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Seven-Coordinate Carbonyl Complexes of Molybdenum(II) and Tungsten(II)

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Tetrabutylammonium trihalogenotetracarbonylmolybdate(II) and -tungstate(II) undergo substitution reactions with triphenylphosphine and with a variety of phosphorus-, arsenic-, and sulfur-donor polydentate ligands to yield seven-coordinate molybdenum(II) and tungsten(II) carbonyl complexes. The interaction of equimolar amounts of $P(C_6H_5)_3$ with $(R_4N)[M(CO)_4I_3]$ (M = Mo and W) yields $(R_4N)[M(CO)_3I_3(P(C_6H_5)_3)]$; all bidentate ligands (L-L) afford $M(CO)_3(L\text{-}L)X_2$ (X = Br and I); tridentate ligands (L-L-L) give $M(CO)_2(L\text{-}L\text{-}L)X_2$, except 1,1,1-tris(diphenylphosphinomethyl)ethane (PPP), which yields $M(CO)_3(PPP)X_2$, with one phosphorus uncoordinated; and tetradentate ligands, $L\text{-}L_3$, afford $M(CO)_2(L\text{-}L_3)X_2$, with only three donor atoms of the tetradentate participating in bonding. The properties of these complexes, their infrared carbonyl stretching frequencies, and their proton magnetic resonance spectra are listed and, where appropriate, discussed in the context of structural assignments.

Introduction

The most common synthetic procedures for seven-coordinate metal carbonyl complexes have utilized (a) halogen oxidation of substituted metal carbonyls[1-7] and (b) interaction of metal carbonylates with halogen-containing species.[8,9] Thus, for example, bromine oxidation of $Mo(CO)_4$(diphos) (diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) in dichloromethane yields $Mo(CO)_3(\text{diphos})Br_2$,[2] and treatment of $V(CO)_6^-$ with $(C_6H_5)_3PAuCl$ affords $(C_6H_5)_3PAuV(CO)_6$.[8] More recently, the carbonyl halides $[M(CO)_4X_2]_2$ (M = Mo, W; X = Cl, Br) have been synthesized[10-12] and their substitution reactions with several monodentate (L) and bidentate (L-L) ligands have been reported to give $M(CO)_3L_2X_2$ and $M(CO)_3(L\text{-}L)X_2$, respectively.[10-13]

Our interest in the stereochemistry of seven-coordinate complexes prompted us to explore different preparative routes to new derivatives of metal carbonyls possessing this coordination number. A particularly attractive complementary feature appeared to be the use of polydentate ligands, since one ligand molecule may bond to several sites in a complex and should facilitate elucidation of structures of the seven-coordinate complexes. Reported in this paper are substitution reactions of the anions $M(CO)_4X_3^-$ (M = Mo, W; X = Br, I) with various mono-, bi-, tri-, and tetradentate phosphorus-, arsenic-, and sulfur-donor ligands, resulting in the synthesis of seven-coordinate molybdenum(II) and tungsten(II) compounds.

Experimental Section

Materials.—Halogenopentacarbonyl anions of molybdenum(0) and tungsten(0) were prepared from tetrabutylammonium halides and molybdenum or tungsten hexacarbonyl as described by Abel, *et al.*[14] The appropriate anions were then oxidized with halogens to give tetrabutylammonium trihalogenotetracarbonylmolybdate(II) or -tungstate(II), $[(n\text{-}C_4H_9)_4N][M(CO)_4X_3]$, where M = Mo or W and X = Br or I, according to the method of Ganorkar and Stiddard.[4] Tetrabutylammonium bromodiiodotetracarbonyltungstate(II) was prepared by oxidizing tetrabutylammonium bromopentacarbonyltungstate(0) with an equimolar quantity of iodine.[4] Tris(acetonitrile)tricarbonylmolybdenum(0) was obtained[15] by refluxing molybdenum hexacarbonyl in excess acetonitrile for 4 hr. Cycloheptatrienetricarbonylmolybdenum was synthesized[16] by refluxing cycloheptatriene and molybdenum hexacarbonyl and then purified by sublimation. Vanadium hexacarbonyl was prepared[17] by acidifying bis(diglyme)sodium hexacarbonylvanadate(−I) (Alfa Inorganics, Inc.) and then purified by sublimation.

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(1) J. Lewis, R. S. Nyholm, C. S. Pande, and M. H. B. Stiddard, *J. Chem. Soc.*, 3600 (1965).
(2) J. Lewis and R. Whyman, *ibid.*, 5486 (1965).
(3) J. Lewis and R. Whyman, *ibid.*, *A*, 77 (1967).
(4) M. C. Ganorkar and M. H. B. Stiddard, *ibid.*, 3494 (1965).
(5) R. B. King, *Inorg. Chem.*, **3**, 1039 (1964).
(6) R. S. Nyholm, M. R. Snow, and M. H. B. Stiddard, *J. Chem. Soc.*, 6570 (1965).
(7) W. J. Kirkham, A. G. Osborne, R. S. Nyholm, and M. H. B. Stiddard, *ibid.*, 550 (1965).
(8) A. S. Kasenally, R. S. Nyholm, R. J. O'Brian, and M. H. B. Stiddard, *Nature*, **204**, 871 (1964).
(9) K. A. Keblys and M. Dubeck, *Inorg. Chem.*, **3**, 1646 (1964).
(10) R. Colton and I. B. Tomkins, *Australian J. Chem.*, **19**, 1143 (1966).
(11) R. Colton and I. B. Tomkins, *ibid.*, **19**, 1519 (1964).
(12) M. W. Anker, R. Colton, and I. B. Tomkins, *ibid.*, **20**, 9 (1967).
(13) R. Colton and I. B. Tomkins, *ibid.*, **20**, 13 (1967).
(14) E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 2068 (1963).
(15) D. P. Tate, W. R. Knipple, and J. M. Augl, *Inorg. Chem.*, **1**, 433 (1962).
(16) E. W. Abel, M. A. Bennett, R. Burton, and G. Wilkinson, *J. Chem. Soc.*, 4559 (1958).
(17) R. Ercoli, F. Calderazzo, and A. Alberola, *J. Am. Chem. Soc.*, **82**, 2965 (1960).

