the degree of overlap should be nearly the same in the two species. However, the orbital energies are lower for the Mn-Mn case, since the Cr^- level is higher than the Mn^0 level, and a stronger bond is expected. The same argument holds for the pair Mn-Re, Mn-W.

The results discussed above are consistent with dissociation energies found for M-M bonds from electron impact measurements,[38,39] observations of mass spectral fragmentation patterns,[40-42] and previous force constant calculations[7] all of which indicate an increase in metal-metal bond strength as a row of the periodic table is descended.

Analysis of the k_{C-O} and k_{M-C} values reveals several interesting relationships. The $k_{C-O(eq)}$'s are larger than the corresponding $k_{C-O(ax)}$ values, and the reverse is true for the k_{M-C} values. This follows from preferential back-donation into the π^*(CO) of the axial CO which is trans to the $M'(CO)_5$, since that increases the π character of the M-C axial bond and the π^* character of the axial CO bond, as is the general case in which the trans ligand acts as a weak π base.

Comparisons can also be made for $k_{M'-C(eq)}$ and $k_{C-O(eq)}$ between members of the M-M' series. The $k_{C-O(eq)}$ values are in the relationship $k_{C-O(eq)}(Mo) > k_{C-O(eq)}(Cr) \simeq k_{C-O(eq)}$(W) which indicates that the amount of π bonding between Mo and the equatorial ligands associated with it is lower than that for either Cr or W. This decrease in the π bonding for Mo is also reflected in the Mo-C equatorial force constant, which is the lowest of the three $k_{M'-C(eq)}$ values. This result is in agreement with recent vibrational analyses by Jones, *et al.*,[35] and the photoionization and bonding results of Schlag and Lloyd[37] on the metal hexacarbonyls.

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Registry No. $Et_4NMnCr(CO)_{10}$, 40664-55-9; $Ph_4AsMnCr(CO)_{10}$, 40605-02-5; $Et_4NMnMo(CO)_{10}$, 40605-03-6; $Ph_4AsMnMo(CO)_{10}$, 40629-31-0; $Et_4NMnW(CO)_{10}$, 40605-04-7.

Supplementary Material Available. Table VI, a listing of band positions, intensities, physical states, and assignments for each compound studied, along with Table VII, a listing of normalized symmetry coordinates, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2349.

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Reactions of Halocarbonyls of Group VIb Elements. II. Complexes of Molybdenum and Tungsten Containing Group Va Donors or Phenyl Isocyanide

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Halocarbonyls of molybdenum and tungsten, $Mo(CO)_4X_2$ and $W(CO)_4X_2$ (X = Cl, Br), reacted with PEt_3, $P(OEt)_3$, $AsEt_3$, py, and CNPh to form substituted halocarbonyls, $M(CO)_xL_yX_2$ and $W(CO)_xL_yX_2$. The use of neat pyridine, 2,6-lutidine, and NCPh led in some cases to products containing no carbonyl groups. In such cases molybdenum underwent a facile disproportionation to produce compounds of Mo(0) and Mo(III). A similar disproportionation occurred much less readily in the case of tungsten halocarbonyl. With $W(CO)_4Br_2$ and NCPh, $WBr_2(NCPh)_2$ was produced. Complexes of various types containing 2,2'-bipyridine and 1,10-phenanthroline were obtained by reaction with $MoBr_3(NCR)_3$ or MoI_3. Compounds of mixed oxidation state, $Mo_3Br_8(NCPh)_6$ and $W_3I_8(NCCH_3)_6$, were obtained when trivalent and tetravalent compounds, respectively, were heated in the presence of a nitrile. Physical examination of some of the compounds is reported.

Introduction

There are two well-established methods for making substituted halocarbonyl complexes of the type $M(CO)_xL_yX_2$ where M = Mo or W, X = Cl, Br, or I. The first, introduced by Nyholm and coworkers,[1] involves treating the hexacarbonyl with a neutral electron donor L followed by halogen oxidation of the resulting substituted carbonyl.[1-7] A second method involves treatment of the halocarbonyl complexes $M(CO)_4X_2$ with the appropriate donor.[8-11] It has been reported recently that reduction of $MoCl_4(PPh_3)_2$ and $WOCl_4$

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Table I. Analyses of Some Substituted Halocarbonyl Complexes of Bivalent Molybdenum and Tungsten

		% found						% calcd					
No.	Compd	Mo or W	Cl, Br, or I	C	H	N, P or As	O	Mo or W	Cl, Br, or I	C	H	N, P, or As	O
I	$Mo(CO)_3(PEt_3)_2Cl_2$	19.36	16.27	37.90	6.65	13.80		19.21	14.55	36.98	6.21	12.72	
II	$Mo(CO)_2[P(OCH_3)_3]_3Cl_2$		11.92	23.31	4.68	16.37			12.02	22.20	4.57	15.62	
III	$[Mo(CO)_2(AsEt_3)Cl_2]_x$		18.55	25.66	4.61	20.07			18.42	24.96	3.93	19.46	
IV	$Mo(CO)(CNPh)_3Cl_2$	18.58	14.07					19.03	14.06				
V	$Mo(CO)(CNPh)_4Cl_2$	15.50	11.97					15.80	11.67				
VI	$Mo(CO)_3(OPPh_3)Cl_2$	18.21	13.36	51.10	3.45			18.21	13.40	47.80	2.86		
VII	$W(CO)_3(py)_2Cl_2$	36.70	14.27	29.66	2.36	5.66	9.86	36.99	14.27	31.42	2.03	5.64	9.66
VIII	$W(CO)_3(py)_2Br_2$	31.55	27.84	24.92	1.65	4.76	8.03	31.38	27.28	26.65	1.72	4.78	8.19
IX	$W(CO)_3(py)_2I_2$	27.42	37.22	22.88	1.51	4.25	7.13	27.04	37.33	22.96	1.48	4.12	7.06

with $EtAlCl_2$ in the presence of carbon monoxide gives acetone-soluble products from which $Mo(CO)_3(PPh_3)_2Cl_2$ and $W(CO)_3(PPh_3)_2Cl_2$ could be precipitated by the addition of triphenylphosphine.[12] In the present work, some complexes of bivalent molybdenum and tungsten, prepared by the first two methods, are reported. The complexes $WCl_3(py)_3$ and $WBr_3(py)_3$ which were mentioned briefly in an earlier paper[13] are discussed more fully. Some bipyridine and phenanthroline complexes are also reported.

