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

Organometallic Compounds with Metal–Metal Bonds. X. Oxidative Elimination Reactions of Tetracarbonylbipyridylmolybdenum and -tungsten with Halides and Organometallic Halides of Germanium(IV) and Tin(IV)[1]

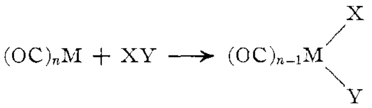
BY RUDOLF KUMMER AND W. A. G. GRAHAM

Received June 22, 1967

Reactions of bipy$M(CO)_4$ (bipy = 2,2′-bipyridyl; M = Mo, W) with the tetrahalides $M'X_4$ (M' = Ge, Sn; X = Cl, Br, I) yield new seven-coordinate compounds bipy$(CO)_3XMM'X_3$ having metal–metal bonds. A variety of organometallic halides ($C_6H_5GeCl_3$, CH_3SnCl_3, n-$C_4H_9SnCl_3$, $CH_2{=}CHSnCl_3$, $C_6H_5SnCl_3$, and $(C_6H_5)_2SnCl_2$) undergo a similar reaction. Several compounds have also been prepared with *o*-phenanthroline and 1,2-bis(diphenylphosphino)ethane as ligands. Infrared studies of the carbonyl stretching region suggest that the compounds may exist in solution in two isomeric forms. The nmr spectrum of bipy$(CO)_3ClMoSnCH_3Cl_2$ is consistent with the existence of isomers and establishes that the methyl group remains on the tin atom when the compound is formed from CH_3SnCl_3.

Introduction

The term "oxidative elimination" has been applied to a rather general reaction of metal carbonyls in which one of the carbon monoxide ligands is expelled and replaced by two univalent ligands,[2] as illustrated by the general process



$$(OC)_nM + XY \longrightarrow (OC)_{n-1}M\begin{smallmatrix}X\\ Y\end{smallmatrix}$$

In such a reaction, the coordination number of M increases by 1, while its formal oxidation state increases by 2 units. Typically, XY would be a halogen molecule, and one of the earliest examples of the reaction is[3]

$$(OC)_5Fe + I_2 \longrightarrow cis\text{-}(OC)_4FeI_2 + CO$$

More recently, novel seven-coordinate derivatives have been prepared by reactions of the same general type[4]

$$\text{diars}(OC)_4Mo + I_2 \longrightarrow \text{diars}(OC)_3MoI_2 + CO$$

In two reported instances, oxidative elimination processes have led to the formation of bonds between mercury and a transition metal

$$(OC)_5Fe + HgCl_2 \longrightarrow cis\text{-}(OC)_4Fe(HgCl)_2{}^5$$

$$\text{bipy}(OC)_4W + HgCl_2 \longrightarrow \text{bipy}(OC)_3W(HgCl)_2{}^6$$

There is some uncertainty at present as to why these reactions do not yield "mixed" derivatives such as $(OC)_4Fe(Cl)HgCl$, and we shall return to this problem in a later paper of this series. For the present, it is sufficient to note that the reaction provides, in the case of mercury at least, a convenient route to metal–metal bonds.

The work reported here was undertaken with the hope of extending the oxidative elimination reaction to the formation of other metal–metal bonds, in particular those involving metals and metalloids of the fourth main periodic group.

Experimental Section

All reactions were carried out under a nitrogen atmosphere, mainly by the use of Schlenk-tube techniques. Solvents were dried and saturated with nitrogen. Published procedures were used for the preparation of germanium(IV) iodide,[7] tin(IV) bromide[7] and iodide,[7] phenyltrichlorogermane,[8] and methyltin trichloride.[9] Other reagents were available commercially and were used without further purification. The known tetracarbonyl complexes of molybdenum and tungsten with 2,2′-bipyridyl and *o*-phenanthroline were prepared by heating the components in xylene,[10a,b] while the 1,2-bis(diphenylphosphino)ethane complex was prepared by heating the components in a sealed tube without solvent.[10c]

Infrared spectra were obtained using a Perkin-Elmer Model 337 (grating) spectrometer, with scale expansion and CO–DBr calibration as previously described.[11] Conductivities were measured using a Phillips Type PR-9500 conductivity bridge and a cell with a constant of 0.28 cm^{-1}. The solvent for conductivity measurements was acetone which had been dried over sodium carbonate and distilled from potassium permanganate. Reported values are extrapolated to zero time after a 10–30-min observation, during which a steady increase in conductance was observed. Microanalyses were performed by Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany, with results as given in Table I.

In Table I are also summarized some properties of the compounds and the reaction conditions. Several representative procedures are described in detail in this section.

---

[1] Part IX: J. A. J. Thompson and W. A. G. Graham, *Inorg. Chem.*, **6**, 1875 (1967).

[2] J. Lewis and S. B. Wild, *J. Chem. Soc., Sect. A*, 69 (1966).

[3] W. Hieber and G. Bader, *Ber.*, **61**, 1717 (1928).

[4] H. L. Nigam, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 1806 (1960). "diars" represents *o*-phenylenebisdimethylarsine.

[5] Originally observed by H. Hock and H. Stuhlmann, *Ber.*, **61**, 2097 (1928); more recently investigated by Lewis and Wild.[2]

[6] M. C. Ganorkar and M. H. B. Stiddard, *Chem. Commun.* (London), 22 (1965).

[7] G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry," Vol. 1, 2nd ed, Academic Press Inc., New York, N. Y., 1963.

