Table IV. Pertinent Ir Bands for the Two S-Donor Ligands and Their Corresponding Mo(IV) Complexes (in cm^{-1})

Compd	Mo-O-Mo or Mo=O	Amide C=O	Ester C=O	S-H	N-H
$Mo_2OCl_4(HCEE)_2$	740		1738		3020
H_2CEE			1750	2480	3100
$MoOCl_2(DACDEE)\cdot 3HCl$	987	1590	1745		3310
DACDEE		1655	1743		3325

the complex. One interpretation that can be based on this fact is that the molybdenum(IV)-flavine complex is in equilibrium with a very small amount of molybdenum(V)-flavine-semiquinone complex and that at least for the latter species there is no difference in the solid complex and its solution species.

The Mo(IV)-HCEE and Mo(IV)-DACDEE complexes were prepared in the anticipation that they would further react with flavine ligands to produce mixed-ligand species. This hope faded when these two S-ligand compounds proved to be very insoluble in the required reaction solvents. Since these compounds were not useful for our purposes, we did not study them extensively. However, their pertinent ir spectral bands are listed in Table IV. We formulate the DACDEE compound as a monomeric oxomolybdenum(IV) complexed by at least two chlorides and by the DACDEE, probably *via* a sulfur atom and the amide oxygens. Evidence for the latter is the observed decrease in the C=O stretching frequency from 1655 to 1590 cm^{-1} on going from ligand to complex. The HCEE compound is formulated as a monooxo-bridged dimer on the basis of the absence of a Mo=O frequency and the clear presence at 740 cm^{-1} of a band assignable to the Mo-O-Mo stretching frequency.[15] The cysteine ethyl ester is probably bound to the molybdenum *via* all *three* of its potential ligand atoms, as was suggested[15] in the case of a Mo(V) complex with this same ligand.

Finally, the mixed-ligand (flavine and S-donor) complexes of Mo(IV) were prepared by allowing the S-donor ligand to react with the flavine complex. The pertinent ir bands for the two complexes are recorded in Table V. Since the ir spectra are so complicated, most of the assignments, with the exceptions of those for Mo=O, S–H, and N–H stretching frequencies, are quite tentative. However, they are consistent with the models put forth earlier in this paper for the Mo(IV) complexes containing one or the other of the two ligands. We believe that the first coordination sphere of the Mo(IV) contains a multiply bonded oxygen, two chloride ions, and each of the polydentate ligands bound through at least two ligand atoms.

Table V. Pertinent Ir Bands for the Mixed-Ligand Complexes and the Appropriate Ligands (in cm^{-1})

Compd	Mo=O	TMIA		Ester C=O	Amide C=O	S-H	N-H[a]
		C=O- (2)	C=O- (4)				
$MoOCl_2(HCEE)(HTMIA)\cdot 2HCl$	984	1715	1600	1740			2960
H_2CEE				1750		2480	3100
TMIA		1705	1670				
$MoOCl_2(DACDEE)(HTMIA)\cdot 2HCl$	980	1715	1600	1738	1660		3280
DACDEE				1743	1655		3325

[a] For the complexes these bands are broad and probably include the band due to the cysteine derivative N–H stretch as well as that due to the HTMIA N(1)–H formed in the complex.

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Registry No. $PTMoO_2Cl_2$, 52195-42-3; $PTMoOCl_4$, 41391-14-4; $MoOCl_3(TMIA)\cdot HCl$, 52239-46-0; $MoOCl_3(HEAMIA)\cdot HCl$, 52195-43-4; $MoOCl_3(HTMIA)\cdot 0.5HCl$, 52195-44-5; $MoOCl_3(HRTB)$, 52195-45-6; $MoOCl_3(HRTA)\cdot HCl$, 52195-46-7; $MoOCl_3(HTMAZ)\cdot 1.5HCl$, 52195-47-8; $Mo_2OCl_4(HCEE)_2$, 52195-49-0; $MoOCl_2(DACDEE)\cdot 3HCl$, 52195-48-9; $MoOCl_2(HCEE)(HTMIA)\cdot 2HCl$, 52239-47-1; $MoOCl_2(DACDEE)(HTMIA)\cdot 2HCl$, 52239-48-2; 7,8-dimethylalloxazine, 1086-80-2; 1,3,7,8-tetramethylalloxazine, 14684-48-1; methylalloxan, 2757-83-7; 2-amino-*N*,4,5-trimethylaniline hydrochloride, 52176-12-2; 3,7,8,10-tetramethylisoalloxazine, 18636-32-3.