TABLE I

DETAILS OF SYNTHESIS, ANALYTICAL DATA, AND PHYSICAL PROPERTIES OF THE COMPLEXES

		Approx reacn time,	Alcohol used	Yield,	Analyses, %								Mp (dec),	Λ_M,[b]
					Calcd				Found					cm²/
No.	Compound[a]	hr	in crystn	%	C	H	X	O	C	H	X	O	°C	ohm *M*
I	$[(n\text{-}C_4H_9)_4N][Mo(CO)_3I_3(P(C_6H_5)_3)]$[c]	1	Ethyl	62	41.67	4.79	35.76	4.51	41.61	4.92	36.57	4.44	155	(93.3)
II	$Mo(CO)_3(diphos)I_2$[d]	1	Ethyl	60	41.83	2.88	30.53	5.77	41.85	2.98	30.67	5.61	190	(13.6), 1.13
III	$Mo(CO)_3(diars)I_2$	1	Ethyl	45	37.83	2.61	27.61	5.22	37.97	2.86	27.66	5.25	140	(9.02)
IV	$Mo(CO)_3(AP)Br_2$	1.5	Methyl	53	47.71	2.89	19.28	5.78	47.61	3.06	19.42	5.93	194	0.79
V	$Mo(CO)_3(AP)I_2$	1.5	Methyl	60	42.86	2.60	27.49	5.19	43.02	2.55	27.78	5.37	160	1.2
VI	$Mo(CO)_3(SP)I_2$	0.5	Methyl	59	35.58	2.29	34.23	6.47	35.76	2.03	33.99	6.54	160	0.95
VII	$Mo(CO)_2(DSP)Br_2$	4	Methyl	68	39.63	2.85		4.80	39.81	2.84		4.93	175	1.49
VIII	$Mo(CO)_2(DSP)Br_2\cdot CH_3OH$				39.54	3.29	22.89		39.80	3.23	22.9			
IX	$Mo(CO)_2(DSP)I_2\cdot CH_3OH$	3	Methyl	65	34.84	2.90	32.06	6.06	34.88	2.90	31.91	5.87	160	0.55
X	$Mo(CO)_2(DSA)Br_2$	4	Methyl	37	37.18	2.68	22.51		37.32	2.82	22.23		185	*e*
XI	$Mo(CO)_2(DSA)I_2\cdot CH_3OH$[f]	15	Methyl	34	33.01	2.75	30.38	5.74	33.0	2.61	31.52	5.61	156	1.74
XII	$Mo(CO)_3(PPP)I_2$				49.91	3.69	24.01	4.54	50.20	3.90	23.82	4.56	130	(25.3), 4.11
XIII	$Mo(CO)_2(TSP)I_2$				34.23	2.60	31.50		34.42	2.75	31.22			1.99
XIV	$[(n\text{-}C_4H_9)_4N][W(CO)_3I_3(P(C_6H_5)_3)]$[c]	2	Ethyl	64	38.51	4.42	33.04	4.16	38.54	4.24	33.22	4.20	198	20
XV	$W(CO)_3(diphos)I_2\cdot CH_2Cl_2$[d]	3	Methyl	46	35.82	2.59	25.27	4.78	35.63	2.56	25.24	4.76	195	1.02
XVI	$W(CO)_3(diars)I_2\cdot CH_2Cl_2$	8	Methyl	56	32.94	2.38	23.24	4.39	32.49	2.22	23.40	4.47	200	0.36
XVII	$W(CO)_3(AP)I_2$	4	Methyl	59	39.13	2.37	25.10	4.74	39.01	2.50	24.96	4.61	242	1.46
XVIII	$W(CO)_3(SP)I_2$				31.81	2.05	30.60	5.78	32.02	1.90	30.48	5.93	150	(13.3)
XIX	$W(CO)_2(DSP)Br_2$	18	Methyl	25	35.01	2.51	21.19		34.92	2.38	21.44		199	0.59
XX	$W(CO)_2(DSP)BrI$				32.95	2.37	15.85 (I)		33.03	2.39	15.76 (I)		200	*e*
XXI	$W(CO)_3(PPP)BrI$				48.05	3.55	11.56 (I)		47.27	3.68	14.15 (I)		167	4.75
XXII	*cis*-$Mo(CO)_3(DSP)$				51.66	3.56		8.98	51.91	3.61		9.10	188	
XXIII	*cis*-$Mo(CO)_3(TSP)$				49.63	3.62		8.27	49.93	4.43		8.39	198	
XXIV	*cis*-$Mo(CO)_3(TAP)$				60.87	3.74		4.27	60.55	3.52		4.33	278	
XXV	$V(CO)_3(PPP)I$				59.59	4.40	14.33		57.26	4.72	14.12			

[a] All of the compounds are diamagnetic. [b] For approximately 10^{-3} *M* nitromethane (values in parentheses) or nitrobenzene solutions at 25°. [c] The anion was prepared earlier and isolated as the triphenylphosphonium salt.[3] [d] The compound was reported previously.[2] [e] The compound is sparingly soluble in organic solvents. [f] Excess ligand was used.

Triphenylphosphine, bis(1,2-diphenylphosphino)ethane (diphos), bis(1,2-diphenylarsino)ethane (diars) (Alfa Inorganics, Inc.), and 1,1,1-tris(diphenylphosphinomethyl)ethane (PPP) (Orgmet, Inc.) were purchased and used without further purification. Diphenyl(*o*-diphenylarsinophenyl)phosphine (AP),[18] diphenyl(*o*-methylthiophenyl)phosphine (SP),[19] phenylbis(*o*-methylthiophenyl)phosphine (DSP),[20] tris(*o*-methylthiophenyl)phosphine (TSP),[21] and tris(*o*-diphenylarsinophenyl)phosphine (TAP)[22] were prepared by established procedures.