[8] F. Rijkens and G. J. M. Van der Kerk, "Investigations in the Field of Organogermanium Chemistry," Germanium Research Committee, Utrecht, The Netherlands, 1964, p 123.

[9] A. C. Smith and E. G. Rochow, *J. Am. Chem. Soc.*, **75**, 4103 (1953).

[10] (a) W. Hieber and F. Mühlbauer, *Z. Anorg. Allgem. Chem.*, **221**, 337 (1935); W. Hieber and E. Romberg, *ibid.*, **221**, 349 (1935); (b) M. H. B. Stiddard, *J. Chem. Soc.*, 4712 (1962); (c) J. Chatt and H. R. Watson, *ibid.*, 4980 (1961).

[11] W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966).

TABLE I

PROPERTIES, REACTION CONDITIONS, AND ANALYTICAL RESULTS[a]

Compound	Mp,[b] °C	Color	Conditions[c]	Anal, %									
				Calcd					Found				
				C	H	N	O	X	C	H	N	O	X
bipy$(CO)_3$ClMoGeCl_3	135 d	Yellow-red	D, 2 hr, 90°	28.4	1.5	5.1	8.7	25.8	28.4	1.8	5.3	8.9	25.7
bipy$(CO)_3$IMoGeI_3	164 d	Red-brown	X, 2 hr, 100°	17.0	0.9	3.1	5.2	55.4	17.6	1.4	3.0	5.1	55.1
bipy$(CO)_3$ClMoSnCl_3	150 d	Orange	A, 3 hr, 20°	26.2	1.4	4.7	8.0	23.8	25.7	1.5	4.6	...	23.1
bipy$(CO)_3$MoSnBr_3	160 d	Red	B, 6 hr, 20°	20.2	1.0	3.6	6.2	41.3	20.3	1.0	3.7	...	41.1
bipy$(CO)_3$IMoSnI_3	160 d	Orange-brown	B, 2 hr, 30–40°	16.2	0.8	2.9	5.0	52.7	16.6	0.5	2.9	4.9	53.3
bipy$(CO)_3$ClMoSnCH_3Cl_2	190 d	Orange	A, 4 hr, 40–50°	29.2	1.9	4.9	8.3	18.5	29.4	2.0	4.8	...	18.5
bipy$(CO)_3$ClMoSn$C_4H_9Cl_2$	166–168[d]	Yellow	A, 5 hr, 40–50°	33.0	2.8	4.5	7.8	17.2	33.0	3.1	4.7	...	17.8
bipy$(CO)_3$ClMoSn$C_2H_3Cl_2$	161 d	Orange	A, 7 hr, 20°	30.6	1.9	4.8	8.2	18.1	30.8	2.1	4.6	8.2	18.1
bipy$(CO)_3$ClMoSn$C_6H_5Cl_2$	168 d	Yellow-orange	A, 5 hr, 20°	35.8	2.1	4.4	7.5	16.7	35.6	2.1	4.6	...	17.3
bipy$(CO)_3$ClMoSn$(C_6H_5)_2$Cl	212 d	Yellow	T, 5 hr, reflux	44.2	2.7	4.1	7.1	10.4	44.3	2.8	4.4	...	10.9
bipy$(CO)_3$ClWGeCl_3	210 d	Yellow-red	D, 12 hr, 105°	24.5	1.2	4.4	7.5	22.2	24.6	1.2	4.4	7.6	22.2
bipy$(CO)_3$BrWGeBr_3	180 d	Red	A, hal exchange	19.1	1.0	3.4	5.9	39.2	20.0	1.0	3.6	...	39.1
bipy$(CO)_3$ClWGe$C_6H_5Cl_2$	190 d	Yellow	D, 16 hr, 115°	33.6	1.9	4.1	7.1	15.6	33.2	2.2	4.1	...	15.5
bipy$(CO)_3$ClWSnCl_3	150 d	Orange	A, 3 hr, 20°	22.8	1.2	4.1	7.0	20.7	22.9	1.5	...	7.4	20.8
bipy$(CO)_3$BrWSnBr_3	160 d	Red	A, 3 hr, 20°	18.1	0.9	3.3	5.6	37.1	18.2	0.9	3.4	5.6	36.9
bipy$(CO)_3$IWSnI_3	154 d	Yellow-orange	B, 3 hr, 45°	14.9	0.8	2.7	4.6	48.3	15.0	0.8	2.6	...	47.0
bipy$(CO)_3$ClWSnCH_3Cl_2	215 d	Golden yellow	A, 2 hr, 50–60°	25.3	1.7	4.2	7.2	16.0	25.3	1.5	4.1	7.2	15.9
bipy$(CO)_3$IWSnCH_3I_2[e]		Red	A, hal exchange	17.9	1.2	3.0	5.1	40.6	17.0	1.1	...	...	36.9
bipy$(CO)_3$ClWSn$C_4H_9Cl_2$	153–155[d]	Orange	A, 4 hr, 60°	28.9	2.4	4.0	6.8	15.0	29.1	2.4	3.9	7.1	15.6
bipy$(CO)_3$ClWSn$C_2H_3Cl_2$	192 d	Orange	A, 12 hr, 20°	26.7	1.6	4.1	7.1	15.7	26.7	1.5	4.2	7.3	15.6
bipy$(CO)_3$ClWSn$C_6H_5Cl_2$	184 d	Orange	A, 4 hr, 20°	31.4	1.8	3.9	6.6	14.7	31.1	1.9	4.0	...	15.0
bipy$(CO)_3$ClWSn$(C_6H_5)_2$Cl	225 d	Red	D, 6 hr, 120°	39.1	2.4	3.7	6.3	9.2	38.8	2.4	3.8	...	9.5
o-phen$(CO)_3$ClMoSnCl_3	170 d	Orange	A 5 hr, 20°	29.0	1.3	4.5	7.7	22.9	29.1	1.0	4.6	...	22.8
o-phen$(CO)_3$IMoSnI_3		Orange-brown	B, 16 hr, 20°	18.3	0.8	2.8	4.9	51.5	18.5	0.7	3.0	4.7	51.5
o-phen$(CO)_3$ClMoSnCH_3Cl_2	180 d	Yellow-orange	A, 3 hr, 40–50°	32.0	1.9	4.7	8.0	17.7	32.2	2.0	4.5	...	17.6
o-phen$(CO)_3$ClWSnCH_3Cl_2	195 d	Yellow-orange	A, 4 hr, 40–50°	27.9	1.6	4.0	7.0	15.5	28.6	1.8	3.9	...	14.8
o-phen$(CO)_3$ClWSn$C_2H_3Cl_2$	218 d	Orange	A, 12 hr, 20°	29.2	1.6	4.0	6.9	15.2	29.7	1.6	4.0	...	15.5
diphos$(CO)_3$BrMoSnBr_3	179 d	Red	C, 30 min, 25°	34.3	2.4	...	4.7	31.8	35.3	2.6	...	4.4	32.8
diphos$(CO)_3$BrWSnBr_3	185 d	Light red	C, 30 min, 25°	31.5	2.2	...	4.4	28.9	33.6	2.5	...	4.3	29.0