Experimental Section

All reaction vessels were normally dried under vacuum and filled with dry, oxygen-free nitrogen before introducing reagents. Samples were handled under nitrogen and preserved in nitrogen-containing ampoules.

Halocarbonyl, $M(CO)_4X_2$. Molybdenum and tungsten chlorocarbonyl and bromocarbonyl were prepared following published methods[8-10] and the products were isolated as described elsewhere.[13]

$Mo(CO)_xL_yX_2$ Where $L = P(OCH_3)_3$, PEt_3, or $AsEt_3$, $X = Cl$ or $L = P(OCH_3)_3$, $X = Br$. A filtered solution of $Mo(CO)_4X_2$ in the donor liquid, L, was stirred at room temperature for 24 hr. Trimethyl phosphite complexes precipitated within a few minutes. Complexes of PEt_3 and $AsEt_3$ were precipitated by the addition of ether. The products were separated by filtration, washed with several portions of ether and dried at room temperature under vacuum. Analyses for these compounds are given in Table I.

$Mo(CO)(CNPh)_3Cl_2$ and $Mo(CO)(CNPh)_4Cl_2$. Initial experiments showed that phenyl isocyanide reacted with $Mo(CO)_4Cl_2$ in two different stoichiometric ratios. The preparations were repeated by using the stoichiometric amount of reagent in ether and stirring the mixture for 12 hr. Products IV and V were recovered by filtration, washed with ether, and dried at room temperature under vacuum.

$Mo(CO)_3(OPPh_3)Cl_2$. Excess triphenylphosphine oxide gave only monosubstitution. The complex was best prepared in the same manner as the phenyl isocyanide complexes by reaction of stoichiometric quantities of the reagents.

$W(CO)_3(py)_2X_2$. When $W(CO)_4X_2$ was treated with pyridine in methylene chloride, one carbonyl group was replaced by two pyridine molecules. Compounds of this type were prepared in two ways.

(a) The halocarbonyl was dissolved in methylene chloride and filtered. The stoichiometric amount of pyridine in methylene chloride was added to the filtrate and the resulting yellow solution stirred for 12 hr. Most of the solvent was removed by pumping and the product precipitated with ether. This was washed with several portions of ether-methylene chloride (1:1) and then pure ether and dried at 50° under vacuum.

(b) $W(CO)_4(py)_2$ was obtained by heating a mixture of $W(CO)_6$ and pyridine for 12 hr at 100-110°. Upon cooling the solution, orange crystals were recovered and these were washed with small portions of methylene chloride and dried at room temperature under vacuum. *Anal.* Calcd for $C_{14}H_{10}N_2O_4W$: W; 40.49. Found: W, 40.18. A 2-3-g sample of $W(CO)_4(py)_2$ was put into a Schlenk tube with 50 ml of freshly distilled methylene chloride. The tube was evacuated and refilled with nitrogen. The tube was cooled to $-78°$ and the stoichiometric quantity of liquid bromine or chlorine was added from a measuring syringe. The mixture was thoroughly stirred as it was allowed to warm up to room temperature. The resulting yellow solution was filtered to remove possible side products. The required products were isolated as described in section (a).

The iodo complex IX was prepared from the reaction of $W(CO)_4(py)_2$ with the stoichiometric amount of iodine. The reaction was carried out at room temperature in benzene and was allowed 12 hr for completion. The reddish brown solid formed was isolated by filtration, washed with ether, and dried at room temperature under vacuum.

Molybdenum(III) Iodide. Molybdenum hexacarbonyl (4-6 g) and a stoichiometric quantity of iodine were suspended in 50 ml of benzene-toluene (1:1). The mixture was outgassed briefly and the reaction vessel was refilled with nitrogen. The system was slowly heated to 100° and the mixture was stirred for 6 hr. The gray solid which formed was separated and washed with benzene until it was free of iodine and finally with two portions of ether. The product was dried at room temperature under vacuum. *Anal.* Calcd for MoI_3: Mo, 20.13; I, 79.87. Found: Mo, 19.50; I, 80.00.

1,10-Phenanthroline and 2,2'-Bipyridine Complexes of Molybdenum. Considerable effort was devoted to obtaining the maximum degree of coordination of these diamines. Once the coordination limits were found, final preparations were carried out with stoichiometric quantities of the reagents. $Mo(phen)_2Br_3$, $Mo(phen)_2I_3$, and $Mo(bipy)_2I_3 \cdot NCCH_3$ were prepared as follows. A 2-3-g sample of MoI_3 or a bromo complex of the type $MoBr_3(NCR)_3$ was treated with the stoichiometric quantity of phenanthroline or bipyridine in 50 ml of tetralin. The mixture was stirred at 160-170° for at least 24 hr. The solid which separated was washed thoroughly with benzene and the product was recrystallized from acetonitrile followed by further washing with acetonitrile.

