Table I. Data of Lanthanide Fluorosulfate Preparations

Starting material	Wt of starting material, g	Product	Wt of product expected, g	Wt of product found, g
Nd_2O_3	0.0605	$Nd(SO_3F)_3$[a]	0.1585	0.1382
Sm_2O_3	0.0869	$Sm(SO_3F)_3$[a]	0.2230	0.1801
Eu_2O_3	0.0988	$Eu(SO_3F)_3$[a]	0.2521	0.1502
$Sc_2(CO_3)_3$	0.0895	$Sc(SO_3F)_3$	0.2267	0.2235
$Y_2(CO_3)_3$	0.0960	$Y(SO_3F)_3$	0.2087	0.2092
$La_2(CO_3)_3$	0.0919	$La(SO_3F)_3$	0.1750	0.1754
$Pr_2(CO_3)_3$	0.0200	$Pr(SO_3F)_3$	0.0386	0.0385
$Nd_2(CO_3)_3$	0.0608	$Nd(SO_3F)_3$	0.1145	0.1153
$Sm_2(CO_3)_3$	0.0655	$Sm(SO_3F)_3$	0.1218	0.1175
$Eu_2(CO_3)_3$	0.0646	$Eu(SO_3F)_3$	0.1200	0.1159
$Gd_2(CO_3)_3$	0.1004	$Gd(SO_3F)_3$	0.1845	0.1923
$Tb_2(CO_3)_3$	0.1242	$Tb(SO_3F)_3$	0.2276	0.2343
$Dy_2(CO_3)_3$	0.1643	$Dy(SO_3F)_3$	0.3031	0.2989
$Ho_2(CO_3)_3$	0.0994	$Ho(SO_3F)_3$	0.1800	0.1786
$Er_2(CO_3)_3$	0.1893	$Er(SO_3F)_3$	0.3416	0.3360
$Tm_2(CO_3)_3$	0.1715	$Tm(SO_3F)_3$	0.3087	0.3170
$Yb_2(CO_3)_3$	0.1346	$Yb(SO_3F)_3$	0.2406	0.2462
$Lu_2(CO_3)_3$	0.1133	$Lu(SO_3F)_3$	0.2029	0.2068

[a] Not obtained pure by this reaction (see text).

Table II. Data from the Analysis of Lanthanide Fluorosulfates

	% M		% S		% F	
Compd	Calcd	Found	Calcd	Found	Calcd	Found
$Sc(SO_3F)_3$	13.0	12.9	28.0	28.1	17.1	15.9
$Y(SO_3F)_3$	23.1	23.4	24.8	24.7	14.7	13.6
$La(SO_3F)_3$	31.9	31.5	22.0	21.3	13.1	12.7
$Nd(SO_3F)_3$	32.7	32.3	21.8	21.9	12.9	12.6
$Sm(SO_3F)_3$	33.6	33.3	21.5	21.5	12.7	12.6
$Eu(SO_3F)_3$	33.9	35.4	21.4	21.6	12.7	12.0
$Gd(SO_3F)_3$	34.6	35.0	21.5	21.6	12.6	12.0
$Tb(SO_3F)_3$	34.7	34.9	21.1	20.8	12.5	11.7
$Dy(SO_3F)_3$	35.3	36.9	20.9	20.4	12.4	11.7
$Ho(SO_3F)_3$	35.7	36.0	20.8	20.2	12.3	11.5
$Er(SO_3F)_3$	35.9	35.0	20.6	20.0	12.3	11.9
$Tm(SO_3F)_3$	36.3	37.4	20.5	19.8	12.2	11.8
$Yb(SO_3F)_3$	36.8	36.9	20.4	22.4	12.1	12.1
$Lu(SO_3F)_3$	37.1	37.4	20.4	20.4	12.0	12.3

After the reaction had gone to completion, the vessel was pumped to constant weight under dynamic vacuum. The carbonates of lanthanum, praseodymium, and neodymium as prepared for this work required a reaction temperature of about 60 °C and a period of 5–10 days. Cerium carbonate gave a Ce(IV) compound which is discussed elsewhere.[2] Table I gives data regarding the preparations.

Oxides of only three of the rare earth elements, Nd, Sm, and Eu, gave indications of reacting extensively with $S_2O_6F_2$. Results obtained for these are included in Table I. Raman spectra indicated the products to be mixtures of fluorosulfate with oxide. Complete reaction of these oxides was not obtained even at 75 °C with a reaction period up to 17 days.

Analysis. For each salt, with the exception of $Pr(SO_3F)_3$, M, S, and F were determined, and the results are shown in Table II.

Properties. The various fluorosulfates had the colors characteristic of the metals in the III oxidation state. All of the salts were soluble in water or in dimethyl sulfoxide. They also dissolved, but to a much smaller extent, in formamide. They appeared to be essentially insoluble in fluorosulfuric acid, acetonitrile or *N*,*N*-dimethylformamide.