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Complexes of Di(tertiary stibines). Group VIb Metal Carbonyl Halide Derivatives of Bis(diphenylstibino)methane

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The potentially bidentate antimony ligand $(C_6H_5)_2SbCH_2Sb(C_6H_5)_2$ (Dpsm) reacts immediately with the molybdenum and tungsten tetracarbonyl dihalides to yield $M(CO)_3(Dpsm)_2X_2$ (M = Mo, X = Cl, Br; M = W, X = Cl, Br, I) and $Mo(CO)_3(Dpsm)I_2$. Under more vigorous conditions most of the tricarbonyls lose 1 mol of ligand and carbon monoxide to produce species of the type $M(CO)_2(Dpsm)X_2$. Structural and bonding assignments are based upon the interpretation of nmr and infrared spectral data. The types of Dpsm derivatives, their relative stabilities, and spectral data are compared with those for the known phosphorus and arsenic ligand complexes.

Introduction

Compared to the extensive investigations of transition metal carbonyl derivatives of amine, phosphine, and arsine mono- and polydentate ligands relatively few studies of analogous stibine Lewis bases have been conducted.[1-9] In fact, there are only four reports describing reactions of metal carbonyls

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Table I. Analytical Data and Physical Properties for Halogenated Dpsm Metal Carbonyls

Compd	Color	Mp,^{a} °C	Reacn time^b	Mol wt^c		Analyses, %							
						C		H		Sb		X	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Mo(CO)_3(Dpsm)_2Cl_2$^{d}	Orange	132–133	A	1383	1050	46.03	46.21	3.21	3.45			5.13	5.35
$W(CO)_3(Dpsm)_2Cl_2$^{d}	Orange	104–106	A			43.28	43.53	3.02	3.10	33.12	32.90	4.82^e	5.85
$Mo(CO)_3(Dpsm)_2Br_2$^{d}	Orange	125–127	A	1472	1390	43.25	42.95	3.01	3.21	33.10	33.20	10.86	11.06
$W(CO)_3(Dpsm)_2Br_2$	Light orange	130–131	A	1560	1580	40.81	40.30	2.84	2.61	31.23	32.20	10.25	9.40
$Mo(CO)_3(Dpsm)I_2$	Orange	104–105	A	1000	990	33.62	32.98	2.22	2.30	25.39	24.80	24.36	28.60
$W(CO)_3(Dpsm)_2I_2$	Yellow	151–152	A	1654	1540	38.49	38.25	2.68	2.45	29.46	32.10	15.35	17.30
$Mo(CO)_2(Dpsm)Cl_2$^{d}	Brown-orange	110–111	B 4 hr			41.10	41.12	2.81	2.38	30.88	28.30	8.99	8.36
$W(CO)_2(Dpsm)Cl_2$^{d}	Brown-orange	103–104	B 4 days	877	966	36.98	36.41	2.53	2.54	27.78	30.40	8.09	6.60
$Mo(CO)_2(Dpsm)I_2$	Brown-orange	112–113	B 20 hr	976	1140	33.37	33.45	2.28	2.70	25.08	25.90	26.12	24.00