Diiodobis(bipyridine)molybdenum(III) Tetraphenylborate. Sodium tetraphenylborate in acetonitrile was added to a solution of $Mo(bipy)_2I_3$ in acetonitrile. The resulting solution was concentrated by pumping at room temperature whereupon orange crystals were formed. The product XIII was washed with acetonitrile-ether (1:1) and finally with ether and dried at room temperature under vacuum.

Dihalobis(bipyridine)molybdenum(III) Tetrahalobipyridinemolybdate(III). Two or three grams of a nitrile complex (*e.g.*, propionitrile) or a tetrahydrofuran complex of the type $MoCl_3L_3$ or $MoBr_3L_3$ was treated with 2,2'-bipyridine in a 1:2 mole ratio in 30 ml of tetralin. The system was heated with stirring for 13 hr at 170°. The brown solid XIV or XV which was formed was separated and washed with several portions of hot benzene. The chloro compound was alternatively obtained by refluxing a solution in tetrahydrofuran of $Mo(C_4H_8O)_3Cl_3$ and 2,2'-bipyridine in a 1:2 mole ratio.

Reaction of $Mo_2Br_6(bipy)_3$ with Excess Bipyridine. A steel bomb was charged with 1.5 g of $Mo_2Br_6(bipy)_3$, 1.5 g of 2,2'-bipyridine, and 100 ml of freshly distilled acetonitrile. The bomb was evacuated, closed, and kept in an oven at 180° for 3 days. After cooling, the bomb was filled with nitrogen; the red solution was filtered and concentrated to about 20 ml. The product was precipitated by adding small portions of ether. This was separated, washed with several portions of acetonitrile-ether (1:1) and ether, and dried at 50° under vacuum. Elemental analysis showed that the product was probably impure but it approximated to the composition $Mo(bipy)_3Br_2$. *Anal.* Calcd for $C_{30}H_{24}Br_2MoN_3$: Br, 22.07; C, 49.34; H, 4.18; N, 11.60. Found: Br, 22.98; C, 46.65; H, 4.14; N, 12.15.

Diiodobis(phenanthroline)molybdenum(II). A mixture of MoI_3 and anhydrous 1,10-phenanthroline in a 1:3 mole ratio in 50 ml of freshly distilled benzonitrile were heated at 180° for 3 days. The purple solid XVI which formed was separated, washed with hot acetonitrile, and dried at room temperature under vacuum.

Tribromobis(2,6-lutidine)molybdenum(III). Molybdenum bromocarbonyl (4.0 g) was dissolved in 30 ml of 2,6-lutidine, the mixture was filtered, and the filtrate was stirred for 24 hr. The dark yellow solid XVII which formed was isolated, washed with chloroform, and dried at room temperature under vacuum.

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[13] A. D. Westland and N. Muriithi, *Inorg. Chem.*, 11, 2971 (1972).

Table II. Analyses of Molybdenum and Tungsten Halide Complexes Containing Nitrogen Donors

			% found					% calcd				
No.	Compd	Color	Mo or W	Cl, Br, or I	C	H	N	Mo or W	Cl, Br, or I	C	H	N
X	$[Mo(phen)_2Br_2]Br$	Brown	13.54	34.33	41.13	2.36	8.13	13.78	34.44	41.41	2.32	8.05
XI	$[Mo(phen)_2I_2]I$	Violet		44.35	35.05	2.14	6.43		45.48	34.44	1.93	6.69
XII	$[Mo(bipy)_2I_2]I \cdot NCMe$	Dark red		45.35	32.55	2.53	8.28		45.86	34.73	2.31	8.44
XIII	$[Mo(bipy)_2I_2]BPh_4$	Orange		25.30	55.08	4.11	5.61		25.86	53.84	3.70	5.71
XIV	$Mo_2Cl_6(bipy)_3$	Brown		24.29	41.13	3.13	9.45		24.36	41.26	2.77	9.62
XV	$Mo_2Br_6(bipy)_3$	Brown	16.98	42.27	31.46	1.96	7.50	16.83	42.06	31.60	2.12	7.37
XVI	$Mo(phen)_2I_2$	Violet	13.09	36.44	38.92	2.30	8.01	13.51	35.74	40.59	2.27	7.89
XVII	$MoBr_3(lut)_2$[a]	Yellow	16.03	43.10	32.36	3.23	5.50	17.44	43.58	30.57	3.30	5.10
XVIII	$Mo_3Br_8(NCPh)_6$	Green	18.72	41.37	27.56	1.79	5.29	18.62	41.36	32.63	1.96	5.44
XIX	$WCl_4(py)_2$	Brown	38.20	29.08	24.96	2.15	5.83	38.00	28.48	24.82	2.08	5.79
XX	$WCl_3(py)_3$	Red	34.27	19.77	34.43	3.11	7.70	34.85	20.16	34.15	2.87	7.97
XXI	$WBr_3(py)_3$	Red	27.72	36.02	27.09	2.38	6.18	27.82	36.27	27.27	2.29	6.36
XXII	$W_3I_8(NCCH_3)_6$	Gray	30.12	55.42	7.39	1.18	3.78	30.41	55.99	7.95	1.00	4.64

[a] lut = 2,6-lutidine.

Octabromohexakis(benzonitrile)trimolybdenum. $MoBr_3(NCPh)_3$ (2 g) prepared as previously[13] was added to hot benzene (70°) to give a green solution. This was filtered and concentrated by pumping. The green solid XVIII which formed was isolated and washed with several portions of ether. The product was dried at 50° under vacuum.

Trihalotris(pyridine)tungsten(III). The chloro or bromocarbonyl, $W(CO)_4X_2$, was dissolved in pyridine and, after filtering, the solution was heated at 140° for 12 hr. To obtain the chloro complex XX, the hot solution was filtered and concentrated to a small volume. The bromo complex XXI was obtained by removing all of the solvent by pumping and extracting the residue with methylene chloride. The extract was filtered and concentrated to produce crystals. The products were washed with small portions of methylene chloride and dried at 50° under vacuum.

