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The Chemistry of the Dinuclear Metal Carbonyl Anions. I. Insertion Reactions

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The anions $Cr_2(CO)_{10}^{2-}$ and $W_2(CO)_{10}^{2-}$ have been found to react with SnI_2, GeI_2, and SO_2 to produce products of the type $(CO)_5MSnI_2M(CO)_5^{2-}$, $(CO)_5MGeI_2M(CO)_5^{2-}$, and $(CO)_5MSO_2M(CO)_5^{2-}$, respectively. Indium(I) bromide behaved differently when treated with these anions and the mononuclear derivatives $M(CO)_5InBr_3^{2-}$ were obtained. The spectra of these compounds are discussed.

Insertion reactions in metal carbonyl chemistry have been recognized for several years. However, it was not until recently that this type of reaction has been utilized in the formation of metal–metal bonds. Two recent examples involve the dinuclear metal carbonyl derivatives that contain bridging carbonyl groups, $[C_5H_5Fe(CO)_2]_2$ and $Co_2(CO)_8$.[1-4] Insertion of $SnCl_2$, GeI_2, or InBr was found to occur readily to give products in which the nontransition metal was bonded to two transition metals, *e.g.*

$$Co_2(CO)_8 + GeI_2 \longrightarrow (CO)_4CoGeI_2Co(CO)_4$$

The insertion reaction did not occur when bridging carbonyl groups were absent as in $Mn_2(CO)_{10}$ and $[C_5H_5Mo(CO)_3]_2$.[4] This reaction has now been extended to include the dinuclear metal carbonyl anions $Cr_2(CO)_{10}^{2}$ and $W_2(CO)_{10}$.^{2} In addition, it has been found that SO_2 will insert in these anions in a similar manner.

Experimental Section

Materials.—The preparation of the starting materials followed the literature method[5] except that $[(C_6H_5)_3P]_2NCl$[6] or $(CH_3)_4NCl$ was employed instead of $(C_2H_5)_4NCl$. Germanium diiodide[7] and tin diiodide[8] were also prepared by the published methods. The sulfur dioxide was obtained from the Matheson Co. and used without further purification. The metal hexacarbonyls were obtained from Alfa Inorganics.

Preparation of $[((C_6H_5)_3P)_2N]_2M_2(CO)_{10}M'I_2$.—All four of the insertion products were prepared in the same manner. A typical example is given; to 1.41 g of $[((C_6H_5)_3P)_2N]_2Cr_2(CO)_{10}$ dissolved in 25 ml of CH_2Cl_2, a 0.33-g sample of GeI_2 was added. The mixture was stirred at ambient temperature for 0.5 hr and then filtered. The filtrate was evaporated to dryness and then dissolved in 10 ml of CH_2Cl_2. Ethyl acetate, 30 ml, was added and the mixture cooled. A 0.6-g sample of product crystallized out. The work-up of the reaction mixture when SnI_2 was used was slightly different. After filtering and evaporating the reaction mixture the residue was washed twice with small amounts of ether. Then it was extracted with 25 ml of hot ethanol. The product crystallized from the ethanol extract on cooling. All of the products are listed in Table I.

Preparation of $[((C_6H_5)_3P)_2N]_2M(CO)_5InBr_3$.—Both the tungsten and chromium derivatives were prepared in the same manner. A 1.46-g sample of $[((C_6H_5)_3P)_2N]_2Cr_2(CO)_{10}$ was dissolved in 40 ml of THF and 10 ml of CH_2Cl_2. Then 0.55 g of InBr was added and the mixture was stirred for 3 hr. The reaction mixture was dark gray presumably owing to the presence of metallic indium. After filtering the mixture, 100 ml of ether was added to the filtrate. Then pentane was added to precipitate the product. It was recrystallized from THF and CH_2Cl_2.

Preparation of $[(CH_3)_4N]_2M_2(CO)_{10}SO_2$.—Both of the metal derivatives were prepared in the same manner. A 0.75-g sample of $[(CH_3)_4N]_2W_2(CO)_{10}$ was dissolved in 75 ml of dry acetone and the solution was filtered to remove a small amount of residual solid. The solution was attached to the vacuum line and evacuated. Sulfur dioxide, 1.06 mmoles, was condensed into the mixture. The mixture was allowed to warm to ambient temperature and was stirred for 0.5 hr. It was then concentrated to 35 ml and filtered. The product, 0.31 g, was obtained.