Dichloromethane, methanol, petroleum ether (bp 30–60°), hexane, absolute ethyl alcohol, and anhydrous ether were analytical reagent grade chemicals.

Synthesis of Phenylbis(*o*-methylthiophenyl)arsine, $C_6H_5As(o\text{-}C_6H_4SCH_3)_2$ (DSA).—The reaction of *o*-mercaptoaniline with sodium and iodomethane, as described by Livingstone,[23] gave *o*-aminothioanisole in 87% yield. This compound was converted to *o*-bromothioanisole in 57% yield by the method Brand and Stallman.[24] A solution of *n*-butyllithium (1.72 g) in hexane (16.6 ml total volume) was added dropwise at 0° to a solution of *o*-bromothioanisole (5.46 g) in 3.6 ml of anhydrous ether. After complete addition, the mixture was stirred at room temperature for 1 hr. Then, phenyldichloroarsine (3 g) in 7 ml of anhydrous ether was added dropwise with stirring. After complete addition, the mixture was stirred at room temperature for 2 hr. The reaction mixture was then hydrolyzed with 2.8 ml of water followed by 5.3 ml of saturated ammonium chloride solution. The white solid was collected on a filter, washed with ethanol, dried, and finally recrystallized from 1-butanol (mp 120°); yield 4.5 g (84%). *Anal.* Calcd for $C_{20}H_{19}AsS_2$: C, 60.30; H, 4.77; As, 18.84. Found: C, 60.32; H, 4.96; As, 18.72.

General Procedure for Preparation of Complexes I–XIX (Except XII, XIII, and XVIII).—The seven-coordinate trihalogenotetracarbonyl complexes of molybdenum(II) or tungsten(II) (1 g) were stirred with an equimolar quantity of the appropriate ligand in dichloromethane at 25° and under nitrogen until the evolution of carbon monoxide ceased. Approximate reaction times are listed in Table I. The resulting mixture was filtered, the filtrate was concentrated in a stream of nitrogen, and then alcohol (specified in Table I) was added. The crystals, which formed on standing, were filtered off by suction and washed with petroleum ether. The filtrate was evaporated to dryness and the infrared spectra of the solid residues showed the presence of tetrabutylammonium iodide or bromide.

Reaction of $[(n\text{-}C_4H_9)_4N][Mo(CO)_4I_3]$ with a Twofold Excess of Triphenylphosphine.—One gram of tetrabutylammonium triiodotetracarbonylmolybdate(II) was stirred with 0.63 g of triphenylphosphine in dichloromethane for 4 hr under nitrogen. The solution was filtered and concentrated, and to this methanol was added. Yellow crystals were deposited. The crystals became pale yellow to white on repeated recrystallization from dichloromethane–methanol. Infrared spectroscopy[25] and elemental analyses identified this product as *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$; yield 0.25 g (28.4%). *Anal.* Calcd for $C_{40}H_{30}MoO_4P_2$: C, 65.57; H, 4.10. Found: C, 65.51; H, 4.05.

Preparation of $W(CO)_3(SP)I_2$ (XVIII).—One gram of tetrabutylammonium triiodotetracarbonyltungstate(II) was stirred under nitrogen with 0.335 g of SP for 30 min in 50 ml of dichloromethane. The solution was filtered and white crystals were deposited when diethyl ether was added to the reaction mixture. Infrared spectroscopy confirmed that the white crystals were tetrabutylammonium iodide. After filtration, more diethyl ether was added to the filtrate and an orange-red oil separated. The oil was separated by decantation and dried in a stream of nitrogen. Small amounts of methanol were added and orange-red crystals were deposited. The crystals were collected on a filter and washed with petroleum ether; yield 0.3 g (33%).

Preparation of $W(CO)_2(DSP)BrI$ (XX).—One gram of tetrabutylammonium bromodiiodotetracarbonyltungstate(II) was stirred with 0.5 g of DSP in 50 ml of dichloromethane for 24 hr under nitrogen. The reaction mixture was filtered, the filtrate was concentrated to 6 ml, and then methanol was added. Red crystals were deposited; yield 0.19 g (21%).

Preparation of *cis*-$Mo(CO)_3(DSP)$ (XXII).—The tricarbonyl

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[18] P. Nicpon and D. W. Meek, *Inorg. Chem.*, **6**, 145 (1967).

[19] S. E. Livingstone and T. N. Lockyer, *Inorg. Nucl. Chem. Letters*, **3**, 35 (1967).

[20] M. O. Workman, G. Dyer, and D. W. Meek, *Inorg. Chem.*, **6**, 1404 (1967).

[21] G. Dyer and D. W. Meek, *ibid.*, **4**, 1398 (1965).

[22] T. E. W. Howell, S. A. J. Pratt, and L. M. Venanzi, *J. Chem. Soc.*, 3167 (1961).

[23] S. E. Livingstone, *ibid.*, 437 (1956).

[24] K. Brand and O. Stallman, *Chem. Ber.*, **54**, 1578 (1921).

[25] R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962).

$(CH_3CN)_3Mo(CO)_3$ (0.822 g) was refluxed under nitrogen with 0.96 g of DSP in acetonitrile (50 ml) for 5 min. The resulting yellow solution was filtered and evaporated to dryness. The yellow residue was recrystallized from dichloromethane–methanol; yield 0.7 g (36%).

Reaction of *cis*-$Mo(CO)_3$(DSP) with Iodine.—*cis*-$Mo(CO)_3$(DSP) (0.5 g) and iodine (0.238 g) were allowed to react in 50 ml of dichloromethane for 16 hr under nitrogen. The resulting red solution was filtered and the filtrate was concentrated to about 6 ml. Upon addition of methanol, orange-red crystals of $Mo(CO)_2(DSP)I_2 \cdot CH_3OH$ were formed.