[a] Abbreviations: bipy = 2,2′-bipyridyl, $C_{10}H_8N_2$; *o*-phen = *o*-phenanthroline, $C_{12}H_8N_2$; diphos = 1,2-bis(diphenylphosphino)ethane, $[(C_6H_5)_2PCH_2]_2$; X = halogen. [b] Kofler hot-stage microscope; temperatures marked d are those at which darkening became noticeable, with the sample turning black over a 10–20° range, without melting. [c] Solvent, reaction time, reaction temperature. Abbreviations: A = acetone, B = benzene, C = dichloromethane, D = diglyme, T = tetrahydrofuran, X = xylene. [d] Melting sharply but with darkening and gas evolution. [e] Calcd: Cl, 0.0. Found: Cl, 0.0.

Formation of bipy$(CO)_3$ClMoSnCl_3.[12]—Tin(IV) chloride (1 ml, 8.5 mmoles) was added to a stirred suspension of bipy$(CO)_4$Mo (1 g, 2.7 mmoles) in 15 ml of acetone. The starting material quickly dissolved and there was vigorous evolution of carbon monoxide. After about 3 min the solution cleared, and fine orange crystals were soon deposited. Stirring was continued at room temperature until gas evolution ceased. The precipitate was removed by filtration, washed with three 10-ml portions of ether, and dried under vacuum for 6 hr. The yield is almost quantitative. The compound may be recrystallized from THF–ether, a procedure which affords larger orange-red crystals, but this is not necessary as the original orange crystals are analytically pure. The compound is moderately soluble in THF, acetone, and dichloromethane but insoluble in petroleum ether (bp 30–60°), benzene, carbon tetrachloride, and ether. It is completely stable to air and moisture.

Formation of bipy$(CO)_3$ClWSn$(C_6H_5)_2$Cl.—Tetracarbonylbipyridyltungsten(0) (0.45 g, 1.0 mmole) and diphenyltin dichloride (0.8 g, 2.3 mmoles) were slowly heated to 120° in 10 ml of diglyme. Starting materials dissolved and brown crystals formed after 3–4 hr. After 6 hr the solution was cooled to room temperature and 10 ml of ether was added. The solution was cooled to 0° to complete crystallization. After 2 days, solvent was decanted from the crystals, which were then washed thoroughly with ether and with methanol and dried under vacuum; the yield was 0.5 g (65%). The product is very sparingly soluble in THF, acetone, and dichloromethane.

Formation of *o*-phen$(CO)_3$IMoSnI_3.—To a solution of tin(IV) iodide (1.5 g, 2.4 mmoles) in 10 ml of benzene was added (*o*-phen)$(CO)_4$Mo (0.5 g, 1.3 mmoles). The mixture was stirred at room temperature until gas evolution ceased, about 16 hr. Then the brown crystalline product was filtered off and washed three times with carbon disulfide–ether (1:1) and with ether. After drying under vacuum, the yield was 1.0 g, 78%. The compound is slightly soluble in acetone, THF, dichloromethane, and chloroform.

Formation of bipy$(CO)_3$ClMoGeCl_3.—Germanium(IV) chloride (2 ml, 2.7 g, 17 mmoles) and bipy$(CO)_4$Mo (0.5 g, 1.37 mmoles) were heated at 90° in 10 ml of diglyme solution for 2 hr. After filtration and concentration at reduced pressure to about 5 ml, addition of 20 ml of diethyl ether and 5 ml of pentane precipitated orange crystals. These were recrystallized from THF–ether affording brown crystals which were washed with ether and vacuum dried; yield, 0.3 g, 40%.