Tetrachlorobis(pyridine)tungsten(IV). Tungsten carbonyl chloride was dissolved in pyridine and the solution filtered. The filtrate was heated at 80° for 6 hr. The brown solid XIX which formed was separated and washed with small portions of methylene chloride and dried at 80° under vacuum.

Tungsten(IV) Iodide. The procedure for preparing this compound was identical with that used in the preparation of MoI_3 except that much longer reactions times are required. *Anal.* Calcd for WI_4: W, 26.59. Found: W, 26.74.

Reaction of WI_4 with Acetonitrile. Two grams of WI_4 was dissolved in 25 ml of acetonitrile. The solution was filtered and heated at 80° for 12 hr. Upon adding ether a gray solid XXII was formed. This was washed with several portions of ether and dried at room temperature under vacuum.

Analytical Methods. The method of analysis of molybdenum complexes containing chloride or bromide has been described previously.[13] It was modified as follows for determination of chloride or bromide in tungsten complexes. After fusion with sodium peroxide, aliquot portions of the filtered extract were treated with a large excess of tartaric acid and acidified with dilute sulfuric acid employing Methyl Red. The halogens were determined as before.[13]

Iodine was determined as follows. A weighed sample was put into a two-necked flask which was fitted with an air-cooled condenser. The metal was oxidized to the hexavalent state and the iodide to iodine by the addition of excess cerium(IV) sulfate and sulfuric acid. The flask was quickly stoppered after addition of the reagents and heated gently. The liberated iodine was swept with a stream of nitrogen into a 5% solution of potassium iodide which was cooled in ice. The solution of KI_3 was titrated with standard arsenic(III) solution.[14]

Tungsten was determined gravimetrically by weighing as oxide. Samples of compound, contained in a porcelain crucible, were carefully oxidized with nitric acid after which the acid was expelled by heating and the oxide was brought to constant weight at 750°.

Carbon, hydrogen, and nitrogen were determined by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany. See Table II for the analyses of compounds X–XXII.

Physical Measurements. Electrical Conductivity. Samples were dissolved in acetonitrile and measurements made using an Industrial Instruments Model RC-16B2 conductivity bridge.

Molecular Weights. Molecular weights were estimated by Alfred Bernhardt Mikroanalytisches Laboratorium by osmometer.

Infrared Spectra. Spectra of $WX_3(py)_3$ in the range 340–200 cm^{-1} were recorded on a Perkin-Elmer Model 225 spectrometer, the Nujol mull being contained in cesium iodide disks. Other spectra were obtained with a Beckman Model IR-20 spectrometer.

Results and Discussion

It was shown in a previous publication[13] that donor substances such as nitriles which have no special ability to stabilize low oxidation states react with $Mo(CO)_4Cl_2$ and $Mo(CO)_4Br_2$ to give complexes of trivalent and zerovalent molybdenum by disproportionation. Donor molecules which may form π bonds with metal d orbitals yield yellow complexes of bivalent molybdenum. These latter compounds are in many cases too unstable to permit isolation of analytically pure products. Thus, while $Mo(CO)_2[P(OCH_3)_3]_3Cl_2$ is stable, a preparation of the bromo analog was somewhat impure and appeared to be incompletely substituted with the phosphorus-containing ligand. Moreover, the preparation turned to a paste after a few days.

When $Mo(CO)_3(PEt_3)_2Cl_2$ was allowed to stand, a strong odor of PEt_3 developed and the aged preparation gave a violet solution when added to ether, carbon tetrachloride, or methylene chloride. This indicated a tendency for the compound to decompose. The substance formed initially when $Mo(CO)_4Cl_2$ was treated with $AsEt_3$ approximated to the composition $Mo(CO)_3(AsEt_3)Cl_2$. When maintained for a few hours at 50° *in vacuo*, this gave a product of empirical formula, $Mo(CO)_2(AsEt_3)Cl_2$, which is probably dimeric. A molecular weight determination in acetone gave the value 515 while the molecular weight for a monomer would be 385.

Phenyl isocyanide in ether solution with $Mo(CO)_4Cl_2$ gave $Mo(CO)(CNPh)_3Cl_2$ or $Mo(CO)(CNPh)_4Cl_2$ depending upon the ratio of reagents used. On the other hand, neat phenyl isocyanide reacted very exothermally to give a dark resinous material which resisted attempts at crystallization. When the reaction was carried out just above the melting point of phenyl isocyanide, *i.e.*, at about −30°, a light pink solid of approximate composition $MoCl_3(CNPh)_4 \cdot 2CH_2Cl_2$ precipitated upon the addition of methylene chloride. *Anal.* Calcd for $C_{30}H_{24}Cl_7MoN_4$: Mo, 12.20; Cl, 31.6; C, 45.8; H, 3.1; N, 7.2. Found: Mo, 11.70; Cl, 30.1; C, 44.2; H, 4.7; N, 8.07. Although the product was not pure, its magnetic susceptibility indicated that disproportionation had occurred. The magnetic moment, assuming that all of the molybdenum was in a single oxidation state, was 3.7 BM. This indicates that the molybdenum was in the 3+ oxidation state. Complexes of the type $Mo(CNR)_5X_2$ are diamagnetic.[15] A dis-

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(14) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," 3rd ed, Longmans, Green and Co., New York, N. Y., 1961, p 355.