[a] Decomposition point. [b] A, immediately upon mixing; B, refluxing methylene chloride; for $Mo(CO)_2(Dpsm)Br_2$ 42 hr and for $W(CO)_2(Dpsm)Br_2$ 9 days. [c] Chloroform at 37°. [d] Molar conductivities: 3.26–5.58 $cm^2\ ohm^{-1}\ mol^{-1}$. [e] For W: calcd, 12.50; found, 11.20.

with potentially bidentate organoantimony ligands.[6-9] Because of this dearth of information and the comparative possibilities with bis(diphenylphosphino)methane (Dpm) and bis(diphenylarsino)methane (Dam) metal carbonyls,[10-20] we have extended our investigations to include the halogenated group VIb metal carbonyl chemistry of bis(diphenylstibino)methane.

Experimental Section

Microanalyses and molecular weights were performed by M-H-W Laboratory, Garden City, Mich. The latter were determined by osmometry at 37° in chloroform. Infrared spectra were recorded in methylene chloride solutions on a Model 621 Perkin-Elmer spectrometer. Proton nmr spectra were taken in chloroform-*d* on a Varian Associates Model T-60 instrument with tetramethylsilane as an internal standard. Conductivity measurements were obtained in nitrobenzene solutions at 27°. Melting points were taken in open capillaries and are uncorrected. Dry nitrogen was used routinely for deaeration of solvents, maintenance of an inert atmosphere over reaction mixtures, and admission to evacuated vessels.

$M(CO)_3(Dpsm)_2X_2$ (M = Mo, X = Cl, Br; M = W, X = Cl, Br, I). The impure tetracarbonyl halide $M(CO)_4X_2$, prepared by allowing the hexacarbonyl to react with chlorine or bromine at −78°[21-24] or with iodine at 25° under ultraviolet irradiation,[25] was dissolved in methylene chloride and filtered into a solution of Dpsm[26] (2 times the carbonyl concentration) in the same solvent. Purification was accomplished by solvent evaporation (25°, 30 mm) and recrystallization of the residue by the addition of pentane to a CH_2Cl_2 solution saturated with carbon monoxide. Yields were usually between 10 and 25% with the exception of $W(CO)_3(Dpsm)_2I_2$ which was 70%.

$W(CO)_3(Dpsm)_2Cl_2$ was prepared by adding solid Dpsm to a filtered acetone solution of $W(CO)_4Cl_2$. Hexane was added and the blue solution was evaporated until a blue solid precipitated. The resulting orange solution was filtered and evaporated to dryness. Subsequent recrystallization as above yielded orange crystals.

$M(CO)_2(Dpsm)X_2$. The dicarbonyl complexes of molybdenum and tungsten were produced by refluxing the tricarbonyls in methylene chloride until conversions were complete as determined by monitoring the ν(CO) stretching region. Recrystallized products were obtained only in 2 to 7% yields.

See Table I for analyses of compounds.

Results and Discussion

While there are generally two methods utilized to synthesize halogenated group VIb metal carbonyls, (1) halogen oxidation of substituted derivatives and (2) ligand replacement of carbonyls in $M(CO)_4X_2$ species,[27] only the latter led to isolable and pure bis(diphenylstibino)methane (Dpsm) complexes. Immediately upon mixing methylene chloride solutions of Dpsm and $M(CO)_4X_2$ (M = Mo, W; X = Cl, Br, I) an orange color developed. Solvent evaporation yielded an orange solid but ν(CO) bands for the tricarbonyl $M(CO)_3(Dpsm)_2X_2$ and a dicarbonyl derivative were observed. Since attempts to recrystallize the products led to oils, purification was accomplished by concentrating the methylene chloride solution with carbon monoxide (which converted the dicarbonyl present to the tricarbonyl) and adding pentane to effect precipitation. Unlike their Dpm[16] and Dam[17] counterparts none of the dichloro and dibromo metal carbonyls of Dpsm showed signs of solvent adduct formation.

