0.08	$Ag–O_2–N$	117.8	2.1
$C_3–C_4$	1.57	0.11	$Ag–O_3–N$	115.6	2.9
$C_4–C_5$	1.39	0.05	$C_2–C_1–C_3$	97.2	7.8
$N–O_1$	1.33	0.04	$C_1–C_3–C_4$	103.3	8.1
$N–O_2$	1.19	0.05	$C_1–C_2–C_5$	90.4	5.2
$N–O_3$	1.24	0.05	$C_3–C_4–C_5$	92.6	4.2
			$C_2–C_5–C_4$	123.4	4.6

Comparable Distances in $COT \cdot AgNO_3$[2]

Ag–C	2.46, 2.51 A	O–Ag–O	80°
Ag–O	2.36, 2.43 A	O–Ag–C	123.2°, 124.4°
		C–Ag–C	31.8°

[a] s = estimated standard deviation.

planar. Each double bond in the norbornadiene molecule is coordinated to an Ag atom, and thus the norbornadiene molecule serves as a cross-link between two $Ag–NO_3$ chains.

The occurrence of the $Ag–NO_3$ chains and the coordination of the olefin to the chain is very similar to that observed in the cyclooctatetraene–silver nitrate complex. A list of bond distances and angles in the $NBD \cdot 2AgNO_3$ complex and a comparison to the comparable values in the $COT \cdot AgNO_3$ complex are given in Table III. Owing to the small contribution of the light atoms to the total structure factor in the $NBD \cdot 2AgNO_3$ complex, the errors in the interatomic distances are large, and no significant statements concerning them can be made. The general configuration of the complex can be considered reliable however.

Acknowledgment.—This work has been supported by Grant No. DA-ARO(D)-31-124-G26 of the Army Research Office (Durham) and Grant No. AF-AFOSR-763-65 of the Air Force Office of Scientific Research.

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

Organometallic Compounds with Metal–Metal Bonds. I. Tricarbonyl-π-cyclopentadienylchromium, -molybdenum, and -tungsten Bonded to Methyl and Phenyl Derivatives of Germanium, Tin, and Lead[1]

BY H. R. H. PATIL AND W. A. G. GRAHAM

Received May 9, 1966

By reaction of the anions $[\pi\text{-}C_5H_5(CO)_3M]^-$ (M = Cr, Mo, W) with halides $R_3M'X$ (M' = Ge, Sn, Pb; R = CH_3, C_6H_5), 12 compounds $\pi\text{-}C_5H_5(CO)_3M–M'R_3$ have been prepared. General stability increases markedly from Cr to W. From R_2SnCl_2, $R_2Sn[Mo(CO)_3C_5H_5]_2$ is obtained. Carbonyl-stretching frequencies and nmr spectra are reported and discussed. Proton–tin coupling constants in the methyltin derivatives are smaller than in tetramethyltin, which is taken to indicate enhanced s character in the hybrid tin orbitals bonding to the transition metal.

Introduction

The possibility of strong covalent bonding between transition metals was not seriously considered prior to 1957. In that year, X-ray crystallographic results revealed the existence of such bonds in the dimers of pentacarbonylmanganese[2] and of tricarbonyl-π-cyclopentadienylmolybdenum.[3] In these compounds, the metal–metal bonds alone, unsupported by bridging carbonyls or other groups, give rise to the dimers. These results stimulated an overdue recognition of the widespread occurrence of covalent metal–metal bonding in inorganic chemistry. The scope of metal–metal bonding, as it is presently known, leads us to expect that more than 30 metals are capable of forming covalent bonds with one another. The number of binary bonding systems is therefore very large, to say nothing of ternary combinations.[4]

The basis for our expectation is the proposition that a metal capable of forming σ-bonded organometallic compounds is also capable of forming covalent bonds to other metals. Indeed, Chatt has previously pointed out that a common factor—the presence of ligands of high ligand field strength—can render a transition metal capable of forming stable σ bonds to hydrocarbon radicals as well as stable metal–metal bonds.[5] It is an object of this and succeeding papers to clarify the relationship which evidently exists between metal–carbon and metal–metal bonding.

In the past 25 years, many compounds have been

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[1] Presented in part at the 48th Canadian Chemical Conference, Montreal, June 1965.

