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A Photolytic Preparation of Metal–Metal Bonds between Some Group VI and Group IV Metals

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Received February 24, 1967

The photolytic reaction of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ with either $(C_6H_5)_4AsSnCl_3$ or $(C_6H_5)_4AsGeCl_3$ produced complexes of the type $(C_6H_5)_4AsM(CO)_5M'Cl_3$ where M = Cr, Mo, or W and M′ = Sn or Ge. Similar derivatives of $Fe(CO)_5$ were also prepared.

The formation of metal–metal bonds between the group IV metals and transition metal derivatives has been a subject of recent widespread interest and several synthetic routes have been developed. The most direct method involves a halide displacement reaction utilizing a metal carbonyl anion.[1-4] Alternately, an insertion reaction between a lower valent metal halide such as $SnCl_2$ or GeI_2 with a metal carbonyl dimer can be used.[5-7]

A new method for the formation of metal–metal bonds has been developed: the displacement of carbon monoxide by a MCl_3^- ion. This method relies on the Lewis basicity possessed by the $GeCl_3^-$ and $SnCl_3^-$ anions. This basicity is amply demonstrated by their reaction with boron trifluoride to produce the complex anions $BF_3GeCl_3^-$ and $BF_3SnCl_3^-$.[8] Furthermore, evidence has been presented for the π-electron-acceptor ability of the $SnCl_3^-$ ion.[9-12] Since these are the requisites for a good ligand for metal carbonyls, a study was made of the interaction of these anions with the hexacarbonyls of chromium, molybdenum, and tungsten and with iron pentacarbonyl.

Results and Discussion

The group VI metal carbonyls form adducts with a larger number of Lewis bases. These have been reviewed recently.[13] Methods for the preparation of these adducts from the parent carbonyl generally involved either thermal or photolytic activation.[14] This latter method of activation was readily applied to this study. The reaction of either $(C_6H_5)_4AsSnCl_3$ or $(C_6H_5)_4AsGeCl_3$ with the group VI hexacarbonyls was found to give high yields of the corresponding monosubstituted products

$$(C_6H_5)_4AsM'Cl_3 + M(CO)_6 \xrightarrow[CH_2Cl_2]{h\nu} (C_6H_5)_4AsM(CO)_5M'Cl_3 + CO$$

where M = Cr, Mo, or W and M′ = Sn or Ge.

In only one case was a disubstituted product isolated, $[(C_6H_5)_4As]_2Mo(CO)_4(GeCl_3)_2$, although evidence for the formation of the disubstituted products $[(C_6H_5)_4As]_2Mo(CO)_4(SnCl_3)_2$, $[(C_6H_5)_4As]_2W(CO)_4(GeCl_3)_2$, and $[(C_6H_5)_4As]_2W(CO)_4(SnCl_3)_2$ was obtained from infrared spectroscopy. However, the amount of these latter materials produced was too small to permit isolation *via* the fractional crystallization technique employed. In addition to the group VI hexacarbonyls, $Fe(CO)_5$ was found to react with both the $SnCl_3^-$ and $GeCl_3^-$ anions under similar conditions. The yields of the monosubstitution products $(C_6H_5)_4AsFe(CO)_4SnCl_3$ and $(C_6H_5)_4AsFe(CO)_4GeCl_3$, however, were much lower than for the other derivatives.

All of the products are yellow to orange solids which are stable in air for short periods of time. However, in solution they undergo oxidation rapidly. The complexes are soluble in polar organic solvents such as CH_2Cl_2, CH_3CN, and CH_3NO_2, and to a lesser extent in ether. No evidence for the presence of any hydridic hydrogen or paramagnetic impurities in the complexes was found by proton nmr. The molar conductance of all of the complexes in nitromethane was in the range of 60–70 for approximately 10^{-3} *M* solutions. This is indicative of 1:1 electrolyte behavior.[15]

The reaction of the complexes with triphenylphosphine was explored in an effort to obtain a comparison of the relative donor strengths of the $SnCl_3^-$ ion, the $GeCl_3^-$ ion, and triphenylphosphine. At room temperature in methylene chloride neither of the chromium or tungsten derivatives underwent reaction. However the molybdenum compounds did. The complex anions $Mo(CO)_5SnCl_3^-$ and $Mo(CO)_5GeCl_3^-$ were found to behave differently when treated with 1 equiv of triphenylphosphine. A stepwise displacement reaction apparently occurred. In the case of the germanium derivative it was possible to isolate the intermediate mixed adduct (I) in low yield

$$Mo(CO)_5GeCl_3^- + (C_6H_5)_3P \longrightarrow \underset{\text{I}}{cis\text{-}Mo(CO)_4GeCl_3(C_6H_5)_3P^-} + CO$$

$$\underset{\text{II}}{cis\text{-}Mo(CO)_4[(C_6H_6)_3P]_2} + GeCl_3^- \xleftarrow{(C_6H_5)_3P} \text{I}$$