(15) F. Bonati and G. Minghetti, *Inorg. Chem.*, 9, 2642 (1970).

proportionation similar to that which occurs here is found also when Cr(II) reacts with an isocyanide.[16]

The reactions of tungsten halocarbonyls were somewhat different from those of the molybdenum analogs. Both $W(CO)_4Cl_2$ and $W(CO)_4Br_2$ reacted with pure pyridine at room temperature to give tetravalent and zerovalent[17] tungsten complexes. The disporportionation was complete only at 80°. The bromo complex of tungsten(IV) was very soluble in pyridine and could not be isolated in a pure state. The ratio of bromine to tungsten was found to be 3.6:1 indicating that tungsten(IV) was probably present. The chloro complex XIX was less soluble and was obtained pure.

The complexes $WCl_3(py)_3$ and $WBr_3(py)_3$ were isolated only after the reaction mixture of carbonyl halide and pyridine was heated to 140°. These were presumably formed by reduction of tungsten(IV) by pyridine. The oxidation product was not isolated but it was probably the 1-(4-pyridyl)-pyridinium ion.[18] The infrared spectra of the solution in the reaction of $W(CO)_4X_2$ with neat pyridine showed that the initial products were $W(CO)_3(py)_2Cl_2$ and $W(CO)_3(py)_2Br_2$. These substituted carbonyl compounds reacted further with pyridine to give the complexes $WX_4(py)_2$ and $W(CO)_3(py)_3$. The reaction of $W(CO)_3(py)_2I_2$ with neat pyridine at 140° gave $W(CO)_3(py)_3$ as one of the products. The other major product was an impure adduct of WI_4 containing approximately four pyridine molecules. A substance of this approximate composition was prepared by the reaction of WI_4 with neat pyridine and also by treating $W(CO)_3(py)_3$ [14] with iodine in benzene. None of the preparations could be obtained pure. In the reaction of $W(CO)_3(py)_2I_2$ with neat pyridine, it is probable that $WI_3(py)_3$ was initially formed at the high temperature along with free iodine. Unlike chlorine and bromine, iodine is not a sufficiently powerful oxidant to oxidize pyridine. Rather, it oxidized the $WI_3(py)_3$ to give the tungsten(IV) adduct when the temperature was lowered. A similar behavior was noted in the reaction of NbI_5 with pyridine to produce $NbI_4(py)_2$ and iodine, the latter existing as a complex with pyridine.[18]

Attempts to prepare $WX_3(NCPh)_3$ (X = Cl, Br) by treating the halocarbonyl with benzonitrile at room temperature gave only substituted tungsten(II) carbonyl halides. These were not isolated but infrared spectra of their solutions showed three carbonyl bands very similar to those of $W(CO)_3(py)_2X_2$ thus suggesting that their formulation is similar. At elevated temperature these complexes lost carbon monoxide and impure, diamagnetic solids of approximate formula $WX_2(NCPh)_2$ were readily isolated.

The reaction of iodine and the metal hexacarbonyl was also studied. Djordjevic, *et al.*,[19] obtained MoI_3 from the reaction of $Mo(CO)_6$ and I_2 in a sealed tube. This method of preparation gave a very reactive product but it could be carried out only on a small scale. The procedure described in the present work takes advantage of the fact that in a benzene-toluene solution the volatility of the reagents is suppressed. Reaction commenced at about 90° but loss of both $Mo(CO)_6$ and I_2 was appreciable above 110°. Good yields were obtained.

Tungsten hexacarbonyl reacted much more slowly with iodine and the tetraiodide was produced. This served as a convenient starting material for the preparation of complexes of tungsten(IV) iodide. Tungsten here again shows a greater tendency than does molybdenum to go to the 4+ oxidation state. A further example is the reaction of $W(CO)_3(py)_3$ with iodine to give an adduct of tetravalent tungsten.

Many metal ions form complexes of the type $[M(chel)_2X_2]^{n+}$ where chel = 2,2′-bipyridine or 1,10-phenanthroline.[20] However, apart from $[Mo(phen)_2Cl_2]Cl$,[21] no other complexes of this type containing Mo(III) have been reported. In our efforts to prepare $[Mo(bipy)_2X_2]X$ we succeeded only in obtaining the iodo salt XII and this was a solvate containing acetonitrile. The uncomplexed iodide was readily replaced by treating an acetonitrile solution of $[Mo(bipy)_2I_2]I \cdot NCCH_3$ with $NaBPh_4$ to give $[Mo(bipy)_2I_2]BPh_4$. Molar conductivities of these compounds measured in acetonitrile solution at concentrations between 5×10^{-4} and 40×10^{-4} M lay in the range 110-140 ohm^{-1} cm^2. This is typical of 1:1 electrolyte behavior.

Treatment of $MoBr_3(bipy)(NCCH_3)$ with 1 equiv of bipyridine gave the known complex $[Mo(bipy)_2Br_2][Mo(bipy)Br_4]$.[22] Phenanthroline does not appear to form a similar complex anion under these conditions although the anion is formed in aqueous HCl.[23]

When the preparation of bipyridine and phenanthroline complexes was carried out in a nitrile as solvent, Mo(III) was reduced to Mo(II). Thus when MoI_3 and 1,10-phenanthroline in a 1:3 mole ratio were heated to 180° in benzonitrile, product XVI was obtained. The magnetic susceptibility of this substance was 130×10^{-6} cgsu which suggests that the electronic configuration was spin-paired d^4. The pairing of spins is to be expected for a highly distorted octahedral structure. Partial reduction occurred also when $MoBr_3(NCPh)_3$ was heated in benzene.

Infrared Spectra. The band positions for carbonyl stretching in some substituted carbonyl complexes of bivalent molybdenum and tungsten are given in Table III.