Reaction of $[(n\text{-}C_4H_9)_4N][Mo(CO)_4I_3]$ with $CH_3C[CH_2P(C_6H_5)_2]_3$.—Tetrabutylammonium triiodotetracarbonylmolybdate(II) (0.8 g) was mixed with 0.581 g of 1,1,1-tris(diphenylphosphinomethyl)ethane in dichloromethane under nitrogen. After 2 hr, the solution became orange-red. It was then filtered and concentrated. Upon addition of methanol, a pink precipitate formed and was filtered off. The filtrate was concentrated and chilled at −20°, yielding yellow crystals; yield 0.33 g. The compound was identified by elemental analyses, electrical conductivity, and infrared spectroscopy to be $Mo(CO)_3(PPP)I_2$.

The pink product was purified by chromatography on an alumina column using dichloromethane as eluent. White crystals were obtained upon removal of the solvent; yield 0.31 g. This complex was identified as *cis*-$Mo(CO)_3$(PPP), previously reported by Chatt and Watson.[26] *Anal.* Calcd for $C_{44}H_{39}MoO_3P_3$: C, 65.7; H, 4.85; O, 5.97. Found: C, 65.8; H, 4.86; O, 6.07.

Reaction of $[(n\text{-}C_4H_9)_4N][W(CO)_4BrI_2]$ with $CH_3C[CH_2P(C_6H_5)_2]_3$.—Tetrabutylammonium bromodiiodotetracarbonyltungstate(II) (1.008 g) and 1,1,1-tris(diphenylphosphinomethyl)ethane (0.72 g) were dissolved in 50 ml of dichloromethane under nitrogen. The solution became brown over a period of 5 hr. The mixture was then filtered and the filtrate was concentrated to 6 ml before addition of methanol. Yellow crystals of $W(CO)_3$(PPP)BrI were deposited on cooling the solution to −20° overnight. They were filtered off and washed with petroleum ether; yield 0.87 g (69%).

Reaction of $[(n\text{-}C_4H_9)_4N][Mo(CO)_4Br_3]$ with $CH_3C[CH_2P(C_6H_5)_2]_3$.—Tetrabutylammonium tribromotetracarbonylmolybdate(II) (1 g) was added to 0.9 g of 1,1,1-tris(diphenylphosphinomethyl)ethane in 50 ml of dichloromethane under nitrogen. A large amount of gas (presumably carbon monoxide) was evolved immediately and the solution turned dark purple. The mixture was stirred at room temperature for 2 hr and filtered. The filtrate was concentrated to 6 ml and then methanol was added. A pale pink solid was deposited; it was collected on a filter and washed first with methanol and then with petroleum ether. The product was identified by infrared spectroscopy[26] as *cis*-$Mo(CO)_3$(PPP). Its purification was effected by chromatography on an alumina column using dichloromethane as eluent; yield 0.61 g (52%).

Preparation of *cis*-$Mo(CO)_3$(PPP).—(a) Tris(acetonitrile)tricarbonylmolybdenum(0) (0.4 g) was stirred with 0.83 g of 1,1,1-tris(diphenylphosphinomethyl)ethane in 50 ml of dichloromethane for 16 hr under nitrogen. The mixture was filtered and the filtrate was concentrated in a stream of nitrogen. The white crystals were collected on a filter and washed with methanol; yield 0.68 g (64%).

(b) Cycloheptatrienetricarbonylmolybdenum (0.388 g) and 1,1,1-tris(diphenylphosphinomethyl)ethane (0.89 g) were refluxed in 50 ml of dichloromethane for 5 hr under nitrogen. The solution changed from red to orange; it was filtered and concentrated to 10 ml. White crystals were collected on a filter and washed with methanol; yield 0.85 g (74%).

Reaction of *cis*-$Mo(CO)_3$(PPP) with Iodine.—Iodine (0.228 g) in 40 ml of dichloromethane was added dropwise to 0.723 g of *cis*-$Mo(CO)_3$(PPP) in 20 ml of dichloromethane. After 3 hr the resulting brown solution was filtered and concentrated to 6 ml; then 30 ml of methanol was added giving a light purple precipitate (0.34 g). After chromatographing this material on an alumina column using dichloromethane as eluent, white crystals of the unreacted *cis*-$Mo(CO)_3$(PPP) were obtained. The filtrate was concentrated to 20 ml and then cooled to −20°, affording yellow crystals of $Mo(CO)_3(PPP)I_2$; yield 0.2 g (21%).

Reaction of $[(n\text{-}C_4H_9)_4N][Mo(CO)_4I_3]$ with TSP.—Tetrabutylammonium triiodotetracarbonylmolybdate(II) (0.83 g) was refluxed under nitrogen with 0.4 g of TSP in dichloromethane (50 ml). The solution became dark red after about 1.5 hr. It was then filtered and concentrated, and methanol was added. Dark brown powder was deposited on chilling the filtrate at −15° overnight. The solid was filtered off, and on concentrating the filtrate, purple powder was deposited. Infrared spectroscopy, electrical conductivity, and elemental analyses identified the latter as $Mo(CO)_2(TSP)I_2$; yield 0.2 g (24.8%). The dark brown powder was shown by infrared spectroscopy to be impure $Mo(CO)_2(TSP)I_2$.

Preparation of *cis*-$Mo(CO)_3$(TSP) (XXIII).—Tris(acetonitrile)tricarbonylmolybdenum(0) (0.85 g) was dropped into a warm suspension of 1.12 g of TSP in 50 ml of acetonitrile under nitrogen, giving immediately a clear yellow solution. After this solution was refluxed for 2 hr, the solvent was evaporated under reduced pressure. The resulting yellow paste was extracted with dichloromethane. The extract was filtered and concentrated in a stream of nitrogen, and methanol was added. Bright yellow crystals separated; yield 0.86 g (53%).

Preparation of *cis*-$Mo(CO)_3$(TAP) (XXIV).—Tris(acetonitrile)tricarbonylmolybdenum(0) (0.3 g) was dropped into a warm suspension of 0.944 g of TAP in 50 ml of acetonitrile under nitrogen. After refluxing for 15 min, the suspension turned into a clear yellow solution. Continued refluxing for *ca.* 1.5 hr resulted in the formation of a yellow precipitate, which was collected on a filter and recrystallized from dichloromethane–methanol; yield 0.7 g (63%).