Infrared Spectra.—The infrared spectra in the carbonyl region were obtained on solutions of approximately 0.010 g/ml of the compounds in methylene chloride or THF when the cation was $[(C_6H_5)_3P]_2N^+$ or in nitromethane when the cation was $(CH_3)_4N^+$. The instrument, a Perkin-Elmer Model 521 spectrometer, was calibrated with indene. The SO_2 bands were observed in spectra obtained on Nujol mulls using cesium bromide plates.

Conductivity Measurements.—The conductivity of the salts in nitromethane solution was determined using equipment previously described.[9] The specific conductivity of the nitromethane used was 5.63×10^{-7} ohm^{-1}. The anion, concentration (*M*), and equivalent conductance (cm^{-1}/ohm equiv) are as follows: $W(CO)_5InBr_3^{2-}$, 9.936×10^{-4}, 71.0; $Cr(CO)_5InBr_3^{2-}$, 1.028×10^{-3}, 68.1; $Cr_2(CO)_{10}GeI_2^{2-}$, 0.692×10^{-4}, 70.4; $Cr_2(CO)_{10}SnI_2^{2-}$, 1.024×10^{-3}, 67.7; $W_2(CO)_{10}GeI_2^{2-}$, 1.036×10^{-3}, 67.1; and $W_2(CO)_{10}SnI_2^{2-}$, 10.17×10^{-3}, 68.2.

Results and Discussion

The recently reported spectra of the dinuclear metal carbonyl anions,[5] $M_2(CO)_{10}^{2-}$ (M = Cr, Mo, or W), suggested the presence of bridging carbonyl groups in the complex anions. Thus, an investigation was begun to determine whether the chemistry of these anions would be similar to that of $Co_2(CO)_8$. It has been found that like $Co_2(CO)_8$ the dianions $Cr_2(CO)_{10}^{2-}$ and $W_2(CO)_{10}^{2-}$ will react with either SnI_2 or GeI_2 to give a product in which the nontransition metal moiety has inserted between the transition metals to produce anionic species containing metal–metal bonds. Analogous products were obtained with $SnCl_2$ but they were formed in only low yield and were difficult to purify.

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TABLE I

			Calcd, %				Found, %			
Compound	Mp, °C	Yield, %	C	H	N	X or S	C	H	N	X or S
$[((C_6H_5)_3P)_2N]_2Cr_2(CO)_{10}SnI_2$	168–171	40	53.7	3.27	1.53	13.9	53.9	3.21	1.62	13.5
$[((C_6H_5)_3P)_2N]_2Cr_2(CO)_{10}GeI_2$	177–179 dec	35	55.1	3.36	1.57	14.2	55.3	3.52	1.67	14.1
$[((C_6H_5)_3P)_2N]_2W_2(CO)_{10}SnI_2$	173–175	39	47.0	2.86	1.34	12.1	47.3	2.98	1.39	12.2
$[((C_6H_5)_3P)_2N]_2W_2(CO)_{10}GeI_2$	160–163	35	48.1	3.32	1.37	12.4	47.9	3.25	1.96	12.0
$[((C_6H_5)_3P)_2N]_2Cr(CO)_5InBr_3$	255–257	58	56.9	3.70	1.73	14.8	56.8	3.73	1.78	14.6
$[((C_6H_5)_3P)_2N]_2W(CO)_5InBr_3$	253–256	35	52.7	3.42	1.59	13.7	52.4	3.40	1.63	13.5
$[(CH_3)_4N]_2Cr_2(CO)_{10}SO_2$	Dec pt 130–140, without melting	36	36.3	4.03	4.70	5.37	36.5	4.12	4.63	5.49
$[(CH_3)_4N]_2W_2(CO)_{10}SO_2$	Dec pt 150–160, without melting	46	25.1	2.79	3.25	3.72	24.9	2.79	3.27	3.85

$$W_2(CO)_{10}^{2-} + MI_2 \longrightarrow (CO)_5WMI_2W(CO)_5^{2-}$$

$$Cr_2(CO)_{10}^{2-} + MI_2 \longrightarrow (CO)_5CrMI_2Cr(CO)_5^{2-}$$

$$(M = Sn \text{ or } Ge)$$

Therefore, complete characterization was not attempted.