Acknowledgment. This work was performed in part under contract with the Office of Naval Research.

Registry No. $Sc(SO_3F)_3$, 58438-33-8; $Y(SO_3F)_3$, 58438-34-9; $La(SO_3F)_3$, 58438-35-0; $Pr(SO_3F)_3$, 58438-36-1; $Nd(SO_3F)_3$, 58438-37-2; $Sm(SO_3F)_3$, 58438-38-3; $Eu(SO_3F)_3$, 58438-39-4; $Gd(SO_3F)_3$, 58438-40-7; $Tb(SO_3F)_3$, 58438-41-8; $Dy(SO_3F)_3$, 58438-42-9; $Ho(SO_3F)_3$, 58438-43-0; $Er(SO_3F)_3$, 58438-44-1; $Tm(SO_3F)_3$, 58438-45-2; $Yb(SO_3F)_3$, 58438-46-3; $Lu(SO_3F)_3$, 58438-47-4; $S_2O_6F_2$, 13709-32-5.

References and Notes

(1) J. M. Shreeve and G. H. Cady, *Inorg. Synth.*, 7, 124 (1963).
(2) R. Dev, W. M. Johnson, and G. H. Cady, *Inorg. Chem.*, **11**, 2259 (1972).

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Reactions of $Mo_2X_8H^{3-}$ and $Mo_2X_9^{3-}$ with Pyridine[1]

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The dinuclear complexes of molybdenum,[2,3] tungsten,[4] and rhenium[2b,3,5,6a] halides undergo a variety of reactions with various heteroatom-containing ligands. Although they are frequently accompanied by geometric rearrangement and/or reduction of the metal to a lower oxidation state, in general these reactions occur with retention of the dinuclear framework. This paper describes the study of the extended reactions of several dinuclear complexes of molybdenum with pyridine as well as certain related spectroscopic observations about the products.

Experimental Section

General Data. Pyridine (Matheson Coleman and Bell) was distilled from calcium hydride under a nitrogen atmosphere prior to use. Molybdenum hexacarbonyl and molybdenum(III) chloride (Climax Molybdenum) were used without further purification. Optical spectra were recorded using a Cary Model 14 spectrophotometer. Infrared spectra (>400 cm^{-1}) were obtained on a Perkin-Elmer Model 225 grating spectrophotometer employing either KBr disks or Nujol mulls supported on polyethylene plates. Frequencies are precise to ±1 cm^{-1}. Raman spectra were recorded on a Cary Model 82 laser Raman spectrometer equipped with a rotating sample cell similar to that described elsewhere.[6b] Unless otherwise noted, a slit width of 3 cm^{-1} and a scan rate equal to the ratio of the slit width to time constant were employed. Excitation was provided by Coherent Radiation Laboratory Model 52 argon and kryton ion lasers. Reported frequencies are precise to ±1 cm^{-1}. Far-infrared spectra (<400 cm^{-1}) were recorded on a Beckman Fourier Model FS-720 spectrophotometer employing Nujol mulls supported on polyethylene plates. Frequencies are precise to ±0.5 cm^{-1}.

Raman intensities were determined by adding a known amount of internal standard ($KReO_4$ or KNO_2) to a predetermined quantity of the desired complex admixed with an inert substrate (KBr). The resulting mixture was homogenized in a Spex Wig-L-Bug for 3–5 min. A polar planimeter was used to determine the intensity of each band of interest by integrating the area under each envelope and comparing it to the area of a selected band in the internal standard. All intensities were corrected for phototube response.

Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Tricesium 1,1,1,2,2,2-Hexachloro-μ-hydrido-di-μ-chloro-dimolybdenum(III),[7] $Cs_3Mo_2Cl_8H$, **tricesium 1,1,1,2,2,2-hexabromo-μ-hydrido-di-μ-bromo-dimolybdenum(III),** $Cs_3Mo_2Br_8H$, **tricesium enneachlorodimolybdenum,[7]** $Cs_3Mo_2Cl_9$, ***mer*-trichlorotris(pyridine)molybdenum(III),[8]** *mer*-$MoCl_3(py)_3$, **tetrachloro-[2] and tetrabromotetrakis(pyridine)dimolybdenum(II),[2a]** $Mo_2Cl_4(py)_4$ **and** $Mo_2Br_4(py)_4$, **and tetrapotassium octachlorodimolybdenum(II),[9]** $K_4Mo_2Cl_8$, were prepared according to literature procedures.