Preparation of $V(CO)_3$(PPP)I (XXV).—Vanadium hexacarbonyl (0.312 g) was introduced into a suspension of powdered PPP (0.89 g) in hexane (35 ml) under nitrogen. A bright yellow precipitate started forming gradually. After about 1 hr, iodine (0.181 g) in hexane (25 ml) was added dropwise to the suspension. The bright yellow precipitate turned darker yellow. The suspension was stirred for about 30 min; the precipitate was filtered off and dried on filter paper inside a dry, nitrogen atmosphere box. The yield was 1.03 g (81.5%).

Melting Points.—Melting points were determined in sealed capillary tubes and were not corrected.

Infrared Spectra.—Spectra of dichloromethane solutions were recorded in the metal carbonyl stretching region on a Beckman Model IR-9 spectrophotometer using a matched set of 0.1-mm NaCl cells. Spectra of solids were examined on a Perkin-Elmer Model 337 spectrophotometer either as KBr pellets or as hexachlorobutadiene and Nujol mulls, polystyrene being used as a reference.

Proton Magnetic Resonance Spectra.—Nmr spectra were obtained using a Varian Associates A-60 spectrometer. Tetramethylsilane was employed as an internal standard and deuteriochloroform as solvent in all cases.

Conductivity.—Measurements were made on 10^{-3} *M* nitromethane or nitrobenzene solutions using an Industrial Instruments Co. Model RC 16B2 conductivity bridge and a cell with platinum electrodes.

Magnetism.—Measurements were made at room temperature on a Faraday magnetic balance constructed in this laboratory.

Analyses.—Microanalyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn., by Dr. Alfred Bernhardt, Mikroanalytisches Laboratorium im Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr), West Germany, and by Dr. Franz Pascher, Mikroanalytisches Laboratorium, Bonn, West Germany.

Results and Discussion

Properties of Seven-Coordinate Complexes.—Reactions of the anions $M(CO)_4X_3^-$ (M = Mo, W; X = Br,

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[26] J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961).

I) with several different ligands containing phosphorus-, arsenic-, and sulfur-donor groups have yielded the following types of seven-coordinate complexes: $[(n\text{-}C_4H_9)_4N][M(CO)_3I_3(P(C_6H_5)_3)]$, $M(CO)_3(L\text{-}L)X_2$, $M(CO)_3(PPP)X_2$, $M(CO)_2(L\text{-}L\text{-}L)X_2$, and $M(CO)_2(TSP)I_2$ (L-L and L-L-L are bidentate and tridentate ligands, respectively). Generally, it was found that the molybdenum halogenocarbonyl anions undergo substitution more readily than the corresponding anions of tungsten and that phosphine ligands are more reactive than the corresponding arsines.

The interaction of $M(CO)_4I_3^-$ (M = Mo, W) with an equimolar amount of triphenylphosphine yields the diamagnetic anions $M(CO)_3I_3P(C_6H_5)_3^-$ isolated as the orange, crystalline tetrabutylammonium salts. These solids decompose only very slowly in air, but their solutions are much less stable. The same anions were synthesized earlier by Lewis and Whyman[3] employing iodine oxidation of $M(CO)_3[P(C_6H_5)_3]_3$ (M = Mo, W). It is interesting that the reaction of $Mo(CO)_4I_3^-$ with 2 mol of triphenylphosphine yields *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$ rather than $Mo(CO)_3I_2[P(C_6H_5)_3]_2$, since the chloro and the bromo analogs of the latter have been recently prepared by the action of triphenylphosphine on $[Mo(CO)_4X_2]_2$ (X = Cl, Br).[10,11]

The triiodotetracarbonyl anions of molybdenum(II) and tungsten(II) react with an equimolar quantity of each of the ligands diphos, diars, AP, and SP (L-L) to give $M(CO)_3(L\text{-}L)I_2(CH_2Cl_2)_x$, where x is 0 or 1. A similar reaction occurs between $Mo(CO)_4Br_3^-$ and AP. These complexes are yellow-orange, diamagnetic, crystalline solids, which exhibit slight conductivity in nitromethane or nitrobenzene. They are more stable than the seven-coordinate anions containing triphenylphosphine, the tungsten compounds having higher stability than the molybdenum counterparts. The complexes are soluble in dichloromethane, chloroform, and acetone, but are insoluble in petroleum ether and methanol. Further, it is of interest that compounds XV and XVI each contained one molecule of dichloromethane. This is supported by elemental analyses and by the proton magnetic resonance spectrum of XVI, given in Table II. Lewis and Whyman[2] previously synthesized the diphosphine derivative by oxidation of $W(CO)_4$(diphos) with iodine and reported that the dichloromethane can be removed by heating *in vacuo* at 80°.

The reactions of $Mo(CO)_4X_3^-$ (X = Br, I) with DSP and DSA (L-L-L) yield complexes of general formula $Mo(CO)_2(L\text{-}L\text{-}L)X_2(CH_3OH)_x$, where x is 0 or 1. The presence of methanol is confirmed by elemental analyses in conjunction with the infrared spectral data. Accordingly, complexes VIII, IX, and XI show O–H stretching frequencies at 3485, 3513, and 3505 cm^{-1} (hexachlorobutadiene mull), respectively. The methanol can be removed from complex VIII by heating *in vacuo* at 80° for 8 hr; however, IX and XI remain unchanged after similar treatment.

Under conditions analogous to those employed above, there is no apparent reaction between $W(CO)_4Br_3^-$ and DSA and between $W(CO)_4I_3^-$ and DSP. However, DSP reacts with $W(CO)_4Br_3^-$ and with $W(CO)_4BrI_2^-$ to give $W(CO)_2(DSP)Br_2$ and $W(CO)_2(DSP)BrI$, respectively. All of these dicarbonyls are stable, orange-red, crystalline solids.