Although $W(CO)_4I_2$ reacted with Dpsm to give $W(CO)_3(Dpsm)_2I_2$, the molybdenum iodide produced $Mo(CO)_3(Dpsm)I_2$ which contains only 1 mol of ligand. This is in contrast to results with Dam where complexes containing 1 and 2 mol of ligand were isolated.[28] Distinct differences exist in the stability of the dihalotricarbonylmetal complexes of Dpsm and the analogous ones of phosphorus and arsenic. The $M(CO)_3(Dpm)_2X_2$ compounds were generally too unstable to be isolated[16] and some of the Dam complexes were converted to dihalodicarbonyl derivatives by simply dissolv-

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Table II. Infrared and Proton Nmr Spectra for Halogenated Dpsm Metal Carbonyls and Related Compounds

Compd	ν(CO),[a] cm^{-1}	Proton nmr spectra,[b] ppm	
		$\tau(CH_2)$	$\tau(C_6H_5)$
Dpsm[28]		7.96	2.74
$Mo(CO)_3(Dpsm)_2Cl_2$	2032 s, 1958 s, 1919 s	7.16	2.77
$W(CO)_3(Dpsm)_2Cl_2$	2023 s, 1940 s, 1908 s	7.30	2.78
$Mo(CO)_3(Dpsm)_2Br_2$	2030 s, 1958 s, 1920 s	7.03	2.63
$W(CO)_3(Dpsm)_2Br_2$	2023 s, 1941 s, 1908 s	7.08	2.64
$Mo(CO)_3(Dpsm)I_2$	2027 s, 1957 s, 1920 s	7.80	2.65
$W(CO)_3(Dpsm)_2I_2$	2021 s, 1942 s, 1910 s	6.86	2.64
$Mo(CO)_2(Dpsm)Cl_2$	1931 s, 1859 s	7.56[c]	2.66
$W(CO)_2(Dpsm)Cl_2$	1914 s, 1832 s	7.62[c]	2.76
$Mo(CO)_2(Dpsm)Br_2$	1933 s, 1857 s		
$W(CO)_2(Dpsm)Br_2$	1924 s, 1845 s	7.92[c]	2.81
$Mo(CO)_2(Dpsm)I_2$	1939 s, 1858 s	7.93[c]	2.75
$Mo(CO)_3(SbPh_3)_2Cl_2$[22]	2040 m, 1965 s, 1925 m		
$Mo(CO)_3(Ph_3P)_2Cl_2$[21]	2045 m, 1952 s, 1903 m N		
$Mo(CO)_3(Dam)_2Cl_2$[17]	2040 s, 1970 s, 1920 s N		
$W(CO)_3(Dam)_2Cl_2$[17]	2030 s, 1950 s, 1904 s N		
$Mo(CO)_2(Dam)_2Cl_2$[17]	1950 s, 1870 s N		
$Mo(CO)_2(Dpm)_2Cl_2$[16]	1940 s, 1865 s N		

[a] Recorded in methylene chloride except those denoted by N which were run in Nujol. Intensities: medium, m; strong, s. [b] Recorded in chloroform-*d* with TMS as internal standard. [c] Very weak and broad bands.

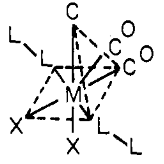
ing them in methylene chloride at 25°.[17,28] In contrast, it was necessary to heat, sometimes extensively, the $M(CO)_3(Dpsm)_2X_2$ complexes to produce stibine dicarbonyls.

Even though the complete conversion to pure dicarbonyls proved difficult and resulted in low yields, refluxing the various $M(CO)_3(Dpsm)_2X_2$ species in methylene chloride did lead to dicarbonyl derivatives of every tricarbonyl except the tungsten iodide. Contrary to the results observed with Dam and Dpm which formed complexes with two ligands per molecule, $M(CO)_2(ligand)_2X_2$,[16,17,28] elemental analyses and molecular weight measurements of Dpsm derivatives were consistent with one ligand per unit, $M(CO)_2(Dpsm)X_2$.