Preparation of Tricesium Enneabromodimolybdenum(III), $Cs_3Mo_2Br_9$. $Cs_3Mo_2Br_8H$ (1.0 g, 0.81 mmol) was placed in a 200-ml beaker along with a Teflon-coated stirrer bar. Deoxygenated hydrobromic acid (75 ml, 48%) was added and the mixture stirred under nitrogen until dissolution was completed. Two platinum electrodes, each measuring ~10 cm^2 in area, were then inserted into the solution, and, with continuous stirring and maintaining a steady stream of nitrogen through the solution, the mixture was electrolyzed for 2 min at 4.0 ± 0.5 A.[10] The red precipitate, which began forming almost immediately, was collected by suction filtration, washed with 50 ml of distilled water, 50 ml of absolute ethanol, and finally 50 ml of anhydrous ether, and dried in vacuo. The isolated yield of tricesium enneabromodimolybdenum was 65%. Anal. Calcd for $Cs_3Mo_2Br_9$: Br, 55.04. Found: Br, 55.08.

Reaction of $Cs_3Mo_2Cl_8H$ **with Pyridine.** Tricesium 1,1,1,2,2,2-hexachloro-μ-hydrido-di-μ-chloro-dimolybdenum(III) (1.5 g, 1.2 mmol) was placed in a 12-in. × 0.5-in. (i.d.) Fischer-Porter combustion tube. Pyridine (20 ml) and a Teflon-coated stirring bar were added and the vessel was tightly sealed with a Teflon-lined cap and placed in a silicone oil bath at 200 °C for 18 h. Shorter or longer reaction times as well as the failure to maintain efficient stirring throughout the course of the reaction led to reduced product yields. The resulting mixture was allowed to cool to an ambient temperature and treated with petroleum ether (bp 30–60 °C, 100 ml). The yellow solid which precipitated was collected by suction filtration, washed with three 10-ml portions of water followed by three 10-ml portions of ether, and then dried in vacuo. The crude product, isolated in 75–80% yield, was recrystallized from hot pyridine. Anal. Calcd for $(C_5H_5N)_3MoCl_3$: C, 40.98; H, 3.44; N, 9.56; Cl, 24.19. Found: C, 41.21; H, 3.52; N, 9.73; Cl, 23.93.

Reaction of $Cs_3Mo_2Cl_9$ with Pyridine. Tricesium enneachlorodimolybdenum(III) (1.2 g, 1.3 mmol) was allowed to react with pyridine under conditions (18 h, 200 °C) equivalent to those described for the similar reaction of $Cs_3Mo_2Cl_8H$. The crude product, isolated in 75% yield, was recrystallized from hot pyridine. Anal. Found: C, 40.80; H, 3.37; N, 9.50; Cl, 24.12.

Reaction of $Cs_3Mo_2Br_8H$ with Pyridine. Into a 12-in. × 0.5-in. Fischer-Porter combustion tube was placed a small Teflon-coated stirrer bar and the vessel was charged with tricesium 1,1,1,2,2,2-hexabromo-μ-hydrido-di-μ-bromo-dimolybdenum(III) (1.50 g, 1.26 mmol) and pyridine (20 ml). The vessel was sealed tightly with a Teflon-lined cap and placed in a silicone oil bath at 200 °C. The reaction mixture was stirred vigorously for 8 h. Longer reaction times or inefficient stirring resulted in lower yields. After it had cooled to room temperature, the reaction mixture was treated with petroleum ether (bp 30–60 °C, 100 ml). The orange-yellow solid that formed was collected by suction filtration, washed with diethyl ether, and dried in vacuo. The crude product, isolated in 65–75% yield, was recrystallized from hot pyridine. Anal. Calcd for $(C_5H_5N)_3MoBr_3$: C, 32.60; H, 2.72; N, 7.33; Br, 41.89. Found: C, 32.49; H, 2.78; N, 7.48; Br, 41.68.

Reaction of $Cs_3Mo_2Br_9$ with Pyridine. A procedure was employed similar to that described for the analogous reaction with $Cs_3Mo_2Br_8H$. Optimum yields (85%) were obtained with a reaction time of 2 h. Anal. Found: C, 33.91; H, 2.81; N, 7.31; Br, 41.16.

Reaction of $Mo_2Cl_4(C_5H_5N)_4$ with Pyridine. Tetrachlorotetrakis(pyridine)dimolybdenum(II) (1.20 g, 1.85 mmol) was placed in a 12-in. × 0.5-in. Fischer-Porter combustion tube containing a Teflon-coated magnetic stirrer bar. Pyridine (20 ml) was added and the vessel was sealed with a Teflon-lined cap and placed in an oil bath at 200 °C for 18 h. Efficient stirring was maintained throughout the reaction period. The resulting mixture was cooled to room temperature and treated with petroleum ether (100 ml, bp 30–60°). The crude brown solid (0.38 g) that precipitated was collected by suction filtration and recrystallized from hot pyridine to yield 80 mg (7.4% based on available chloride) of *mer*-trichlorotris(pyridine)molybdenum(III).