[2] L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).

[3] F. C. Wilson and D. P. Shoemaker, *ibid.*, **27**, 808 (1957).

[4] H. R. H. Patil and W. A. G. Graham, *J. Am. Chem. Soc.*, **87**, 673 (1965), and references cited therein.

[5] J. Chatt, *Proc. Chem. Soc.*, 318 (1962).

reported[6-10] which can now be formulated with some confidence as having main group metals covalently bonded to transition metals. These are altogether too numerous to mention here; most involve a metal of main group IV.[6] One must cite the pioneering investigations of Hieber[7] and of Hein,[8] in which various compounds having organotin or organolead groups in combination with iron tetracarbonyl or cobalt tetracarbonyl moieties were obtained; unfortunately, no spectroscopic data are available for these compounds. Manganese pentacarbonyl derivatives of organotin and organolead groups were prepared by Gorsich,[9] and analogous rhenium pentacarbonyl derivatives have also been reported,[10] although in neither case were the infrared data adequate in terms of the particular requirements of the metal carbonyl field.[11]

It appeared that a useful approach would be the systematic study of series of compounds in which carbon, silicon, germanium, tin, and lead are bonded to a particular transition metal, keeping other ligands constant. One could thus compare trends as metal–carbon bonding progresses through metal–metalloid bonding to metal–metal bonding. We describe in this paper the preparation, properties, and spectra of compounds in which the heavier members of the fourth main group are covalently linked to chromium, molybdenum, and tungsten, with the latter metals in the form of their tricarbonyl-π-cyclopentadienyl complexes.[12] At a late stage of our investigation, we learned that Nesmeyanov and his co-workers[13] had prepared several of the same compounds, with some infrared data obtained on mulls. Methyl and other σ-bonded carbon derivatives of this type have been known for some time,[14] and π-C_5H_5-$(CO)_3Mo$–$SnCl_3$ and its tungsten analog have also been reported.[15]

Experimental Section

Infrared spectra were determined using a Perkin-Elmer Model 421 spectrometer with double-grating interchange. Particular care was used in the measurement of carbonyl-stretching frequencies. This region of the spectrum was measured with a chart speed such that the 2200–1800-cm^{-1} region extended over 13 in. Immediately after each spectrum was taken, the spectrum of gaseous deuterium chloride[16] was superimposed on the same chart paper; the calibrating peaks were spaced about 12 cm^{-1} apart, and carbonyl bands were determined by interpolation. For calibration near and below 1900 cm^{-1}, deuterium bromide was used.[16] Spectra reproduced as Figures 1 and 2 were recorded using a Perkin-Elmer 337 (grating) Infracord with scale expansion on an external recorder and calibration using bands of gaseous carbon monoxide.[16]

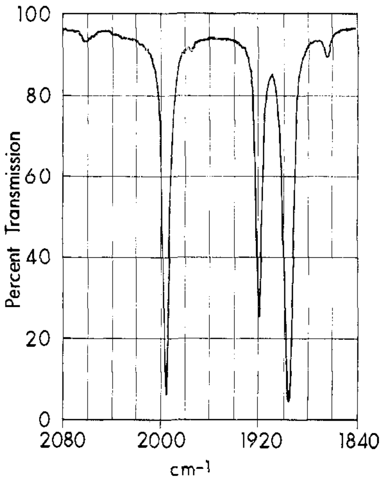

Figure 1.—Carbonyl-stretching region of infrared spectrum of $(CH_3)_3Sn$–$W(CO)_3C_5H_5$; about 1 mg/ml of cyclohexane solution, 0.5-mm cells.

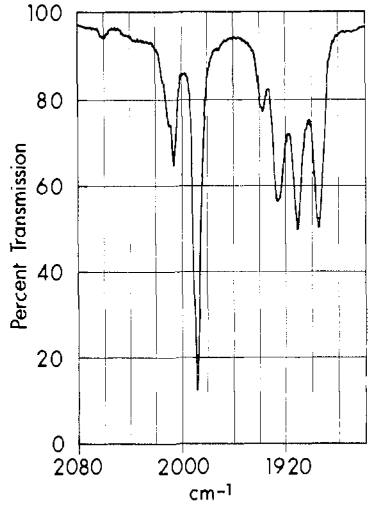

Figure 2.—Carbonyl-stretching region of infrared spectrum of $(CH_3)_2Sn[Mo(CO)_3C_5H_5]_2$; about 1 mg/ml of cyclohexane solution, 0.5-mm cells.