Preparation of bipy$(CO)_3$BrWGeBr_3 by Halogen Exchange.—A stirred solution of bipy$(CO)_3$ClWGeCl_3 (0.32 g, 0.5 mmole) in 30 ml of acetone was treated with finely powdered NaBr (1.85 g, 18 mmoles). After stirring for 4 hr at room temperature, acetone was completely removed at reduced pressure and the residue extracted with three 15-ml portions of warm dichloromethane. The combined extracts were concentrated to 5 ml and filtered, and 25 ml of ether was added. After standing in a refrigerator for several days, this solution afforded red crystals which were washed with ether and dried under vacuum; yield, 0.3 g, 74%.

Discussion

Tetrahalides of germanium and tin have been found to react readily with several substituted carbonyls of molybdenum and tungsten. The following reaction, for example, took place almost quantitatively when the reactants were stirred in acetone at room temperature.[13]

$$\text{bipyMo(CO)}_4 + \text{SnCl}_4 \longrightarrow \text{bipy(CO)}_3\text{ClMoSnCl}_3 + \text{CO}$$

In general, the new compounds produced in these reactions are yellow-to-red crystalline solids of low solubility in polar solvents and are insoluble in nonpolar

---

(12) Abbreviations: bipy = 2,2′-bipyridyl; *o*-phen = *o*-phenanthroline; diphos = 1,2-bis(diphenylphosphino)ethane; THF = tetrahydrofuran; diglyme = dimethyl ether of diethylene glycol.

(13) Abbreviations are given in footnote 12. We write the molecular formula of the reaction product and other compounds so as to imply which ligands are associated with each metal atom and to emphasize the metal–metal bond.

solvents. The solids appear to be indefinitely stable to light and air.

Conductivity measurements on representative compounds (Table II) establish that the products are nonionic, and hence they may be formulated as seven-coordinate derivatives of bivalent molybdenum or tungsten. The reaction can thus be classified as an *oxidative elimination* in the general sense discussed in the Introduction and is the first to be reported involving compounds of elements of the fourth main group. It should be capable of considerable extension as a method for the synthesis of bonds between transition metals and germanium or tin. The coordination geometry of these new compounds is not known. There are a number of possibilities,[14] of which the pentagonal bipyramid originally suggested[4] for the dihalogeno derivative diars$(CO)_3MoI_2$ is one. Indeed, as will emerge from the infrared and nmr studies, it appears that these compounds provide interesting new examples of isomerism in seven-coordinate systems.

TABLE II

CONDUCTIVITIES[a]

Compound	Concn, m*M*	Conductance, mhos cm^2 mole^{-1}
bipy$(CO)_3$ClMoSnCl_3	0.93	0.75
bipy$(CO)_3$ClMoSn$(C_6H_5)_2$Cl	0.78	1.1
bipy$(CO)_3$ClWSnCH_3Cl_2	0.72	0.0
bipy$(CO)_3$IMoSnI_3	0.55	18.3
bipy$(CO)_3$IMoGeI_3	0.59	4.3

[a] In acetone solution, extrapolated to zero time (see text).

The tin and germanium derivatives can usefully be compared with the seven-coordinate dihalogeno compounds. The latter are reported to be unstable to light and air,[10b] while the germanium and tin derivatives, as already noted, exhibit unusually great stability for carbonyl derivatives.[15] Both classes of compounds, on the other hand, show a similar increase in conductivity with time in donor solvents. As previously suggested,[10b] this increase may be due to solvent displacement of halide ion. In most cases the conductivity extrapolates to low values at zero time, but with the iodides the displacement is particularly rapid. Representative conductivity results are given in Table II.[16]

Many reactions have been investigated in order to define the scope of the oxidative elimination process. In particular, it has been possible to carry out reactions using organometallic halides of germanium and tin; $C_6H_5GeCl_3$, CH_3SnCl_3, n-$C_4H_9SnCl_3$, $CH_2{=}CHSnCl_3$, $C_6H_5SnCl_3$, and $(C_6H_5)_2SnCl_2$ react, requiring more vigorous conditions than the tetrahalides. Some reaction was observed with $(CH_3)_2SnCl_2$ and $(C_6H_5)_3SnCl$, but only at high temperatures where the product decomposed. In these reactions, the question arises as to what group is transferred to the transition metal: the halogen or the organic group? On the basis of the nmr evidence to be discussed later in the case of the compound bipy$(CO)_3$ClMoSnCH_3Cl_2, and by inference for the other compounds as well, it is the halogen that is transferred.

These and other successful reactions are summarized in Table I. It is of interest to review the unsuccessful or anomalous reactions as well. There was no reaction of bipyCr$(CO)_4$ with any of the tetrahalides, even though fairly vigorous conditions were used; this is not unexpected, since chromium would be unlikely to form a seven-coordinate derivative of this type. No reaction was observed between the tetrahalides of germanium and tin and the unsubstituted hexacarbonyls. Silicon tetrachloride does not react with bipy(Mo,W)$(CO)_4$ under the conditions investigated, which included a sealed tube reaction with diglyme as solvent at 140° for 3 weeks; this sharp distinction between silicon and germanium is surprising. Although diphos(Mo,W)$(CO)_4$[17] reacted smoothly with tin tetrabromide, it could not be made to undergo reaction with tin tetrachloride or tetraiodide, either at high temperature or with ultraviolet irradiation; an observation that may be pertinent is the immediate formation of a yellow adduct when $SnCl_4$ is added to diphos(Mo,W)$(CO)_4$—the infrared spectrum of this adduct is the same as that of the diphos(Mo,W)$(CO)_4$ starting material. It is not clear why only tin(IV) bromide undergoes the reaction in this case.