TABLE II

PROTON MAGNETIC RESONANCE DATA FOR SOME LIGANDS AND THEIR COMPLEXES

Compound	Chemical shift of protons, τ[a] CH_2 of ligand	CH_3 of coordinated thioether group	CH_3 of free thioether group	Phenyl	CH_2Cl_2
diars	7.86			2.74	
$Mo(CO)_3(diars)I_2$	7.22			2.61	
$W(CO)_3(diars)I_2 \cdot CH_2Cl_2$	7.27			2.47	4.66
SP			7.64	2.3–3.2[b]	
$Mo(CO)_3(SP)I_2$		6.86		1.9–2.5[b]	
$Mo(CO)_2(SP)I_2$		6.74		1.9–2.7[b]	
DSP			7.61	2.6–3.4[b]	
TSP			7.56	2.6–3.4[b]	
cis-$Mo(CO)_3(DSP)$		7.14		2.1–2.7[b]	
cis-$Mo(CO)_3(TSP)$		7.17	7.64	2.1–2.9[b]	

[a] All peaks are singlets unless indicated otherwise. [b] Complex pattern.

By way of contrast, the tridentate ligand PPP reacts with $Mo(CO)_4I_3^-$ to afford *cis*-$Mo(CO)_3(PPP)$ and the tricarbonyl $Mo(CO)_3(PPP)I_2$. Further, under the same experimental conditions, $Mo(CO)_4Br_3^-$ and PPP yield almost exclusively *cis*-$Mo(CO)_3(PPP)$, but $W(CO)_4BrI_2^-$ and PPP give only $W(CO)_3(PPP)BrI$. Thus, with the more stable tungstate anion, simple substitution occurs, whereas with the more reactive $Mo(CO)_4Br_3^-$, reduction is favored.

The tricarbonyls $M(CO)_3(PPP)X_2$ are yellow, crystalline solids, which exhibit only slight conductivity in nitrobenzene and nitromethane. Hence, ionic formulations such as $[M(CO)_3(PPP)X]X$, similar to those of $[M(CO)_3(triars)X]X$ (M = Mo, W; X = Br, I; triars = $CH_3As(CH_2CH_2CH_2As(CH_3)_2)_2$, $CH_3C(CH_2As(CH_3)_2)_3$),[6] in which all three phosphorus atoms coordinate to the metal, may be ruled out. It appears, therefore, that the tridentate ligand utilizes only two phosphorus donor atoms for coordination, the third one being free. Additional support for this formulation is derived from similarity of the infrared carbonyl stretching frequencies of this and the diphosphine complex, listed in Table III. The small conductivity in solution may then be attributed to an equilibrium

$$M(CO)_3(PPP)X_2 \rightleftharpoons M(CO)_3(PPP)X^+ + X^-$$

Our attempts to displace one carbonyl group from $Mo(CO)_3(PPP)I_2$ to form $Mo(CO)_2(PPP)I_2$ proved unsuccessful. After 5 hr of uv irradiation, most of the $Mo(CO)_3(PPP)I_2$ was recovered, together with a small quantity of decomposition material containing no carbonyl groups. Iodine oxidation of *cis*-$Mo(CO)_3(PPP)$ also afforded $Mo(CO)_3(PPP)I_2$ rather than $Mo(CO)_2(PPP)I_2$. This is in contrast to the oxidation of *cis*-$Mo(CO)_3(DSP)$, which gives the dicarbonyl, $Mo(CO)_2(DSP)I_2 \cdot CH_3OH$.

There appear two plausible explanations for the

TABLE III
INFRARED METAL CARBONYL STRETCHING BANDS (CM^{-1})

		CO absorptions[d]	
No.	Compound	CH_2Cl_2 soln	Solid
I	$[(n\text{-}C_4H_9)_4N][Mo(CO)_3I_3P(C_6H_5)_3]$	2023 m, 1948 s, 1900 m, sh	2008 m, 1943 s, 1925 s[a]
II	$Mo(CO)_3(\text{diphos})I_2$	2040 s, 1976 vs, 1920 m	2033 s, 1982 s, 1924 s[a]
III	$Mo(CO)_3(\text{diars})I_2$	2047 s, 1974 vs, 1922 m	2028 s, 1966 s, 1913 s[a]
IV	$Mo(CO)_3(AP)Br_2$	2063 s, 1979 vs, 1919 m	2059 s, 1975 s, 1917 s[b]
V	$Mo(CO)_3(AP)I_2$	2045 s, 1972 vs, 1920 m	2036 s, 1975 s, 1911 s[a]
VI	$Mo(CO)_3(SP)I_2$	2046 s, 1971 vs, 1920 m	2053 s, 1973 s, 1940 s[b]
VII	$Mo(CO)_2(DSP)Br_2$	1978 s, 1912 m	1972 s, 1900 s[b]
VIII	$Mo(CO)_2(DSP)Br_2 \cdot CH_3OH$	1977 s, 1910 m	1973 s, 1900 s[b]
IX	$Mo(CO)_2(DSP)I_2 \cdot CH_3OH$	1966 s, 1910 m	1971 s, 1900 s[b]
X	$Mo(CO)_2(DSA)Br_2$	1976 s, 1908 m	1964 s, 1890 s[b]
XI	$Mo(CO)_2(DSA)I_2 \cdot CH_3OH$	1963 s, 1903 m	1962 s, 1900 s[b]
XII	$Mo(CO)_3(PPP)I_2$	2037 s, 1969 vs, 1915 s	2032 s, 1954 s, 1924 s[c]
XIII	$Mo(CO)_2(TSP)I_2$	1965 s, 1907 m	1958 s, 1897 s[c]
XIV	$[(n\text{-}C_4H_9)_4N][W(CO)_3I_3P(C_6H_5)_3]$	2017 m, 1938 s, 1888 m, sh	2004 m, 1926 s, 1911 s[c]
XV	$W(CO)_3(\text{diphos})I_2 \cdot CH_2Cl_2$	2039 s, 1963 vs, 1909 m	2055 s, 1950 s, 1904 s[a]
XVI	$W(CO)_3(\text{diars})I_2 \cdot CH_2Cl_2$	2038 s, 1958 vs, 1908 m	2031 s, 1953 s, 1908 s[c]
XVII	$W(CO)_3(AP)I_2$	2041 s, 1959 vs, 1909 m	2037 s, 1965 s, 1904 s[c]
XVIII	$W(CO)_3(SP)I_2$	2042 s, 1961 vs, 1918 m	2048 s, 1958 s, 1923 s[c]
XIX	$W(CO)_2(DSP)Br_2$	1966 s, 1893 m	1959 s, 1877 s[c]
XX	$W(CO)_2(DSP)BrI$	1966 s, 1895 m	1953 s, 1880 s[c]
XXI	$W(CO)_3(PPP)BrI$	2044 s, 1955 vs, 1902 s	2035 s, 1953 s, 1898 s[c]
XXII	*cis*-$Mo(CO)_3(DSP)$	1939 s, 1851 s, 1824 s	1930 s, br, 1873 s, br[b]
XXIII	*cis*-$Mo(CO)_3(TSP)$	1936 s, 1847 m, 1828 m	1940 s, 1858 m, 1810 s[c]
XXIV	*cis*-$Mo(CO)_3(TAP)$	1943 s, 1857 s	1942 s, 1858 s, 1845 s[c]
XXV	$V(CO)_3(PPP)I$		2013 w, 1901 m, 1851 s[a]