Proton magnetic resonance spectra were obtained with a Varian Model A-60 spectrometer. A Varian Model HR-100 instrument was used to measure coupling constants in the methyltin and methyllead derivatives; line positions were measured using a precision audiooscillator monitored by a frequency counter. Ultraviolet spectra were determined using a Cary Model 14M spectrometer.

All reactions were carried out under a nitrogen atmosphere. Melting points were determined in sealed capillaries with a Gallenkamp apparatus and are uncorrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Pascher Mikroanalytisches Laboratorium, Bonn, Germany.

Materials.—Molybdenum and tungsten hexacarbonyls were purchased from Climax Molybdenum Co., New York, N. Y. Chromium hexacarbonyl was prepared by the aluminum alkyl method.[17] Trimethyl or triphenyl derivatives of silicon, german-

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(6) Only a few such compounds involving metals of main group III have been reported: $In[Co(CO)_4]_3$, $Tl[Co(CO)_4]_3$, and $Tl[Co(CO)_4]$ by Hieber,[7a] and other In–Co bonds more recently by D. J. Patmore and W. A. G. Graham, *Chem. Commun.*, 591 (1965). From main group V, a Bi–Re bond has been reported.[10]

(7) (a) W. Hieber and U. Teller, *Z. Anorg. Allgem. Chem.*, **249**, 43 (1942); (b) W. Hieber and R. Breu, *Chem. Ber.*, **90**, 1270 (1957).

(8) (a) F. Hein and H. Pobloth, *Z. Anorg. Allgem. Chem.*, **248**, 84 (1941); (b) F. Hein and E. Heuser, *ibid.*, **254**, 138 (1947); (c) F. Hein, P. Kleinert, and W. Jehn, *Naturwissenschaften*, **44**, 34 (1957); (d) F. Hein and W. Jehn, *Ann.*, **684**, 4 (1965).

(9) R. D. Gorsich, *J. Am. Chem. Soc.*, **84**, 2486 (1962).

(10) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, *Proc. Acad. Sci. USSR, Chem. Sect.*, **156**, 502 (1964).

(11) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

(12) A few of these have been mentioned briefly in a preliminary communication.[4]

(13) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and M. Ya. Zakharova, *Proc. Acad. Sci. USSR, Chem. Sect.*, **156**, 532 (1964).

(14) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

(15) F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 179 (1964).

(16) "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," International Union of Pure and Applied Chemistry, Butterworth and Co. Ltd., London, 1961.

(17) H. E. Podall, J. H. Dunn, and H. Shapiro, *J. Am. Chem. Soc.*, **82**, 1325 (1960).

ium, tin, and lead were obtained commercially or prepared by well-established methods.[18] Diglyme and tetrahydrofuran were distilled from lithium aluminum hydride.

Preparation of the Sodium Salts.—These were prepared on a large scale, and appropriate aliquots were used for reaction with the halides. Diglyme was used in the preparation of $\pi\text{-}C_5H_5(CO)_3CrNa$, as recently described;[19] 0.12 mole of C_5H_5Na with 25.0 g (0.11 mole) of $Cr(CO)_6$ in 100 ml of diglyme was assumed to give a quantitative yield of the sodium salt on refluxing overnight. $\pi\text{-}C_5H_5(CO)_3WNa$ was prepared similarly. $\pi\text{-}C_5H_5(CO)_3MoNa$ was prepared in 300 ml of tetrahydrofuran from 100 g (0.40 mole) of $Mo(CO)_6$ and C_5H_5Na prepared from 9.2 g (0.40 mole) of sodium and freshly cracked cyclopentadiene; the mixture was refluxed overnight.