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TABLE I

	Frequencies, cm^{-1}				Force constants, mdynes/A		
	A_1^2	A_1^1	B_1	E	k_1	k_2	k_i
$Cr(CO)_5SnCl_3^-$	2057 m	~1938	1970 w, sh	1938 vs	15.36	15.74	0.30
$Mo(CO)_5SnCl_3^-$	2070 m	~1948	1978 w, sh	1948 vs	15.52	15.92	0.30
$W(CO)_5SnCl_3^-$	2069 m	~1941	1983 w, sh	1941 vs	15.42	15.84	0.32
$Cr(CO)_5GeCl_3^-$	2059 m	~1937	1980 w, sh	1937 vs	15.35	15.74	0.30
$Mo(CO)_5GeCl_3^-$	2068 m	~1946	1985 w, sh	1946 vs	15.49	15.88	0.30
$W(CO)_5GeCl_3^-$	2067 m	~1936	1983 w, sh	1936 vs	15.35	15.77	0.32

When $(C_6H_5)_4AsMo(CO)_5SnCl_3$ was allowed to react with triphenylphosphine, only the bis-phosphine adduct (II) could be isolated even when an excess of the carbonyl derivative was employed. Treatment of either the tin or the germanium complex with 2 equiv of triphenylphosphine resulted in the formation of *cis*-$M(CO)_4[(C_6H_5)_3P]_2$ in almost quantitative yield. This difference in reactivity between the three group VI metals is not necessarily indicative of the difference in stability of the metal–metal bond in the complex. On the other hand, the isolation of $(C_6H_5)_4AsMo(CO)_4(GeCl_3)[(C_6H_5)_3P]$ perhaps suggests that the $GeCl_3^-$ ion is a better ligand, at least toward molybdenum, than is the $SnCl_3^-$ ion.

In order to better assess the ability of the $GeCl_3^-$ and $SnCl_3^-$ ions to act as ligands toward the group VI transition metals, the infrared spectra of the group VI complexes were analyzed according to the method of Cotton and Kraihanzel.[16] Although three infrared-active bands are expected in the carbonyl region for these complexes ($2\ A_1 + E$), for an idealized C_{4v} symmetry, it is apparent that only two of these three bands are directly observable. The third band observed in the spectra is probably the Raman-active B_1 band which is given some intensity due to a distortion from pure C_{4v} symmetry. The A_1^1 band (in Cotton's notation) is believed to be accidentally degenerate with the E mode. This degeneracy of the A_1^1 and E bands was also found for the monotriphenylphosphine adducts of chromium, molybdenum, and tungsten.[17] The above assignment is based on the calculated force constants because if the band, presently assigned to the B_1 band, is assigned as the A_1^1 mode then k_1 is found to be greater than k_2 for all of the complexes.[18] Since the band assigned to the B_1 mode appears in the spectra as a weak shoulder on the E mode, no attempt was made to calculate its frequency and compare it with the observed frequency due to the uncertainty in determining the latter. A summary of the data is presented in Table I.

Although the calculated force constants do not show a significant difference between the π-bonding ability of the two ligands $SnCl_3^-$ and $GeCl_3^-$, they do show a difference between the group VI metals (*e.g.*, the force constants for the molybdenum derivatives are higher than those of either the corresponding chromium or tungsten compounds). A similar difference in force constants was also observed for the monotriphenylphosphine adducts.[17] Furthermore, the reaction of the complexes prepared in this study with triphenylphosphine also demonstrates the uniqueness of the molybdenum compounds. A comparison of the force constants obtained in this study with Lewis base adducts shows that both anionic species appear to be quite similar to triphenylphosphine in π-bonding ability [*e.g.*, $k_1 = 15.50$ and $k_2 = 15.88$ mdynes/A for $Cr(CO)_5(C_6H_5)_3P$ and $k_1 = 15.57$ and $k_2 = 15.99$ mdynes/A for $Mo(CO)_5(C_6H_5)_3P$]. Although the actual numerical values of the force constants obtained by this method may not be completely reliable owing to the approximations in the force field they should offer a good basis for such relative comparisons for compounds containing the same central element. However, a comparison of the carbonyl stretching frequencies or force constants for isoelectronic species such as $Cr(CO)_5SnCl_3^-$–$Mn(CO)_5SnCl_3$[19] or $Cr(CO)_5X^-$–$Mn(CO)_5X$[17,20] (where X = Cl, Br, or I) is not as straightforward and must be made with more care.