The spectrum of $WCl_3(py)_3$ shows a strong band at 295 cm^{-1} and a series of weaker bands on either side of this. The strong band is attributed to W-Cl stretching since pyridine does not absorb in the region 350-250 cm^{-1} [24] and $WBr_3(py)_3$ does not show any significant absorption in this region. Weak absorptions in the spectrum of $WCl_3(py)_3$ were also observed at 276, 244, and 219 cm^{-1}. The last two are probably due to W-N stretching.

The spectrum of $WBr_3(py)_3$ in the region 260-200 cm^{-1} is shown in Figure 1. The bands are better resolved than those of the chloro analog. Six definite bands are visible and on this basis the complex is tentatively assigned the meridional configuration like the nitrile complexes of molybdenum(III) described earlier.[13]

The infrared spectra of 2,2′-bipyridine and 1,10-phenanthroline do not reveal any significant absorption in the range 350-250 cm^{-1}.[25] Furthermore, Mo-I stretching modes are not likely to occur in this spectral range.[26] It seems reasonable, therefore, to assign bands at 283 and 273 cm^{-1} for

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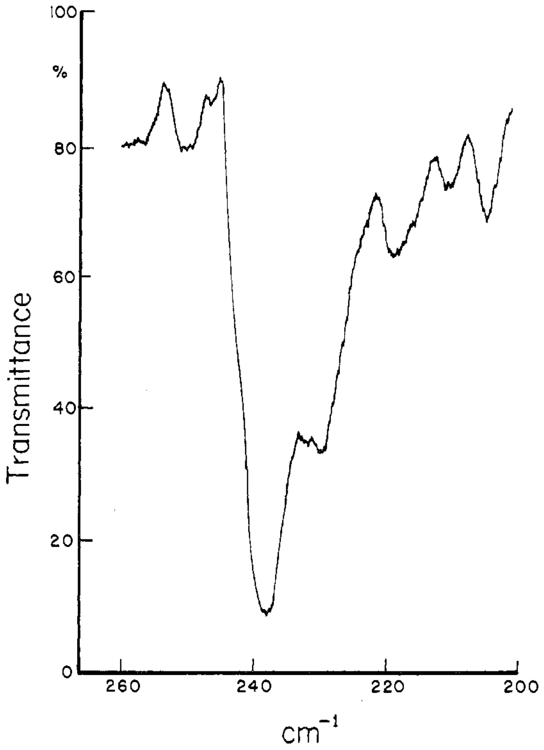

Figure 1. Infrared spectrum of $WBr_3(py)_3$ in the region 260-200 cm^{-1}.

Table III. Carbon-Oxygen Stretching Frequencies (cm^{-1}) of Some Substituted Carbonyls of Molybdenum and Tungsten

Compd		Medium
$Mo(CO)_3(PEt_3)_2Cl_2$	1942 s, 1925 s, 1858 s, 1800 s	Nujol
	1947 s, 1856 s, 1810 sh, w	CH_2Cl_2
$Mo(CO)_2[P(OCH_3)_3]_3Cl_2$	1973 m, 1892 s	Nujol
$Mo(CO)_2[P(OCH_3)_3]_3Br_2$	1978 m, 1885 s	Nujol
$Mo(CO)_2(AsEt_3)Cl_2$	1932 m, 1845 s	Nujol
$Mo(CO)_3(OPPh_3)Cl_2$	2030 w, 1950 w, 1890 s	Nujol
$Mo(CO)(CNPh)_3Cl_2$	1940 m	Nujol
$Mo(CO)(CNPh)_4Cl_2$	2000 m	Nujol
$W(CO)_3(py)_2Cl_2$	2020 s, 1977 sh, 1890 br	Nujol
$W(CO)_3(py)_3Br_2$	2020 s, 1940 s, 1912 s	Nujol
$W(CO)_3(py)_2I_2$	2070 m, 2010 s, 1820 s	Nujol
$W(CO)_3(NCCH_3)_3$	1905 s, 1780 s	Nujol
$W(CO)_3(py)_3$	1888 s, 1747 s	Nujol

$[Mo(bipy)_2I_2]I$, 295 cm^{-1} for $[Mo(phen)_2I_2]I$, and 294 cm^{-1} for $Mo(phen)I_3$ to Mo-N stretching.

Electronic Spectra. Previously,[13] we found that the spin-forbidden bands which appeared in the spectra of Mo(III) complexes were sufficiently well resolved to show the effects of spin-orbit coupling and low ligand field symmetry. We have therefore obtained spectra for the the complexes of W(III) and certain chelate complexes of Mo(III).

The observed band maxima are given in Table IV. All of the compounds (whether cis or trans isomers) have symmetries which yield no degenerate states under the effect of spin-orbit coupling. In consequence, the symmetry type is in no way indicated by the number of allowed transitions. In any case, the band resolution in $[Mo(phen)_2Br_2]^+$ and $[Mo(bipy)_2I_2]^+$ was poor so that the spin-forbidden transitions remained unresolved. On the other hand, the resolution in $WBr_3(py)_3$ was good showing all eight of the spin-forbidden transitions which arise from the $^4A_{2g} \rightarrow {}^2T_{2g}$ and $^4A_{2g} \rightarrow {}^2E_g, {}^2T_{1g}$ transitions in the octahedral case. These bands resemble those of the nitrile complexes of Mo(III).[13] The spin-forbidden bands of these compounds are shown in Figure 2.