Reactions of diars(Mo,W)$(CO)_4$ tended to be complicated and in no case yielded the expected products. diarsMo$(CO)_4$ with $SnCl_4$ in benzene afforded a yellow precipitate showing the unchanged carbonyl stretching bands of diarsMo$(CO)_4$—a behavior essentially similar to that found for diphosMo$(CO)_4$, in which adduct formation seems to prevent further reaction. The diarsine derivatives do react with $SnBr_4$ in a stepwise fashion with loss of CO and $SnBr_2$. In the reaction of diarsMo$(CO)_4$ with $SnBr_4$ (room temperature, dichloromethane) a white precipitate forms ($SnBr_2$) with a red solution showing four carbonyl bands between 1915 and 2060 cm^{-1}. Unstable orange-brown crystals are formed which analyze approximately for [Mo$(CO)_4$-diarsSnBr_3]Br_3. This unstable substance finally decomposes to yield a compound which is obtained as red needles, shows two carbonyl stretching bands at 1906 and 1967 cm^{-1} (dichloromethane), and analyzes as

---

(14) E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 109 (1967).

(15) (a) This relative stability is not unexpected, as there are several known cases in which a trichlorotin derivative, for example, is more stable than its simple halogeno analog; compare the nonexistence of ClCo$(CO)_4$ with the relatively high stability of $Cl_3SnCo(CO)_4$.[15b] It has been suggested that halogen substituents in metal carbonyls are π donors while a ligand such as Cl_3Sn is a strong π acceptor.[11] The stability difference may be due to this factor. (b) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967).

(16) The conclusion that these compounds are nonelectrolytes is not dependent on the extrapolation procedure, which is crude at best. Measured conductivities over periods of 5 or 10 min are far below the range of 130–140 mhos cm^2 mole^{-1} which we have observed for genuine 1:1 electrolytes in acetone. Thus, for bipy$(CO)_3$ClMoSnCl_3, the first entry of Table II, the measured values are 1.5 mhos cm^2 mole^{-1} at 1 min and 3.0 mhos cm^2 mole^{-1} at 5 min. For bipy$(CO)_3$IMoSnI_3, the value at 5 min is 21.2 mhos cm^2 mole^{-1}. In work to be published shortly on related complexes, iodotin derivatives have been found to produce ions fairly rapidly in acetone; they nonetheless seem to have the same constitution as their lighter halogen homologs, which do not do so.

(17) Iodine and bromine reacted with these diphos complexes affording the neutral, seven-coordinate compounds diphos$(CO)_3$(Mo,W)X_2: J. Lewis and R. Whyman, *J. Chem. Soc.*, 5486 (1965).

TABLE III

INFRARED CARBONYL STRETCHING BANDS[a]

Compound	I_1	II_1	I_2	II_2	I_3	II_3
bipy(CO)$_3$ClMoSnCl$_3$	2041 w, sh	2026	1979 vw, sh	1952 m, sh	1917 s, b	
bipy(CO)$_3$BrMoSnBr$_3$	2038 m, sh	2024	1978 w	1953 m, sh	1928 s, b	
bipy(CO)$_3$IMoSnI$_3$[b]	2039 s	2020	1974		1930 b, as	
bipy(CO)$_3$ClWSnCl$_3$	2033 m, sh	2021	1966, w, sh	1940 s, sh	1928 s–vs, b	
bipy(CO)$_3$BrWSnBr$_3$	2030 s, sh	2019	1961 m, sh	1938 s, sh	1924 s–vs	
bipy(CO)$_3$IWSnI$_3$	2031 s–vs	2013 m	1956		1912 s, b, as	
bipy(CO)$_3$ClMoGeCl$_3$[c]	2045	2038 s, sh	1985 m	1964 m–s, sh	1943	. . .
bipy(CO)$_3$IMoGeI$_3$[d]	2030	. . .	1975 m	. . .	1936	. . .
bipy(CO)$_3$ClWGeCl$_3$	2034 s, sh	2028	1965 m, sh	1944 s, sh	1931	
bipy(CO)$_3$BrWGeBr$_3$	2033	. . .	1963	1948 s	1930 s–vs	
bipy(CO)$_3$IWGeI$_3$	2023	. . .	1958 m	. . .	1920 s	. . .
bipy(CO)$_3$ClMoSnCl$_3$	2041 w, sh	2026	1979 vw, sh	1952 m, sh	1917 s, b	
bipy(CO)$_3$ClMoSnC$_6$H$_5$Cl$_2$	. . .	2010	. . .	1921 m	. . .	1899 s
bipy(CO)$_3$ClMoSnC$_2$H$_3$Cl$_2$	. . .	2010	. . .	1921 m, sh	. . .	1900 s
bipy(CO)$_3$ClMoSnCH$_3$Cl$_2$[e]	. . .	2008	. . .	1918 m, sh	. . .	1898 s
bipy(CO)$_3$ClMoSnC$_4$H$_9$Cl$_2$	. . .	2005	. . .	1917 m, sh	. . .	1895 s
bipy(CO)$_3$ClMoSn(C$_6$H$_5$)$_2$Cl	. . .	1993	. . .	1902 s	. . .	1881
bipy(CO)$_3$ClWSnCl$_3$	2023 m, sh	2021	1966 w, sh	1940 s, sh	1928 s–vs, b	
bipy(CO)$_3$ClWSnC$_6$H$_5$Cl$_2$	. . .	2003	. . .	. . .	. . .	1901 s, b
bipy(CO)$_3$ClWSnC$_2$H$_3$Cl$_2$	. . .	2003	. . .	.	. . .	1898 s, b
bipy(CO)$_3$ClWSnCH$_3$Cl$_2$	. . .	2001	. . .	. . .	. . .	1899 s, b
bipy(CO)$_3$ClWSnC$_4$H$_9$Cl$_2$	. . .	1998	. . .	. . .	. . .	1896 s, b
bipy(CO)$_3$ClWSn(C$_6$H$_5$)$_2$Cl	. . .	1983	. . .	1886 s	. . .	1871
bipy(CO)$_3$IMoSnI$_3$	2039 s	2020	1974		1930 b, as	
bipy(CO)$_3$IMoSnCH$_3$I$_2$	. . .	1997	. . .	. . .	. . .	1902 s, b
bipy(CO)$_3$ClWGeCl$_3$	2034 s, sh	2028	1965 m, sh	1944 s, sh	1931	
bipy(CO)$_3$ClWGeC$_6$H$_5$Cl$_2$	2021 s, sh	2011	1945 m, sh		1910 b	
o-phen(CO)$_3$ClMoSnCl$_3$	2039 w, sh	2026	1956 w, sh	1940 s, sh	1916 s, b	
o-phen(CO)$_3$IMoSnI$_3$	2037 s	2020	1973 s		1929 b, as	
o-phen(CO)$_3$ClMoSnCH$_3$Cl$_2$	. . .	2007	. . .	1919 s, sh	. . .	1898 s, b
o-phen(CO)$_3$ClWSnC$_2$H$_3$Cl$_2$	. . .	2001	. . .	. . .	. . .	1899 s, b
o-phen(CO)$_3$ClWSnCH$_3$Cl$_2$	. . .	2001	. . .	. . .	. . .	1900 s, b
diphos(CO)$_3$BrMoSnBr$_3$[f]	2045 m		1972		1933	
diphos(CO)$_3$BrWSnBr$_3$[f]	2037 m		1955		1926	