The infrared spectra in the carbonyl region of the other adducts are tabulated in Table II. The appearance of four infrared-active carbonyl bands in the spectrum of the $Mo(CO)_4(GeCl_3)_2^{2-}$ ion is evidence that the $GeCl_3$ groups are *cis* to each other. The presence of an equal number of carbonyl bands in the spectrum of the mixed adduct $Mo(CO)_4(GeCl_3)(C_6H_5)_3P^-$ and the fact that it is easily converted to *cis*-$[(C_6H_5)_3P]_2Mo(CO)_4$ under mild conditions suggest that the two ligands are also *cis*. The appearance of only three carbonyl bands in the iron carbonyl derivatives suggests that the structure of these complexes is trigonal bipyramidal with the MCl_3 group bonded to an axial position.[21] Although the spectra lack a band required for the two possible isomers based on a tetragonal pyramidal structure, these possibilities cannot be completely eliminated since an accidental degeneracy or poor resolution is always possible.

TABLE II

Anion	Frequencies, cm^{-1}			
$Fe(CO)_4SnCl_3^-$	2039 ms	1959 w	1934 vs	
$Fe(CO)_4GeCl_3^-$	2042 ms	1961 m, sh	1935 vs	
$Mo(CO)_4(GeCl_3)_2^{2-}$	2018 w	1943 m	1914 s	1877 m
$Mo(CO)_4(GeCl_3)$-$(C_6H_5)_3P^-$	1025 ms	1948 w, sh	1917 vs	1880 m

As was the case with the group VI carbonyl deriva-

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TABLE III

ANALYTICAL DATA FOR COMPOUND PREPARATION

Compound	Mp, °C	Yield, %	Analyses, % Calcd C	Calcd H	Calcd Cl	Found C	Found H	Found Cl
$(C_6H_5)_4AsCr(CO)_5SnCl_3$	124–125	70	43.52	2.50	13.3	43.34	2.70	13.5
$(C_6H_5)_4AsMo(CO)_5SnCl_3$	120–121	77	41.23	2.37	12.6	41.06	2.44	12.6
$(C_6H_5)_4AsW(CO)_5SnCl_3$	129–130	70	37.35	2.15	11.5	37.18	2.29	11.6
$(C_6H_5)_4AsCr(CO)_5GeCl_3$	116–117	68	46.55	2.67	14.2	46.63	2.81	13.9
$(C_6H_5)_4AsMo(CO)_5GeCl_3$	110–112	56	43.63	2.51	13.3	43.87	2.74	13.3
$(C_6H_5)_4AsW(CO)_5GeCl_3$	110–111	74	39.30	2.25	12.0	39.60	2.41	12.3
$(C_6H_5)_4AsFe(CO)_4SnCl_3$	96–97	33	43.33	2.58	13.7	43.6	2.65	13.6
$(C_6H_5)_4AsFe(CO)_4GeCl_3$	113–114	32	46.01	2.74	14.6	46.06	2.97	14.9
$(C_6H_5)_4AsMo(CO)_4GeCl_3(C_6H_5)_3P$	162–163	8	53.53	3.39	10.3	53.38	3.20	10.5
$[(C_6H_5)_4As]_2Mo(CO)_4(GeCl_3)_2$	180–182	9	46.88	3.60	16.0	46.57	2.98	15.6

tives, little difference in the CO stretching frequencies is observed in changing from tin to germanium.

Experimental Section

Materials.—The tetraphenylarsonium salts of the $SnCl_3^-$ and $GeCl_3^-$ ions were prepared by the literature method.[8] The metal carbonyls were obtained from commercial sources.

Preparation of $(C_6H_5)_4AsM(CO)_5M'Cl_3$ Complexes.—The preparation for all the complexes involving the group VI metals was carried out in an identical manner. The analytical data, yields, etc., for these materials are presented in Table III. A typical preparation is described below. A 1.2-g sample of $(C_6H_5)_4AsGeCl_3$ was dissolved in 100 ml of CH_2Cl_2. The solution was irradiated for 20 minutes to reach thermal equilibrium before being attached to a gas-measuring system. Molybdenum hexacarbonyl, 1.5 g, was added. After 60 cc of gas at STP had been evolved, the mixture was stripped and the excess $Mo(CO)_6$ was sublimed away from the product. The residue was dissolved in 20 ml of CH_2Cl_2 and then 100 ml of ether was added. The solid 0.41 g which formed was filtered off. Pentane, 75 ml, was added to the initial filtrate. The product $(C_6H_5)_4AsMo(CO)_5GeCl_3$ (0.82 g) was precipitated. The initial solid was recrystallized twice from CH_2Cl_2 and ether to yield 0.15 g of $[(C_6H_5)_4As]_2Mo(CO)_4(GeCl_3)_2$. In the other cases where bisadduct formation was observed by infrared spectroscopy, the amount of the initial solid, ~0.1 g, was too small to permit successive recrystallizations.