Molybdenum Derivatives.—The preparation of $\pi\text{-}C_5H_5(CO)_3MoSn(CH_3)_3$ is described as representative of reactions with molybdenum: to a 30-ml aliquot of the $\pi\text{-}C_5H_5(CO)_3MoNa$ solution (40 mmoles) in a 100-ml flask fitted with condenser, nitrogen inlet, and magnetic stirring bar was added 7.5 g (37.6 mmoles) of trimethyltin chloride; dropwise addition of the latter in tetrahydrofuran solution did not improve the yield. After stirring for 15 hr at room temperature, solvent was removed on a rotary evaporator using a water aspirator. The residue was extracted with four 60-ml portions of pentane. The combined extracts were concentrated and cooled to yield 7.3 g (17.9 mmoles, 47.5%) of product, which was purified by recrystallization from a dichloromethane–pentane mixture. **$Cl(CH_3)_2Sn\text{–}Mo(CO)_3C_5H_5$** resulted from the *slow* addition of a tetrahydrofuran solution of $(CH_3)_2SnCl_2$ to an equimolar amount of $\pi\text{-}C_5H_5Mo(CO)_3Na$ solution, which was stirred overnight; after removal of tetrahydrofuran at reduced pressure, the product was extracted with *n*-hexane and recrystallized from the same solvent.

Tungsten Derivatives.—Preparation and isolation was straightforward owing to the relatively high stability to air and water. The solid organometallic halide was added to the diglyme solution of $\pi\text{-}C_5H_5(CO)_3WNa$ and stirred overnight at room temperature. The solid residue was removed by filtration, and water was added to the filtrate until the product precipitated. Recrystallization from dichloromethane–pentane yielded a pure product.

Chromium Derivatives.—These derivatives were extremely air and water sensitive in solution, and it was found desirable to work up the reaction mixture in a nitrogen-filled glove box. By working with concentrated solutions, the product could be recovered by filtration of the reaction mixture. Thus $(C_5H_5)_3PbCl$ (5.4 g, 11.4 mmoles) was added to $\pi\text{-}C_5H_5(CO)_3CrNa$ (11.0 mmoles) contained in 10 ml of diglyme. After stirring overnight, the mixture was filtered and the residue was extracted with four 50-ml portions of dichloromethane giving 3.2 g (5.0 mmoles, 45%) of product. Infrared cells and nmr tubes were filled with solutions of the chromium compounds in the glove box. The purified solid compounds were stable for short periods in air and were light sensitive.

Discussion

The molybdenum and tungsten derivatives reported here are beautifully crystalline substances, stable indefinitely in closed containers, and surviving exposure to air for several days without appreciable oxidation. The chromium derivatives, however, decompose under an inert atmosphere over a period of several weeks at room temperature. Phenyl derivatives are in general more stable than methyl, and the lead compounds are less stable than their germanium and tin analogs.

We have not as yet been successful in obtaining the silicon analogs, and whether this is due to instability of the silicon derivatives or a consequence of metal–halogen exchange reactions that yield dimers of the starting materials we have not ascertained. It may be noted, however, that the trend in stability of transition metal–silicon bonds appears to be Si–Co > Si–Fe > Si–Mn. Thus, $(C_6H_5)_3Si\text{–}Co(CO)_4$ (mp 135–140°) reacts only slowly with air and water;[20] $(CH_3)_3Si\text{–}Fe(CO)_2\text{-}\pi\text{-}C_5H_5$ is thermally rather stable but easily oxidized,[21] while $(C_6H_5)_3Si\text{–}Mn(CO)_5$ is oxidized with such ease that it has not been characterized.[9, 21a]

Examination of the infrared spectra of compounds containing a single $C_5H_5(CO)_3M$ group (M = Cr, Mo, W) (Table II and Figure 1) reveals three strong terminal CO bands. In this respect, they resemble the halogen derivatives $C_5H_5(CO)_3MX$, but differ from the methyl and ethyl derivatives, which show only two.[14]

We include in Table II our own measurements for the methyl derivatives of molybdenum and tungsten, which are in good agreement with the earlier values,[14] and establish that no additional bands are resolved by a grating instrument.

As Cotton has remarked,[22] it is not clear whether the differing numbers of CO stretching frequencies reflect different structures. It appears most reasonable to suppose that the basic geometry of the compounds here reported is similar to that established for $\pi\text{-}C_5H_5(CO)_3MoC_2H_5$.[23] As Bennett and Mason point out, this structure can be derived from that of dimeric $[\pi\text{-}C_5H_5(CO)_3Mo]_2$ by replacing one of the $\pi\text{-}C_5H_5(CO)_3Mo$ moieties with an ethyl group.