An attempt was made to extend the insertion reaction to include indium(I) bromide since it will insert between the Co–Co bond in $Co_2(CO)_8$.[2] This attempt was not successful and the dinuclear metal carbonyl anions were destroyed. The products that were isolated contain an $M(CO)_5^{2-}$ group bonded to $InBr_3$ (alternately, this can be considered as an $M(CO)_5$ group bonded to a $InBr_3^{2-}$ moiety).

$$M_2(CO)_{10}^{2-} + 6InBr \xrightarrow{THF} 2M(CO)_5InBr_3^{2-} + 4In$$

It is not known whether the product arises from reaction of the dianion directly with InBr or by reaction with $InBr_3$ produced by the disproportionation of InBr. The latter mode appears attractive since treatment of the dianions $Cr_2(CO)_{10}^{2-}$ or $W_2(CO)_{10}^{2-}$ directly with $InBr_3$ produced the product in yields similar to that obtained using excess InBr. Small amounts of $[(C_6H_5)_3P]_2NCr(CO)_5Br$ were also formed. If either BCl_3 or BF_3 were used in place of $InBr_3$, no related products could be isolated. Instead only low yields of the monoprotonated anions, $M_2H(CO)_{10}^-$, were formed. The source of the hydrogen is not known.

Sulfur dioxide was found to react with the dianions $Cr_2(CO)_{10}^{2-}$ and $W_2(CO)_{10}^{2-}$ to give anionic insertion products in moderate yield. The chromium derivative

$$M_2(CO)_{10}^{2-} + SO_2 \xrightarrow{acetone} M(CO)_5SO_2M(CO)_5^{2-}$$

was extremely sensitive to oxygen, turning green on only brief exposure to the atmosphere. The tungsten compound was considerably less reactive. When the above reactions (*e.g.*, reaction of SnI_2, GeI_2, InBr, and SO_2 with $M_2(CO)_{10}^{2-}$) were attempted using the molybdenum-containing dianion, no pure products could be obtained. Evidence for product formation was found by infrared spectroscopy but isolation of the specific species was not possible.

The six new halogen-containing salts are yellow to orange solids, soluble in nitromethane, chloroform, and methylene chloride but insoluble in ether or aromatic solvents. Although they may be handled in air for brief periods of time, they undergo oxidation in solution quite rapidly. No evidence was found for any hydridic hydrogen or paramagnetic impurities by proton nmr. The equivalent conductance of the salts in nitromethane assuming that they are 1:2 electrolytes falls in the expected range of 60–70 for solutions approximately 10^{-3} *M* in concentration. The infrared spectra in the carbonyl region of the new derivatives obtained in CH_2Cl_2 solution are summarized in Table II.

TABLE II

Anion	Frequencies, cm^{-1}			
$Cr_2(CO)_{10}GeI_2^{2-}$	2037 m	1969 w, sh	1933 s	1898 m, sh
$Cr_2(CO)_{10}SnI_2^{2-}$	2051 m	1968 w, sh	1911 vs	1857 s
$W_2(CO)_{10}GeI_2^{2-}$	2050 m	1969 w, sh	1933 s	1898 m
$W_2(CO)_{10}SnI_2^{2-}$	2063 w	1971 w, sh	1923 vs	1850 m
$Cr(CO)_5InBr_3^{2-}$	2015 m	1891 vs	1863 m, sh	
$W(CO)_5InBr_3^{2-}$	2035 m	1904 vs	1865 ms, sh	
$Cr_2(CO)_{10}SO_2^{2-}$	2048 m	1979 w, sh	1941 vs	1888 ms
$W_2(CO)_{10}SO_2^{2-}$	2060 m	1985 w, sh	1937 vs	1882 ms

Although the structures of the products obtained from the reaction of the dianions $Cr_2(CO)_{10}^{2-}$ and $W_2(CO)_{10}^{2-}$ with SnI_2, GeI_2, or SO_2 are not known, the lack of CO evolution during preparation and the apparent simplicity of their infrared spectra in the carbonyl region suggest that insertion of the noncarbonyl reactant between the transition metals has occurred. Half or less than half of the expected number of carbonyl stretching frequencies are observed. This suggests that no coupling occurs between the two $M(CO)_5$ groups[10] which is in contrast with the situation found for species of the type $Co(CO)_4SnR_2Co(CO)_4$[11] or $Mn(CO)_5SnR_2Mn(CO)_5$.[12] If it is assumed that the use of an idealized site symmetry (C_{4v}) for the CO groups is justified, then three active bands (2 A + E) would be expected. In addition, a Raman-active band might be expected at low intensity if distortion from pure C_{4v} occurs. Thus the band at highest frequency is assigned to one of the A_1 modes while the strongest band is assigned to the E mode. The band at lowest frequency is probably the other A_1 mode but since this mode is known to shift considerably, this assignment must be tentative. The bands around 1970–1980 cm^{-1}

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[10] It is possible that the coupling was not observed owing to a lack of resolution in both CH_2Cl_2 and THF solutions although the solid-state spectra show only minor splitting of the strongest band.