[a] Nujol mull. [b] Hexachlorobutadiene mull. [c] KBr pellet. [d] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad.

apparent inability of PPP to displace an additional CO. First, the geometry of this tridentate ligand is such that the three donors can occupy readily adjacent facial positions in a seven-coordinate polyhedron (such as a pentagonal bipyramid). However, its geometry prevents it from coordinating at three meridian sites of such a structure. Therefore, if the stereochemistry of these seven-coordinate complexes is based on a pentagonal-bipyramidal geometry—a pure conjecture at present—the ligand PPP cannot occupy three adjacent equatorial positions, but the ligands DSA and DSP can.

Second, it is possible that two coordinated phosphorus atoms, by virtue of their considerable σ-bonding ability, have strengthened the remaining M–CO bonds to such an extent that displacement of one more CO by the third phosphorus is energetically unfavorable. Some support for this argument is derived from comparison of the CO stretching frequencies of $Mo(CO)_3(PPP)I_2$ and $Mo(CO)_3(SP)I_2$, where both PPP and SP function as bidentate ligands. These frequencies are higher for the latter complex, indicating that one of the three remaining CO's can dissociate more easily from $Mo(CO)_3(SP)I_2$ than from $Mo(CO)_3(PPP)I_2$. Thus it is not surprising that the ligand DSP, structurally similar to SP, displaces one more CO to give the corresponding dicarbonyl $Mo(CO)_2(DSP)I_2 \cdot CH_3OH$.

The reaction of $Mo(CO)_4I_3^-$ with TSP in boiling dichloromethane gives $Mo(CO)_2(TSP)I_2$, a reddish purple, diamagnetic solid. Similarly, $Mo(CO)_4Br_3^-$ and TSA afford $Mo(CO)_2(TSA)Br_2$, the physical and infrared spectral properties of which are similar to those of $Mo(CO)_2(TSP)I_2$; however, the analytical data, especially for carbon, are poor, probably owing to contamination with unreacted TSA.

The complex $Mo(CO)_2(TSP)I_2$ is only slightly ionized in nitrobenzene, precluding its formulation as $[Mo(CO)_2(TSP)I]I$ and suggesting that only two of the three sulfur atoms of TSP are coordinated to the molybdenum. This receives support from comparison of the carbonyl stretching frequencies of $Mo(CO)_2(TSP)I_2$ and $Mo(CO)_2(DSP)I_2 \cdot CH_3OH$ (Table III), which are almost identical.

In an effort to obtain complexes in which all four donor atoms of a tetradentate ligand would be coordinated, we attempted the synthesis of $Mo(CO)_2(TSP)$ and $Mo(CO)_2(TAP)$. However, the products of the reactions of *cis*-$Mo(CO)_3(CH_3CN)_3$ with TSP and with TAP were the tricarbonyls *cis*-$Mo(CO)_3(TSP)$ and *cis*-$Mo(CO)_3(TAP)$, respectively. The nmr spectrum of the former (Table II) showed two kinds of methyl protons in the ratio 2:1. Comparison of this spectrum with that of *cis*-$Mo(CO)_3(DSP)$ leaves little doubt that in *cis*-$Mo(CO)_3(TSP)$ only two of the three sulfurs are coordinated to the molybdenum. Attempts to convert the TSP complex to the corresponding dicarbonyl by heating at 175° *in vacuo* for 15 hr were unsuccessful. Thus it appears that replacement of an additional CO by the uncoordinated sulfur in *cis*-$Mo(CO)_3(TSP)$ and in $Mo(CO)_2(TSP)I_2$ may be unfavorable on electronic grounds, because of the relative strength of the remaining Mo–CO bonds. This behavior is in contrast to that of $Cr(CO)_3(QP)$ ($QP = P(o\text{-}C_6H_4P(C_6H_5)_2)_3$), which loses one CO on heating at 240° (0.1 mm) for 15 hr.[27]

In order to investigate further the synthesis of seven-coordinate metal carbonyl complexes in which all donor atoms of a polydentate ligand are coordinated to the metal, we have turned to vanadium hexacarbonyl, which undergoes substitution more readily than $Mo(CO)_6$. The reaction of $V(CO)_6$ with PPP, followed by oxidation with iodine, yielded an air-sensitive solid, formulated as $V(CO)_3(PPP)I$. This apparently seven-coordinate carbonyl complex is insoluble in methanol and benzene, and decomposes readily in polar solvents such as dichloromethane and acetone, thus precluding purification. The only other seven-coordinate vanadium carbonyl halide reported in the literature, $V(CO)_4(DAS)I$ ($DAS = o\text{-}C_6H_4(As(CH_3)_2)_2$), was prepared by spectrophotometric titration of $[V(CO)_4(DAS)]_2$ with iodine but was not isolated.[8] Because of low stability of these vanadium carbonyl complexes, we decided not to pursue our investigation further.