Preparation of $(C_6H_5)_4AsFe(CO)_4MCl_3$ Complexes.—Both the germanium and the tin complexes were prepared in a similar manner. The analytical data are presented in Table III. A 1.2-g sample of $(C_6H_5)_4AsSnCl_3$ was dissolved in 100 ml of CH_3Cl_2. The solution was irradiated for 20 min to reach thermal equilibrium. Then 0.7 ml of $Fe(CO)_5$ was added. The irradiation was continued until 75 ml of gas was evolved. Then the mixture was stripped to dryness and the residue was extracted with 150 ml of ether. The extract was concentrated to 80 ml and pentane was added to precipitate the product.

Reaction of $(C_6H_5)_4AsMo(CO)_5M'Cl_3$ with $(C_6H_5)_3P$. A.—To 1.645 g of $(C_6H_5)_4AsMo(CO)_5SnCl_3$ in 25 ml of CH_2Cl_2, 0.525 g of $(C_6H_5)_3P$ in 10 ml of CH_2Cl_2 was added. The mixture was stirred for 2 hr at ambient temperature before it was stripped to dryness. The residue was dissolved in 20 ml of CH_2Cl_2 and 100 ml of ether was added. The white precipitate which formed was removed. It was found to be $(C_6H_5)_4AsSnCl_3$, 0.52 g. (*Anal.* Calcd for $(C_6H_5)_4AsSnCl_3$: Cl, 17.5. Found: Cl, 17.3). Pentane was added to the filtrate until light yellow crystals formed. The mixture was cooled and then filtered. A 0.623-g sample of $(C_6H_5)_4AsMo(CO)_5SnCl_3$ was obtained, mp 120°. The filtrate was stripped and extracted with 100 ml of ether. The extract was concentrated to 50 ml and pentane was added. A precipitate of 0.347 g of off-white crystals of *cis*-$Mo(CO)_4[(C_6H_5)_3P]_2$ was obtained.

B.—To 0.802 g of $(C_6H_5)_4AsMo(CO)_5GeCl_3$ in 25 ml of CH_2Cl_2, 0.265 g of $(C_6H_5)_3P$ in 10 ml of CH_2Cl_2 was added. The mixture was stirred for 3 hr at ambient temperature before it was stripped to dryness. The residue was dissolved in 10 ml CH_2Cl_2. Ether, 50 ml, was added and the mixture was cooled. A 0.53-g sample of solid was obtained. It was recrystallized twice from CH_2Cl_2–ether to yield 0.15 g of $(C_6H_5)_4AsMo(CO)_4GeCl_3(C_6H_5)_3P$. The filtrate from above was stripped to dryness and extracted with 50 ml of ether. Pentane was added to the extract and a 0.251-g sample of starting material precipitated. The addition of more pentane to the extract gave 0.15 g of *cis*-$Mo(CO)_4[(C_6H_5)_3P]_2$.

Infrared Spectra.—The infrared spectra were taken on solutions of the complexes in CH_2Cl_2 (concentrations about 8 mg/ml) using a Perkin-Elmer Model 521 spectrometer. The instrument was calibrated with indene.

Conductivity Measurements.—The conductivity of nitromethane solutions of the adducts was determined using equipment already described.[22] The specific conductivity of the nitromethane used was found to be 5.63×10^{-7}. The anion, concentration (*M*), and molar conductance (cm²/ohm equiv) are as follows: $Cr(CO)_5SnCl_3^-$, 1.285×10^{-3}, 64.5; $Cr(CO)_5GeCl_3^-$, 1.066×10^{-3}, 70.1; $Mo(CO)_5SnCl_3^-$, 1.057×10^{-3}, 72.9; $Mo(CO)_5GeCl_3^-$, 1.121×10^{-3}, 73.6; $W(CO)_5SnCl_3^-$, 1.030×10^{-3}, 63.7; $W(CO)_5GeCl_3^-$, 1.052×10^{-3}, 67.1; $Fe(CO)_4SnCl_3^-$, 1.001×10^{-3}, 68.5; and $Fe(CO)_4GeCl_3^-$, 9.864×10^{-4}, 71.6.

Acknowledgment.—This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract No. DA-01-021 AMC-11536(Z).

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