In compounds such as $(CH_3)_2Sn[Mo(CO)_3C_5H_5]_2$, the maximum number of terminal CO bands is six, and all are well resolved in cyclohexane solution (Figure 2).

In the nmr results of Table III, it is the chemical shift and coupling constant values for the methyl derivatives that are of particular interest. Taking tetramethyltin [τ 9.93, $J(^{117}SnCH_3)$ = 51.1 cps, $J(^{119}SnCH_3)$ = 53.4 cps][24] as the basis for comparison, it has been established[25] that the position of the methyl resonance shifts to lower field as methyl groups are replaced by chlorine atoms; this trend may reasonably (though perhaps naïvely) be regarded as an inductive withdrawal of shielding electron density by the chlorine atoms. It is therefore surprising that the present results show a similar shift to lower field as the methyls in tetramethyltin are replaced by $C_5H_5(CO)_3M$ groups; thus, the chemical shift values drop to τ 9.4–9.5 in trimethyltin derivatives and to τ 9.2 in $(CH_3)_2Sn[Mo(CO)_3C_5H_5]_2$. A shift of the resonance to higher

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[18] E. Krause and A. von Grosse, "Die Chemie der metallorganischen Verbindungen," Borntraeger, Berlin, 1937.

[19] R. B. King and F. G. A. Stone, *Inorg. Syn.*, **7**, 105 (1963).

[20] A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 1133 (1965).

[21] T. S. Piper, D. Lemal, and G. Wilkinson, *Naturwissenschaften*, **43**, 129 (1956); unpublished work in these laboratories by Mr. J. Kenney indicates that $(C_6H_5)_3Si\text{–}Fe(CO)_2\text{-}\pi\text{-}C_5H_5$ (mp 162°) is also a stable, easily handled compound.

[21a] NOTE ADDED IN PROOF.—The compound $(C_6H_5)_3Si\text{–}Mn(CO)_5$ has very recently been prepared in this laboratory by Mr. W. Jetz. Contrary to the earlier report,[9] it is a stable, colorless compound, mp 160–163°. The argument presented here must accordingly be modified.

[22] F. A. Cotton in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, John Wiley and Sons, Inc., New York, N. Y., 1960, p 361.

[23] M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 273 (1963).

[24] H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 1514 (1961).

[25] M. P. Brown and D. E. Webster, *J. Phys. Chem.*, **64**, 698 (1960).

Table I

Analytical Data, Colors, Melting Points, and Yields

Compd	Mp,[a] °C	Color	Yield, %	Calcd, %		Found, %	
				C	H	C	H
$(C_6H_5)_3GeCr(CO)_3C_5H_5$	229–230 dec	Yellow-green	24	61.8	4.0	62.3	4.8
$(C_6H_5)_3SnCr(CO)_3C_5H_5$	219–221	Yellow	46	56.6	3.7	55.9	3.8
$(C_6H_5)_3PbCr(CO)_3C_5H_5$	195–197 dec	Yellow	45	48.7	3.1	48.5	3.2
$(C_6H_5)_3GeMo(CO)_3C_5H_5$	219–222 dec	Pale green	74	57.3	3.7	56.5	3.6
$(CH_3)_3SnMo(CO)_3C_5H_5$	97–98.5	Pale yellow	47	32.3	3.5	32.5	3.7
$Cl(CH_3)_2SnMo(CO)_3C_5H_5$[c]	89–90	Pale yellow	50	28.0	2.6	28.3	2.7
$(C_6H_5)_3SnMo(CO)_3C_5H_5$	211–214 dec	Pale green	39	52.7	3.4	53.2	3.5
$(CH_3)_3PbMo(CO)_3C_5H_5$	93–95	Pale orange	6	26.5	2.8	27.2	3.6
$(C_6H_5)_3PbMo(CO)_3C_5H_5$	200 dec	Yellow	. .	45.6	3.0	45.8	3.0
$(C_6H_5)_3GeW(CO)_3C_5H_5$	240 dec	Pale yellow	62	49.0	3.2	49.4	3.5
$(CH_3)_3SnW(CO)_3C_5H_5$[b]	119–120	Pale yellow	90	26.6	2.8	26.7	2.8
$(C_6H_5)_3SnW(CO)_3C_5H_5$	227–228	Pale green	57	45.7	3.0	45.9	3.0
$(C_6H_5)_3PbW(CO)_3C_5H_5$	214–215 dec	Yellow	65	40.5	2.1	40.3	2.8
$(CH_3)_2Sn[Mo(CO)_3C_5H_5]_2$	156–159 dec	Yellow	57	33.8	2.5	32.2	2.3