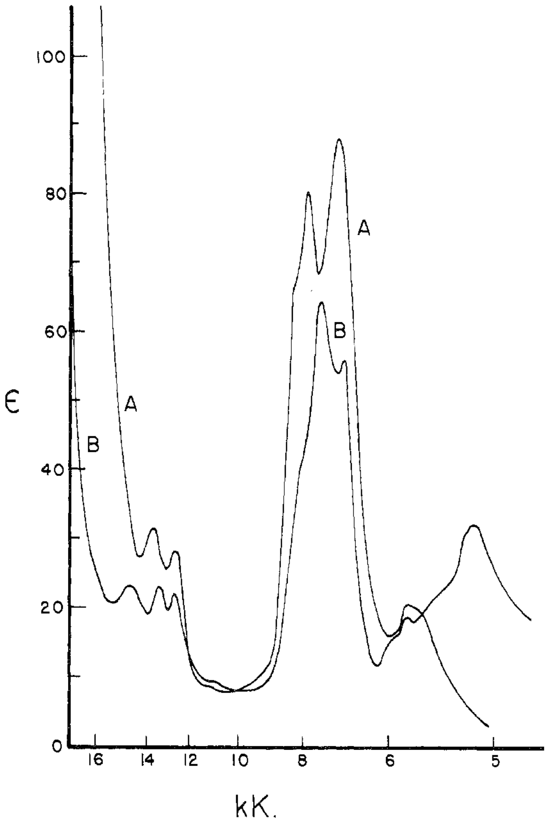

Figure 2. Electronic spectra of tungsten complexes showing spin-forbidden bands: (A) $WCl_3(py)_3$; (B) $WBr_3(py)_3$.

Table IV. Band Maxima in the Electronic Absorption Spectra of Some Trivalent Molybdenum and Tungsten Complexes

Compd	Band energies, kK
$[Mo(phen)_2Br_2]Br$	5.3, 14, 21.7, 23.6, 26.3
$[Mo(bipy)_2I_2]I \cdot NCMe$	7.0, 8.3, 12, 22, 25
$WCl_3(py)_3$	5.2, 5.4, 7.1, 7.8, 8.0, 12.6, 13.5, 22, 30.8, 33.4
$WBr_3(py)_3$	5.8, 6.0, 7.1, 7.7, 8.1, 12.4, 13.3, 14.7, 22.6, 24.7, 33.3

There is a marked difference in relative intensities of the two spin-forbidden band sets in the molybdenum and tungsten compounds, respectively. Greater intensity is expected for tungsten because of its greater spin-orbit coupling but we cannot explain why the lower energy band set in the tungsten compounds is so remarkably intense.

The bands near 22 kK in $WCl_3(py)_3$ and $WBr_3(py)_3$ are assigned to π → d charge transfer associated with pyridine and the bands which are next in increasing energy to charge transfer from halogen. These agree with the assignments of Schlafer and Konig[27] for similar bands in the spectrum of $MoCl_3(py)_3$. The extinction coefficients of the charge transfer bands are of the order of 3×10^3. The spin-allowed d-d absorption is apparently masked by these strong bands.

Magnetic Measurements. The room-temperature value of the effective moment of some of the complexes is given in Table V. Magnetically dilute six-coordinate complexes of Mo(III) are expected to have a moment of 3.6-3.9 BM, while tungsten(III), owing to its larger spin-orbit coupling, should exhibit moments of *ca.* 3.5 BM. The observed values agreed well with these expected values for complexes which can be formulated as mononuclear six-coordinate species. The compounds $WX_3(py)_3$ appear to be the first mononuclear com-

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Table V. Magnetic Moments of Some Complexes of Molybdenum and Tungsten

Compd	Temp, °K	μ_{eff}, BM	Compd	Temp, °K	μ_{eff}, BM
$[\text{Mo(phen)}_2\text{Br}_2]\text{Br}$	297	3.60	$\text{WCl}_4\text{(py)}_2$	298	1.84
$[\text{Mo(phen)}_2\text{I}_2]\text{I}$	293	3.64	$\text{WCl}_3\text{(py)}_3$	299	3.39
$[\text{Mo(bipy)}_2\text{I}_2]\text{I}\cdot\text{NCMe}$	293	3.76	$\text{WBr}_3\text{(py)}_3$	300	3.40
$\text{MoBr}_3\text{(lut)}_2$	299	3.20			

plexes of W(III) containing three unpaired electrons. A facial configuration would have a triply degenerate ground state and therefore a moment not much less than the spin only value would be observed. The ground state in a meridional configuration would be an orbital singlet so that the total spin could equal $^1/_2$. However, if the higher states are not far removed in energy, *S* could equal $^3/_2$. Thus the observed magnetic result cannot be used to confirm the configuration suggested on the basis of the infrared spectrum.

In the case of $\text{MoBr}_3\text{(lut)}_2$, a low moment was observed, and presumably the complex is polynuclear. Measurements have been reported for a number of complexes of W(III), notably $\text{WCl}_3\text{(py)}_2$,[28] WCl_3(bipy),[29] $\text{WCl}_3(\text{NMe}_3)$,[29] and WCl_3(diphos)[30] (diphos = 1,2-bis(diphenylphosphino)ethane). The moments were low for three unpaired electrons; therefore polymeric structures have been proposed. A weak susceptibility of 130×10^{-6} cgsu was found for $\text{Mo(phen)}_2\text{I}_2$ at 300°K. This suggests that the lowest lying orbital is doubly degenerate and fully occupied.

It is difficult to predict a magnetic moment for W(IV). The value recorded in Table V for $\text{WCl}_4\text{(py)}_2$ is reasonable for a distorted d^2 complex.