[a] Band positions in cm^{-1} for dichloromethane solutions. Bands are assigned to postulated isomers I and II, each isomer having three bands designated by subscripts; see text. Band intensities are very strong unless otherwise marked: w, weak; m, medium; s, strong. Band shape designations: b, broad; sh, shoulder; as, asymmetric. [b] See Figure 1d. [c] See Figure 1c. [d] See Figure 1a. [e] See Figure 1b. [f] As Nujol mull.

diarsMo(CO)$_2$Br$_3$; it is evidently related to the reported compound diarsMo(CO)$_2$I$_3$.[18] The latter compound was in fact isolated in minute quantities from the reaction of diarsMo(CO)$_4$ with tin(IV) iodide.

The tungsten analog diarsW(CO)$_4$ reacts with SnBr$_4$ in dichloromethane at room temperature forming a white precipitate (SnBr$_2$) and an unstable compound (perhaps [diars(CO)$_4$WSnBr$_3$]Br) with carbonyl stretching bands at 2099, 2048, 2014, and 1990 cm^{-1}. The only stable product isolated was diars(CO)$_3$WBr$_2$,[18] as shown by analysis and infrared (bands at 2049, 1963, and 1905 cm^{-1} in dichloromethane).

Infrared Spectra.—Typical infrared spectra in the carbonyl stretching region are shown in Figure 1, with band positions for all the compounds given in Table III. Solubility limitations forced the use of dichloromethane as the solvent, which accounts for the rather broad bands. Three bands are observed in some cases (Figure 1a) and in others only two (Figure 1b), but in the latter case the lower band is broad or has a shoulder. In other cases (Figure 1c and d), four or five bands are evident, an anomaly that requires comment in a tricarbonyl molecule.

These supernumerary bands are best accounted for on the assumption that more than one isomer is present in solution. We postulate that there are two possible geometric isomers, designated I and II. The carbonyl stretching frequencies of Table III have been assigned to one or the other of these isomers, and a comparison of all the spectra makes it reasonably clear that there are two sets of three bands, one set increasing in intensity as the other set decreases. A regular trend in the relative intensities is evident as the substituent groups are changed: the bands of set I (designated I_1, I_2, and I_3) become more intense in going from Cl to I, from Mo to W, from Sn to Ge, and from RSnX$_3$ to SnX$_4$. Thus bipy(CO)$_3$IMoGeI$_3$ (Figure 1a) exhibits the bands of only isomer I, while bipy(CO)$_3$ClMoSnCH$_3$Cl$_2$ (Figure 1b) shows only the bands of isomer II.

In Table III, compounds have been grouped to show these trends most clearly. Bands I_3 and II_3 are in no case resolved owing to their proximity and broadness. Also apparent is a drop in frequency of related bands in

---

[18] J. Lewis, R. S. Nyholm, C. S. Pande, and M. H. B. Stiddard, *J. Chem. Soc.*, 3600 (1963).