[a] Melting with decomposition denoted dec. [b] Calcd: W, 37.01; mol wt, 497. Found: W, 36.55; mol wt (benzene, Mechrolab osmometer), 490. [c] Calcd: Cl, 8.3. Found: Cl, 9.1.

Table II

Infrared[a] and Ultraviolet[b] Spectra

Compd	CO stretch, cm^{-1}	λ_{max}, mμ	ϵ_{molar}
$(C_6H_5)_3Ge–Cr(CO)_3C_5H_5$	1996, 1932, 1911		
$(C_6H_5)_3Sn–Cr(CO)_3C_5H_5$	1987, 1923, 1897		
$(C_6H_5)_3Pb–Cr(CO)_3C_5H_5$	1985, 1924, 1902		
$(C_6H_5)_3Ge–Mo(CO)_3C_5H_5$	2008, 1925, 1918	282, 243[c]	5,900, 6,870
$(CH_3)_3Sn–Mo(CO)_3C_5H_5$	1997, 1922, 1895	264	11,600
$Cl(CH_3)_2Sn–Mo(CO)_3C_5H_5$	2013, 1947, 1913		
$(C_6H_5)_3Sn–Mo(CO)_3C_5H_5$	2004, 1934, 1909	283[c]	13,900
$(CH_3)_3Pb–Mo(CO)_3C_5H_5$	1992, 1921, 1895	306, 242[c]	17,700, 9,500
$(C_6H_5)_3Pb–Mo(CO)_3C_5H_5$	2002, 1934, 1910	314[c]	16,800
$(C_6H_5)_3Ge–W(CO)_3C_5H_5$	2004, 1930, 1911	320[d]	2,600
$(CH_3)_3Sn–W(CO)_3C_5H_5$	1994, 1915, 1891	318	2,620
$(C_6H_5)_3Sn–W(CO)_3C_5H_5$	2014, 1927, 1902	320[d]	2,730
$(C_6H_5)_3Pb–W(CO)_3C_5H_5$	1999, 1927, 1907	306	21,500
$CH_3Mo(CO)_3C_5H_5$	2023, 1935	310[d]	2,440
$CH_3W(CO)_3C_5H_5$	2019, 1924	310	2,990
$(CH_3)_2Sn[Mo(CO)_3C_5H_5]_2$	2004, 1988, 1937, 1925, 1910, 1894[c]		
$(C_6H_5)_2Sn[Mo(CO)_3C_5H_5]_2$	2012, 1991, 1933, 1921, 1911, 1898[c]		

[a] In CCl_4 solution except as noted. [b] In CH_2Cl_2 solution except as noted. [c] In cyclohexane. [d] Shoulder.