Molecular Weight and Electrical Conductivity Determinations. Those compounds whose empirical formula suggests that they are seven-coordinate are most probably monomeric. Because of sparing solubility, it was not possible to obtain the molecular weight of $\text{W(CO)}_3\text{(py)}_2\text{Cl}_2$ and $\text{W(CO)}_3\text{py}_2\text{Br}_2$. However, a value of 559 was found for $\text{Mo(CO)}_2[\text{P(OCH}_3)_3]_3\text{Cl}_2$ in benzene (calcd 595). In most cases acetone was required to dissolve a sufficient amount of the compounds but low apparent molecular weights were obtained in this solvent. Thus the apparent molecular weight of $\text{Mo(CO)}_2[\text{P(OCH}_3)_3]_3\text{Br}_2$ in acetone was 429 (calcd 680). Moreover, measurements of electrical conductivity in acetonitrile indicated that in most of the compounds, *e.g.*, in $\text{Mo(phen)}_2\text{I}_2$, ionization to give a 1:1 electrolyte was brought about by interaction with the solvent. Fowles and Hoodless[31] have similarly shown that complexes such as $\text{TiCl}_3\text{(py)}_3$, which were nonionized in solvents of low dielectric constant, behave as 1:1 electrolytes in acetonitrile.

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Registry No. $\text{Mo(CO)}_4\text{Cl}_2$, 15712-13-7; $\text{Mo(CO)}_4\text{Br}_2$, 22172-30-1; $\text{W(CO)}_4\text{Cl}_2$, 22172-29-8; $\text{W(CO)}_4\text{Br}_2$, 22172-31-2; $\text{W(CO)}_4\text{I}_2$, 40813-52-3; W(CO)_6, 14040-11-0; Mo(CO)_6, 13939-06-5; $\text{MoCl}_3(\text{NCCH}_2\text{CH}_3)_3$, 21223-81-4; $\text{MoBr}_3(\text{NCCH}_2\text{CH}_3)_3$, 14175-89-4; $\text{MoBr}_3\text{(NCPh)}_3$, 40813-60-3; $\text{MoCl}_3(\text{C}_4\text{H}_8\text{O})_3$, 31355-55-2; PEt_3, 554-70-1; $\text{P(OCH}_3)_3$, 121-45-9; $\text{C}_5\text{H}_5\text{N}$, 110-86-1; Br_2, 7726-95-6; Cl_2, 7782-50-5; I_2, 7553-56-2; 2,2′-$\text{NC}_5\text{H}_4\text{C}_5\text{H}_4\text{N}$, 366-18-7; CH_3CN, 75-05-8; $\text{Mo(CO)}_3(\text{PEt}_3)_2\text{Cl}_2$, 40904-19-6; $\text{Mo(CO)}_2[\text{P(OCH}_3)_3]_3\text{Cl}_2$, 40804-44-2; $\text{Mo(CO)}_2[\text{P(OCH}_3)_3]_3\text{Br}_2$, 40804-45-3; $\text{Mo}_2\text{(CO)}_4(\text{AsEt}_3)_2\text{Cl}_4$, 39310-34-4; $\text{Mo(CO)(CNPh)}_3\text{Cl}_2$, 40813-47-6; $\text{Mo(CO)(CNPh)}_4\text{Cl}_2$, 40804-46-4; $\text{MoCl}_3\text{(CNPh)}_4$, 40804-47-5; $\text{Mo(CO)}_3(\text{OPPh}_3)\text{Cl}_2$, 40903-13-7; $\text{W(CO)}_3(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2$, 40904-20-9; $\text{W(CO)}_3(\text{C}_5\text{H}_5\text{N})_2\text{Br}_2$, 40904-21-0; $\text{W(CO)}_3(\text{C}_5\text{H}_5\text{N})_2\text{I}_2$, 40904-22-1; $\text{W(CO)}_4(\text{C}_5\text{H}_5\text{N})_2$, 40903-14-8; MoI_3, 14055-75-5; $[\text{Mo}(\text{C}_{12}\text{H}_8\text{N}_2)_2\text{I}_2]\text{I}$, 41119-32-8; $[\text{Mo}(2,2'\text{-NC}_5\text{H}_4\text{C}_5\text{H}_4\text{N})_2\text{I}_2]\text{I}$, 40994-61-4; $[\text{Mo}(2,2'\text{-NC}_5\text{H}_4\text{C}_5\text{H}_4\text{N})_2\text{I}_2]\text{BPh}_4$, 40804-48-6; $[\text{Mo}(\text{C}_{12}\text{H}_8\text{N}_2)_2\text{Br}_2]\text{Br}$, 40813-62-5; $\text{Mo}_2\text{Cl}_6(2,2'\text{-NC}_5\text{H}_4\text{C}_5\text{H}_4\text{N})_3$, 15388-53-1; $\text{Mo}_2\text{Br}_6(2,2'\text{-NC}_5\text{H}_4\text{C}_5\text{H}_4\text{N})_3$, 15388-42-8; $\text{Mo}(2,2'\text{-NC}_5\text{H}_4\text{C}_5\text{H}_4\text{N})_3\text{Br}_2$, 40813-65-8; $\text{Mo}(\text{C}_{12}\text{H}_8\text{N}_2)_2\text{I}_2$, 40813-66-9; $\text{MoBr}_3[2,6\text{-(CH}_3)_2\text{C}_5\text{H}_3\text{N}]_2$, 40804-55-5; $\text{Mo}_3\text{Br}_8\text{(NCPh)}_6$, 39310-37-7; $\text{WCl}_3(\text{C}_5\text{H}_5\text{N})_3$, 40813-67-0; $\text{WBr}_3(\text{C}_5\text{H}_5\text{N})_3$, 40813-68-1; $\text{WCl}_4(\text{C}_5\text{H}_5\text{N})_2$, 20555-48-0; WI_4, 14055-84-6; $\text{W}_3\text{I}_8(\text{NCCH}_3)_6$, 39310-33-3; $\text{W(CO)}_3(\text{NCCH}_3)_3$, 16800-47-8; $\text{W(CO)}_3(\text{C}_5\text{H}_5\text{N})_3$, 40813-70-5.

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