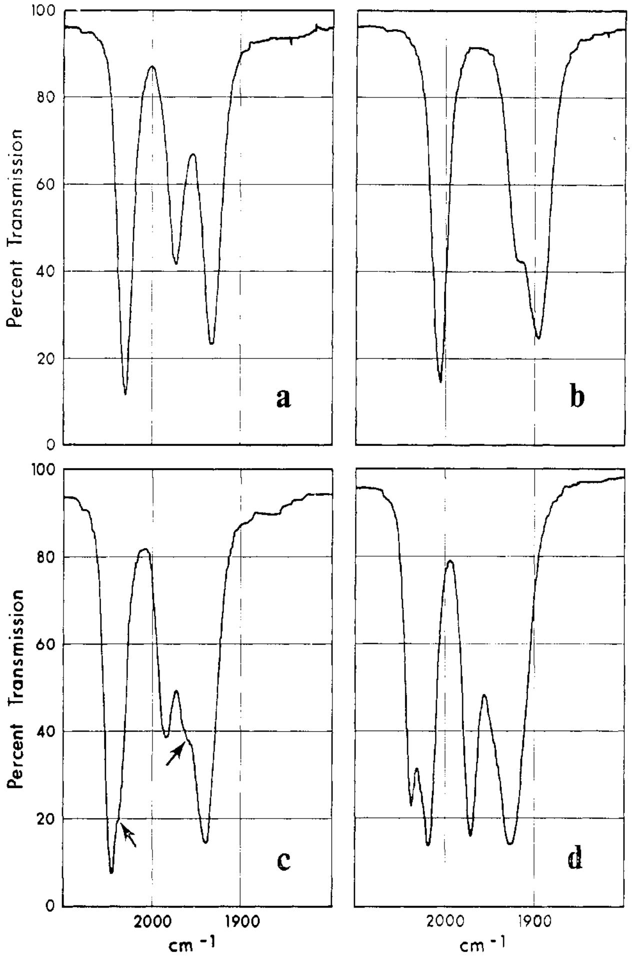


Figure 1.—Carbonyl stretching bands in dichloromethane, saturated or *ca.* 1 mg/ml, 0.5-mm cells: (a) bipy(CO)$_3$IMoGeI$_3$, (b) bipy(CO)$_3$ClMoSnCH$_3$Cl$_2$, (c) bipy(CO)$_3$ClMoGeCl$_3$, with arrows marking shoulders assigned to isomer II, and (d) bipy-(CO)$_3$IMoSnI$_3$.

the series Cl > Br > I and in the replacement of halogens by organic groups; this trend is well established in other germanium and tin derivatives of transition metals.[1,15b] Another observation is that isomer I is favored in the more polar solvents acetone and tetrahydrofuran, which could mean that isomer I is more polar, perhaps with X and MX$_3$ in *cis* positions.[19] At this stage, however, not even the over-all coordination geometry is known, so that speculation about *cis* or *trans* forms is premature. It will be interesting to await the results of X-ray crystallographic studies in this connection.

Five carbonyl stretching bands were observed previously in a chloroform solution of bipy(CO)$_3$MoI$_2$ by Stiddard,[10b] who tentatively suggested an iodine-bridged dimer to account for this unexpected result. The dimer was presumed to involve bipy as a monodentate ligand in order to preserve the rare gas configuration for molybdenum. We suggest that his result is more probably due to the presence of two isomers related to our isomers I and II. Thus it is evident from Stiddard's infrared results that the *three* bands observed for bipy(CO)$_3$MoI$_2$ in nitromethane are very close to three of the bands reported in chloroform; these three bands, moreover, are fairly close to those which we associate in our compounds with isomer I and which we find enhanced in more polar solvents. It also seems unlikely that dimerization could account for the supernumerary bands we observed in compounds of the *o*-phen series, since it is difficult to imagine the rigid *o*-phen ligand as monodentate.

Nmr Spectra.—Only the methyl derivative bipy-(CO)$_3$ClMoSnCH$_3$Cl$_2$ was studied, since it appeared that the simple methyl pattern would be most readily interpreted. The low solubility of the compound made it difficult to obtain nmr spectra of good quality.

In dichloromethane at 33.8°, the main feature of the spectrum is a sharp peak at τ 8.39 with characteristic methyl–tin spin-coupling satellites having $J(^{119}Sn\text{–}CH_3)$ = 70.0 cps and $J(^{117}Sn\text{–}CH_3)$ = 67.2 cps.[20] *This establishes that the methyl group is bonded to the tin atom*, and the coupling constants are reasonable in comparison with those of other methyltin derivatives of transition metals.[11,21] Also clearly evident in the dichloromethane spectrum is a sharp peak at τ 8.49 having approximately 10% of the intensity of the main peak; spin-coupling satellites were not observable for this less intense band. Infrared analysis detected only isomer II for this compound in dichloromethane, and we attribute the weaker τ 8.49 peak to isomer I in a concentration too low to be evident in the infrared spectrum.

An nmr study of the same compound was carried out in dibromomethane so that measurements could be extended to higher temperatures. Only a single sharp peak at τ 8.44 was observed at 40° and below; owing to the lower solubility, spin-coupling satellites were not observable in the normal spectrum. As the temperature was raised, a second broader peak developed at τ 8.54, which at 70° had an intensity almost equal to that of the τ 8.44 peak. At 85°, the highest temperature of the measurements, the τ 8.55 band seemed to be splitting while the τ 8.44 band remained sharp. The process was reversible, and the τ 8.55 band disappeared on cooling. The reason for the broadening of one of the peaks, that which should correspond to isomer I, is not known. Qualitatively, however, the nmr data are consistent with the infrared results, which indicate that isomer I was favored by more polar solvents. Thus a low concentration of I is present in dichloromethane near room temperature, but the concentration of I is too low to be detected in the less polar solvent

---

(19) We consider that the enhancement of bands assigned to isomer I in acetone is not related to the formation of ionic species in such a donor solvent; conductivity values in that solvent indicate a very low concentration of any ionic species over the times required to measure the infrared spectrum, with the exception of the iodotin compound.[16] Moreover, the outstanding example of isomer I is bipy(CO)$_3$IMoGeI$_3$, which exists in essentially pure form in dichloromethane solution, where the formation of an ionic species is not likely; this compound is also a nonelectrolyte in acetone solution (Table II).