Table III

Nmr Spectra

Compd	Solvent	τC_5H_5	τC_6H_5[a]	τCH_3
$(C_6H_5)_3Ge–Cr(CO)_3C_5H_5$	$CDCl_3$	5.10	2.51	
$(C_6H_5)_3Sn–Cr(CO)_3C_5H_5$	$CDCl_3$	5.16	2.57	
$(C_6H_5)_3Pb–Cr(CO)_3C_5H_5$	THF	4.95	2.5	
$(C_6H_5)_3Ge–Mo(CO)_3C_5H_5$	$CDCl_3$	4.79	2.64	
$(CH_3)_3Sn–Mo(CO)_3C_5H_5$[b]	$CHCl_3$	4.59		9.52
$Cl(CH_3)_2Sn–Mo(CO)_3C_5H_5$[c]	CCl_4	4.63		9.02
$(C_6H_5)_3Sn–Mo(CO)_3C_5H_5$	Acetone	4.45	2.57	
$(CH_3)_3Pb–Mo(CO)_3C_5H_5$[d]	$CHCl_3$	4.72		8.83
$(C_6H_5)_3Pb–Mo(CO)_3C_5H_5$	$CDCl_3$	4.74	2.62	
$(C_6H_5)_3Ge–W(CO)_3C_5H_5$	$CDCl_3$	4.64	2.55	
$(CH_3)_3Sn–W(CO)_3C_5H_5$[e]	$CHCl_3$	4.53		9.40
$(C_6H_5)_3Sn–W(CO)_3C_5H_5$	$CDCl_3$	4.61	2.58	
$(C_6H_5)_3Pb–W(CO)_3C_5H_5$	$CDCl_3$	4.57	2.5	
$CH_3Mo(CO)_3C_5H_5$	$CHCl_3$	4.68		9.60
$CH_3W(CO)_3C_5H_5$[f]	Toluene	5.29		9.44
$(CH_3)_2Sn[Mo(CO)_3C_5H_5]_2$[g]	$CDCl_3$	4.65		9.15

[a] Values are the approximate midpoint of broad overlapping multiplet. [b] $J(^{117}SnCH_3)$ = 47.0 cps; $J(^{119}SnCH_3)$ = 49.0 cps. [c] $J(^{117}SnCH_3)$ = 45.6 cps; $J(^{119}SnCH_3)$ = 47.7 cps. [d] $J(^{207}PbCH_3)$ = 44.5 cps. [e] $J(^{117}SnCH_3)$ = 46.4 cps; $J(^{119}SnCH_3)$ = 48.7 cps; $J(^{13}CH_3)$ = 129.0 cps. [f] $J(^{183}WCH_3)$ = 3.9 cps. [g] $J(^{117}SnCH_3)$ = 35.8 cps; $J(^{119}SnCH_3)$ = 37.4 cps.

field might have been expected to result from these electropositive substituents if only inductive effects were considered.

The proton–tin coupling constants of the methyltin derivatives are smaller than in tetramethyltin, decreasing to about 48 cps with one transition metal in the molecule and to 37 cps when two are present. These facts are in harmony with the electropositive character of the metal substituents. Proton–tin coupling will be proportional to the s character in the tin hybrid orbital bonding to the methyl group.[26] This implies that the tin orbitals to carbon are depleted in s character, or equivalently that *the tin atom uses a high degree of s character in its bonds to the transition metals.* This is in harmony with Bent's suggestion that an atom tends to concentrate its s character into orbitals directed toward electropositive substituents.[27] This may be a considerable oversimplification, however.

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(26) This point has been discussed at greater length and applied to methyltin and methyllead hydrides by N. Flitcroft and H. D. Kaesz, *J. Am. Chem. Soc.*, **85**, 1377 (1963).

(27) H. A. Bent, *Chem. Rev.*, **61**, 290 (1961).

Substituent effects on the coupling constant $J(^{119}SnCH_3)$ are not additive, as demonstrated in the series $(CH_3)_3SnCH_3$, $(CH_3)_3Sn–Mo(CO)_3C_6H_5$, $(CH_3)_3SnCl$, and $Cl(CH_3)_2Sn–Mo(CO)_3C_5H_5$. The values are 54.0, 49.0, 59.7, and 47.7 cps, respectively. The chlorine and molybdenum substituents do not offset one another in their effect on $J(^{119}SnCH_3)$ in the last compound.

The ultraviolet absorption data of Table II are reported for the sake of completeness. There is little that can be said by way of interpretation at this stage of development, but it is hoped that correlations will become possible as more data accumulate.

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

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

Organometallic Compounds with Metal–Metal Bonds. II. The Insertion of Tin(II) and Germanium(II) Halides into Metal–Metal Bonds[1]

BY D. J. PATMORE AND W. A. G. GRAHAM

Received December 13, 1965

New examples of insertion reactions into metal–metal bonds are described. Tin(II) chloride reacts smoothly with dicobalt octacarbonyl, $[(C_6H_5)_3PCo(CO)_3]_2$, or dimeric π-cyclopentadienylnickel carbonyl to form $(OC)_4Co–SnCl_2–Co(CO)_4$, $(C_6H_5)_3P(OC)_3Co–SnCl_2–Co(CO)_3P(C_6H_5)_3$, or π-$C_5H_5(OC)Ni–SnCl_2–Ni(CO)$-π-$C_5H_5$, respectively. Germanium(II) iodide and tin(II) bromide and iodide undergo similar reactions with dicobalt octacarbonyl. Infrared spectra of the new compounds are reported.