Three strong bands in the metal carbonyl stretching region of the infrared were observed for the $Mo(CO)_3(Dpsm)_2X_2$ derivatives (Table II), and these are quite comparable to those for $M(CO)_3(ligand)_2X_2$ (ligand = Dam, Dpm, and $(C_6H_5)_3Sb$). Consistent with previously reported results the tungsten complexes exhibited ν(CO) values lower than those for molybdenum. The three halogens produced little variation in the ν(CO) frequencies for the different tricarbonyl derivatives.

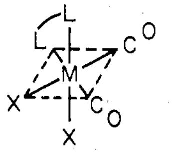
The methylene protons in these metal(II) derivatives exhibited broad singlets shifted further downfield from the free-ligand value than were those for the zerovalent Dpsm complexes.[8] For the tungsten derivatives the downfield shifts (Cl = 0.66, Br = 0.88, I = 1.10 ppm) are just the reverse of that expected from electronegativity trends.

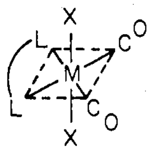
Based on the analytical results, their nonionic behavior in solution (Table I), and the similarity of their infrared spectra to those of the Dpm and Dam complexes, the $M(CO)_3(Dpsm)_2X_2$ derivatives probably attain the seven-coordinate, capped octahedral structure adopted by $M(CO)_3(Dam)_2X_2$ (M = Mo, W)[29]



Although the infrared spectrum of $Mo(CO)_3(Dpsm)I_2$ is similar to those of the other dihalotricarbonyls of Dpsm, the nmr spectrum is quite different. Instead of exhibiting a methylene proton resonance around τ 7.0 it is located at τ 7.80 consistent with the upfield shift observed in monomeric $Mo(CO)_4(Dpsm)$ where Dpsm is chelated. The corroborative spectral and analytical evidence indicates that $Mo(CO)_3(Dpsm)I_2$ is monomeric and seven-coordinate with both antimony atoms bonded to molybdenum similar to the capped octahedral structure of $Mo(CO)_3(Diphos)Br_2$.[30]

Refluxing $M(CO)_3(Dpsm)_2X_2$ in methylene chloride yielded products that exhibited two ν(CO) stretching frequencies similar to those reported for the dihalodicarbonyls of Dam and Dpm.[16,17,28] Unlike the tricarbonyls of Dpsm which showed little variation in the ν(CO) frequencies, the dihalodicarbonyls of both molybdenum and tungsten depicted a slight increase in the order I > Br > Cl which is consistent with the net electron-withdrawing order previously mentioned. The single methylene frequency for the Dpsm dicarbonyls was found to be upfield from those of the dihalotricarbonyl complexes where the ligands are considered to be monodentates. Since an upfield shift in the methylene frequency for $Mo(CO)_3(Dpsm)I_2$ and $M(CO)_4(Dpsm)$[8] (M = Cr, Mo, W) has been associated with ligand chelation and since the two strong infrared bands indicate that the carbonyls are in a cis position, one of the octahedral structures below is suggested for the $M(CO)_2(Dpsm)X_2$ derivatives.





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Registry No. $Mo(CO)_3(Dpsm)_2Cl_2$, 52393-12-1; $W(CO)_3(Dpsm)_2Cl_2$, 52393-13-2; $Mo(CO)_3(Dpsm)_2Br_2$, 52393-14-3; $W(CO)_3(Dpsm)_2Br_2$, 52393-15-4; $Mo(CO)_3(Dpsm)I_2$, 52393-16-5; $W(CO)_3(Dpsm)_2I_2$, 52393-17-6; $Mo(CO)_2(Dpsm)Cl_2$, 52393-18-7; $W(CO)_2(Dpsm)Cl_2$, 52393-19-8; $Mo(CO)_2(Dpsm)Br_2$, 52393-20-1; $W(CO)_2(Dpsm)Br_2$, 52393-25-6; $Mo(CO)_2(Dpsm)I_2$, 52393-26-7.

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