(20) Measurements were made using a Varian HA-100 spectrometer. The low-intensity satellites could be unambiguously located only after an accumulation of 16 scans on a Varian time-averaging computer.

(21) H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, **5**, 1401 (1966); J. A. J. Thompson and W. A. G. Graham, *ibid.*, **6**, 1365 (1967).

dibromomethane. Only isomer II is detectable in dibromomethane near room temperature, and higher temperatures increase the concentration of the higher energy form I. Further quantitative studies of this interesting phenomenon are contemplated; these compounds may provide an important insight into the dynamics of seven-coordination in solution.

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

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

An Approach to the Separation of Inductive and Mesomeric Effects in Complexes of the Types $LMn(CO)_5$ and $LMo(CO)_5$

BY W. A. G. GRAHAM

Received July 17, 1967

It is assumed that inductive effects operating through the ligand–metal σ bond and ligand–metal π bonding are both important in determining the carbonyl stretching force constants in $LMn(CO)_5$ and $LMo(CO)_5$ molecules. It is suggested that the force constants of all carbonyl groups will change by the same amount owing to the change in inductive effect in going from one ligand to another; while the differences in π bonding between two ligands will affect the *trans* force constant twice as much as the *cis*. On this basis, scales of relative σ and π donor or acceptor character for a large number of ligands have been derived. The meaning of the σ and π parameters assigned to the ligands is discussed.

Introduction

In the interpretation of the infrared spectra and bonding of metal carbonyl derivatives, much stress has been placed on metal–ligand[1] π interaction.[2] The influence of inductive effects operating through the metal–ligand σ bond has not been explicitly considered, perhaps because it has not been possible to differentiate the σ effect from the π interaction. In surveying the current literature on metal carbonyls, however, it is difficult to avoid the conclusion that inductive effects have been relegated to a place of secondary importance.

By way of contrast, in discussions of the *trans* effect in square-planar platinum(II) complexes, both σ- and π-bonding effects are considered. Thus, it has been stated that a ligand of high *trans* effect can exert its influence by either electron release in the σ bonds or electron withdrawal in the π-coordinate bonds, the former enhancing S_N1 and the latter S_N2 substitution of the *trans* ligand.[3] From infrared studies of compounds of the type *trans*-$[PtLX(P(C_2H_5)_3)_2]$, Chatt and his coworkers[3] concluded that the lowering of the Pt–X stretching frequency by L was a measure of the inductive electron release by L. This approach has recently been applied to silicon–platinum derivatives of the type *trans*-$[PtX(SiCH_3(C_6H_5)_2)(P(CH_3)_2C_6H_5)_2]$, for which unusually low values of ν(Pt–X) are taken to mean that silicon has the greatest *trans* effect of inductive origin ever observed.[4]

Other spectroscopic techniques have been used to study the bonding in platinum(II) complexes. In hydrides of the type *trans*-$[PtHL(PR_3)_2]$, the *trans* effect of L has been related to both ν(Pt–H) and the chemical shift of H.[5] A particularly elegant approach was that of Parshall,[6] who attempted to discriminate between the σ-donor and π-acceptor aspects of the ligand–platinum bond by an adaptation of the ^{19}F nmr technique developed in organic chemistry by Taft and his school. In short, not only are σ and π effects both considered to be important, but there has been progress in assessing the extent to which each contributes for specific ligands.

Our attention was drawn to the role of inductive effects in metal carbonyl chemistry by the remarkable linearity of the carbonyl stretching frequencies in compounds such as $X_nR_{3-n}GeCo(CO)_4$[7] and $X_nR_{3-n}SnMn(CO)_5$[8] ($X = Cl, Br, I$; $R = CH_3, C_6H_5$) when plotted against the sum of the electronegativities of the halogens on germanium or tin. The trend to higher carbonyl frequencies with increased halogen substitution was explained[7] in terms of enhanced metal to ligand π bonding, the result of a contraction of germanium or tin d orbitals brought about by the increasing electronegativity of the substituents. Further consideration has led us to think that the ligand–metal σ bond might also be appreciably altered by the more electronegative substituents on the ligand and that such alterations could well affect the carbonyl stretching frequencies. Thus, taken as a whole, a Cl_3Sn group should be a

---

(1) We reserve the term "ligand" for the group which is not a carbonyl and designate it by the symbol L.

(2) For example, *cf.* F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1966, p 728 ff.

(3) D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964).

(4) J. Chatt, C. Eaborn, and S. Ibekwe, *Chem. Commun.*, 700 (1966).

(5) J. Chatt, *Proc. Chem. Soc.*, 318 (1962); R. V. Lindsey, Jr., G. W. Parshall, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965).

(6) G. W. Parshall, *ibid.*, **86**, 5367 (1964); **88**, 704 (1966).

(7) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967); similar results in equally extensive series of tin–cobalt derivatives will be described in a forthcoming publication.

(8) J. A. J. Thompson and W. A. G. Graham, *ibid.*, **6**, 1875 (1967).