The general synthetic procedure reported in this paper, *i.e.*, interaction of $M(CO)_4X_3^-$ ($M = Mo, W$;

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(27) I. V. Howell and L. M. Venanzi, *J. Chem. Soc.*, 1007 (1967).

X = Br, I) anions with neutral ligands, provides a convenient route to a variety of seven-coordinate complexes. In terms of yields and experimental simplicity this method is to be rated equal to that involving halogen oxidation of molybdenum(0)- and tungsten(0)-substituted carbonyls for mono-, bi-, and tridentate ligands. However, it is the only known synthetic procedure for seven-coordinate complexes containing tetradentate ligands that do not form the dicarbonyls $M(CO)_2(L\text{-}L)_3$ (M = Mo, W).

Infrared Spectra.—The infrared carbonyl stretching frequencies of the complexes, recorded in solution and in the solid, exhibit several rational trends. Accordingly, for the same ligands, the molybdenum compounds absorb at higher wave numbers than the tungsten analogs. Other factors being equal, complexes containing the more polarizable iodide give rise to carbonyl absorptions at lower wave numbers than those containing coordinated bromide. Further, the anions $M(CO)_3I_3P(C_6H_5)_3^-$ (M = Mo, W) show lower carbonyl stretching frequencies than the neutral tricarbonyls.

Unfortunately, little can be said about the structures of these seven-coordinate complexes from the spectral data. For all of the dicarbonyls in CH_2Cl_2 solution, the symmetric CO stretching frequency is of higher intensity than the asymmetric one, suggesting that the OC–M–CO angle is less than 90°.[28,29] However, there are several structures in which such a bond angle is to be expected, and therefore extensive speculation at this time is inappropriate.

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(28) A. Reckziegel and M. Bigorgne, *J. Organometal. Chem.* (Amsterdam), **3**, 341 (1965).

(29) W. Beck, A. Melnikoff, and R. Stahl, *Angew. Chem.*, **77**, 719 (1965).

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Linkage Isomerism in Carbonyl-π-cyclopentadienyl(thiocyanato)metal Complexes[1]

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Both sulfur- and nitrogen-bonded thiocyanato linkage isomers of dicarbonyl-π-cyclopentadienyliron and tricarbonyl-π-cyclopentadienylmolybdenum have been prepared by air oxidation of dicarbonyldi-μ-carbonyldiπ-cyclopentadienyldiiron in the presence of potassium thiocyanate and hexafluorophosphoric acid and by the reaction of tricarbonyl-π-cyclopentadienylhydromolybdenum with thiocyanogen. The isomers are readily separable by chromatography. The thiocyanato-S complex of iron does not undergo linkage isomerization in chloroform at 36°, in bis(2-methoxyethyl) ether at 50°, and in refluxing acetonitrile but converts readily to the thiocyanato-N form in the solid at 35–40°. Isomerization of tricarbonyl-π-cyclopentadienyl(thiocyanato)molybdenum to the corresponding isothiocyanate either in chloroform or in acetonitrile at 35° is essentially complete in 5 hr. The reaction of tricarbonyl-π-cyclopentadienylhydrotungsten with thiocyanogen affords only the sulfur-bonded thiocyanate, which is stable with respect to linkage isomerization. The previously synthesized π-cyclopentadienyldinitrosyl(isothiocyanato)chromium was shown by infrared spectroscopy, a technique employed throughout this study, to contain a chromium–nitrogen linkage for the thiocyanate. The results of this and of other investigations on thiocyanatocarbonyls are compared.

Introduction

The synthesis of a number of thiocyanatocarbonyl complexes of manganese(I),[3,4] chromium(0),[5] chromium(I),[6] molybdenum(0),[5] tungsten(0),[5] and rhodium(I)[7] has been reported recently. Interestingly, whereas for pentacarbonyl(thiocyanato)manganese both the S- and the N-bonded linkage isomers were detected, the former being the stable species in the solid,[3] the isoelectronic $Cr(CO)_5(NCS)^-$ was found always to contain a Cr–NCS attachment.[5] On the basis of these and some related observations Farona and Wojcicki[4] suggested that in complexes containing strongly π-bonding ligands, higher oxidation states of the metal promote M–SCN bonding, and lower oxidation states favor M–NCS bonding. In order to test this hypothesis over a wider range of oxidation states the synthesis of $Fe(CO)_4(CNS)_2$,[8] expected to contain Fe–SCN linkages, was attempted, albeit unsuccessfully.[3]

Inasmuch as the complexes $C_5H_5M(CO)_xX$ (X = Cl, Br, I) may be formally regarded as containing metal in the +2 oxidation state, we have now prepared several corresponding derivatives with X = NCS and SCN. Reported here are the results of our investigation on the synthesis and on the nature of metal–thiocyanate

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[2] Based on the M.S. thesis submitted by T. E. S. to The Ohio State University, 1968.

(3) M. F. Farona and A. Wojcicki, *Inorg. Chem.*, **4**, 857 (1965).

(4) M. F. Farona and A. Wojcicki, *ibid.*, **4**, 1402 (1965).

(5) A. Wojcicki and M. F. Farona, *J. Inorg. Nucl. Chem.*, **26**, 2289 (1964).

(6) H. Behrens and D. Herrmann, *Z. Naturforsch.*, **21b**, 1236 (1966).

(7) M. A. Jennings and A. Wojcicki, *Inorg. Chem.*, **6**, 1854 (1967).

(8) In this paper NCS designates M–NCS bonding, SCN designates M–SCN bonding, and CNS designates either that the bonding is not known or that both isomers are present.