Introduction

The term "insertion reaction" has been applied to several processes in metal carbonyl chemistry and is best regarded as descriptive of the over-all process, without mechanistic implications. The original[2] and best understood[3] case involves the conversion of methyl- to acetylmanganese pentacarbonyl. More recently, Dighe and Orchin have reported examples of the insertion of mercury into metal–metal bonds,[4] while the reaction of π-cyclopentadienyliron dicarbonyl dimer with tin(II) chloride[5] or germanium(II) iodide[6] affords $[\pi\text{-}C_5H_5Fe(CO)_2]_2SnCl_2$ or $[\pi\text{-}C_5H_5Fe(CO)_2]_2GeI_2$, respectively. The similarity of mercury, tin(II) chloride, and germanium(II) iodide in these reactions is noteworthy and is based on the ability of these reagents to increase their covalency by two units and on the fact that both mercury and tin form strong covalent bonds with transition metals. Our interest in metal–metal bonding has prompted us to explore more fully the scope of the insertion reaction.

Experimental Section

All reactions were carried out in a nitrogen atmosphere. Infrared spectra were determined using a Perkin-Elmer Model 421 spectrometer with double-grating interchange. Carbonyl bands were run on an expanded scale with deuterium chloride calibration on each spectrum.[1] Values are given in cm^{-1}. Color, melting points, and analytical data are given in Table I. Infrared data are given in Table II.

Dichlorobis(tetracarbonylcobalt)tin(IV).—Dicobalt octacarbonyl (10.3 g, 30 mmoles) and anhydrous tin(II) chloride (5.7 g, 30 mmoles) were stirred at room temperature for 15 min in 250 ml of tetrahydrofuran. Solvent was removed at reduced pressure from the deep orange solution, and the residue was dissolved in the minimum amount of dichloromethane. After filtration, slow addition of *n*-pentane to the solution cooled in ice gave orange-red, air-stable, prismatic crystals. Recrystallization from dichloromethane–pentane gave the product in 50% yield. **Dibromobis(tetracarbonylcobalt)tin(IV)** and **diiodobis(tetracarbonylcobalt)tin(IV)** were similarly prepared from the anhydrous halides, *n*-pentane only being used for extraction and recrystallization.

Triphenylphosphinetricarbonylcobalt Dimer.—$[(C_6H_5)_3PCo(CO)_3]_2$ was most conveniently prepared from $Co_4(CO)_{12}$.[7] Triphenylphosphine (4.0 g, 15.3 mmoles) and tetracobalt dodecacarbonyl (2.0 g, 3.5 mmoles) were stirred in 50 ml of *p*-xylene for 1.5 hr. The dark brown product was filtered off and washed with ether to remove unreacted triphenylphosphine; yield 3.6 g.

Reaction of $[(C_6H_5)_3PCo(CO)_3]_2$ with $SnCl_2$.—Anhydrous tin(II) chloride (0.24 g, 1.27 mmoles) and $[(C_6H_5)_3PCo(CO)_3]_2$ (1.0 g, 1.23 mmoles) were refluxed for 3 hr in 50 ml of tetrahydrofuran. Solvent was removed at reduced pressure and the residue extracted with dichloromethane. Addition of *n*-pentane to the extract followed by cooling in Dry Ice gave red crystals. Several recrystallizations from dichloromethane–pentane gave the pure product.

Reaction of $Cl_2Sn[Co(CO)_4]_2$ with $(C_6H_5)_3P$.—Triphenylphosphine (0.55 g, 2.1 mmoles) and $Cl_2Sn[Co(CO)_4]_2$ (0.53 g, 1.0 mmole) were stirred in refluxing tetrahydrofuran for 2 hr. Removal of tetrahydrofuran and extraction with methylene chloride gave a red solution, from which orange crystals were

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(1) Presented in part at the 48th Canadian Chemical Conference, Montreal, June 1965. For Part I of this series, see H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, **5**, 1401 (1966).

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