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in the spectra of the insertion products are probably due to the B mode. Two comparisons can be made. Since the carbonyl stretching frequencies for the $Cr(CO)_5SnCl_3^-$ and $W(CO)_5SnCl_3^-$ ions occur at higher wavenumbers than for $Cr(CO)_5SnI_2Cr(CO)_5^{2-}$ and the corresponding tungsten compound, the $SnCl_3^-$ group appears to be a better π acceptor than the $SnI_2M(CO)_5^-$ group as would be expected. Furthermore a comparison of the carbon stretching frequencies for the isoelectronic species $Cr(CO)_5SnX_3^-$ and $Cr(CO)_5InX_3^{2-}$ and $W(CO)_5SnX_3^-$ and $W(CO)_5InX_3^{2-}$ suggests that the SnX_3^- group is a better π acceptor than InX_3^{2-}. However, since the halogens employed in both cases differ, these conclusions may have to be qualified, although very little differences were noted in the carbonyl stretching frequencies of $Mn(CO)_5SnCl_3$ and $Mn(CO)_5SnBr_3$ and the corresponding rhenium compounds.[13]

The infrared spectra of the two products obtained from the dianions and sulfur dioxide contained, in addition to the above-listed carbonyl bands and bands due to the tetramethylammonium ion, three distinct bands at 1138 (m), 980 (m), and 504 (w) cm^{-1} and 1138 (m), 978 (m), and 504 (w) cm^{-1} for the chromium and tungsten derivatives, respectively. These bands are quite close to those observed in the spectrum of the complex $K_6[(CN)_5CoSO_2Co(CN)_5]$[14] at 1076 (s), 984 (s), and 533 (m) and 525 (m) cm^{-1} which are assigned to the asymmetric and symmetric S–O stretching frequencies and the SO_2 bending frequency, respectively. The observed spectra are indicative of bidentate bonding for the SO_2 group. The absence of a band in the 1300–1350-cm^{-1} region which has been assigned to monodentate SO_2 (and confirmed by X-ray studies in $Ru(NH_3)_5SO_2Br_2$[15]) further supports the assumed structure for the complex anions.

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Kinetic Studies of Group VI Metal Carbonyl Complexes. VI. Substitution Reactions of the Group VI Metal Hexacarbonyls.

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Hexacarbonyl complexes of the group VI transition metals react with phosphine and phosphite ligands, L, in decalin solvent according to the equation: $M(CO)_6 + L \rightarrow M(CO)_5L + CO$. The rate of reaction is governed by the two-term rate law: rate $= k_1[M(CO)_6] + k_2[L][M(CO)_6]$. SN1 and SN2 types of reaction mechanisms are proposed to account for the two terms. Positive ΔS_1^* values for the k_1 paths and negative ΔS_2^* values for the k_2 paths support the proposed mechanisms. The values of ΔH_1^* for the k_1 path decrease in the order: $Cr(CO)_6 \sim W(CO)_6 > Mo(CO)_6$. The magnitude of the second-order rate constants, k_2, was found to be a function of the basicity of the ligand, L, and increases as follows: $As(C_6H_5)_3 < P(OC_6H_5)_3 < P(C_6H_5)_3 < P(OCH_2)_3CC_2H_5 < P(OC_2H_5)_3 < P(n\text{-}C_4H_9)_3$. A comparison of k_2/k_1 ratios for the reaction of the hexacarbonyl complexes with $P(n\text{-}C_4H_9)_3$ suggests that the SN2 path becomes more preferred as the size of the metal atom increases from Cr to Mo to W.

Introduction

Recently several kinetic studies of the substitution and exchange reactions of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ have been reported. Pajaro, Calderazzo, and Ercoli[1] followed the rate of exchange of ^{14}CO with $Cr(CO)_6$ in the gas phase while Cetini and Gambino[2,3] carried out similar studies on the hexacarbonyl complexes of Mo and W. At the time that the present study was in progress Werner and Prinz[4,5] reported a kinetic study of the reactions of $M(CO)_6$ (where M = Cr, Mo, or W) with L (where L is a phosphine or amine) to form $M(CO)_5L$ using a mixture of *n*-decane and cyclohexane as the reaction solvent. Both the results from the ^{14}CO-exchange study and the study conducted in solution indicated that the hexacarbonyl complexes of the group VI metals react with L at a rate which is governed by a simple first-order rate law

$$\text{rate} = k[M(CO)_6] \qquad (1)$$

A more recent study of the reaction of $Mo(CO)_6$ with L conducted in these laboratories[6] indicated that $Mo(CO)_6$, with the proper choice of ligand and ligand concentration, reacted with phosphines and phosphites at a rate

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