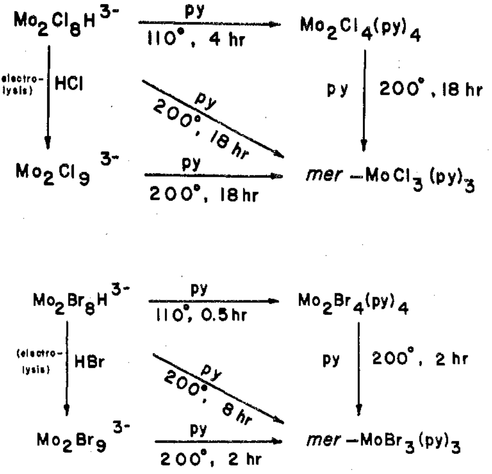
Reaction of $Mo_2Cl_4(py)_4$ with Pyridine and Added Cesium Chloride. The above reaction was repeated in the presence of 0.65 g (3.9 mmol) of added cesium chloride. A similar work-up produced a 75% yield of crude *mer*-trichlorotris(pyridine)molybdenum(III) which was recrystallized from hot pyridine. The isolated yield of pure product was 67%.

Reaction of $W_2Cl_6(py)_4$ with Pyridine. Into a 12-in. × 0.5-in. Fischer-Porter combustion tube were placed a Teflon-coated magnetic stirrer bar, pyridine (20 ml), and $W_2Cl_6(py)_4$[4] (0.50 g, 0.57 mmol). The vessel was tightly sealed with a Teflon-coated cap and placed in an oil bath at 200 °C for 18 h. The reaction mixture was allowed to cool and the brown precipitate (0.35 g) was collected by suction filtration and washed with diethyl ether (20 ml). Neither treatment of the mother liquor with pentane nor its concentration to near dryness produced any further characterizable solid. The Raman spectrum of the isolated solid was equivalent to that of the starting complex $W_2Cl_6(py)_4$. Its elemental analysis was that of the starting complex. Anal. Calcd for $(C_5H_5N)_4W_2Cl_6$: C, 26.77; H, 2.25; N, 6.25; Cl, 23.75. Found: C, 26.08; H, 2.12; N, 6.02; Cl, 22.54.

Results and Discussion

Chemical Work. In a previous investigation we reported that octachloro- and octabromodimolybdates are reduced, respectively, to tetrachloro- and tetrabromotetrakis(pyridine)dimolybdenum(II) by limited reaction with pyridine.[2a] These reactions together with those that occur on extended treatment of both octa- and enneahalodimolybdates with pyridine are summarized in Scheme I. It is apparent that, depending on reaction conditions, the reaction of $Mo_2X_8H^{3-}$ with pyridine can involve overall reduction or oxidation of the molybdenum centers. The ability of pyridine to effect reduction of certain higher valent transition metal ions is well-known,[6a,11] and it is possible that pyridine may, at least in part, be responsible for the reduction of $Mo_2X_8H^{3-}$ to $Mo_2X_4(py)_4$. It is less obvious what oxidant(s) is (are) responsible for the oxidation of $Mo_2X_4(py)_4$ to *mer*-$MoX_3(py)_3$ although disproportionation and/or reaction with dissolved oxygen are two possible ways.

Scheme I. Reactions of the Dinuclear Ions $Mo_2X_8H^{3-}$ and $Mo_2X_9^{3-}$ with Pyridine



The fact that $Mo_2X_4(py)_4$ can be isolated from the incomplete reaction of $Mo_2X_8H^{3-}$ with pyridine suggests that this dinuclear molybdenum(II) complex is an intermediate along the reaction path leading to *mer*-$MoX_3(py)_3$. This suggestion is supported by the further observation that extended treatment of $Mo_2X_4(py)_4$ with pyridine produces *mer*-$MoX_3(py)_3$. In the presence of added cesium halide, the efficiency of this reaction is improved considerably. It appears, therefore, that the overall transformation of $Mo_2X_8H^{3-}$ to *mer*-$MoX_3(py)_3$ proceeds, at least in part, through the intermediacy of the dinuclear complex $Mo_2X_4(py)_4$ which is subsequently oxidized with rupture of the dinuclear framework to yield *mer*-$MoX_3(py)_3$. A similar pathway cannot be excluded for the analogous transformation of $Mo_2X_9^{3-}$ to *mer*-$MoX_3(py)_3$; however, its likelihood is diminished by the fact that no intermediate could be isolated in these reactions. An alternative pathway may be involved.

The reactivity of $Mo_2X_8H^{3-}$ and $Mo_2X_9^{3-}$ varies substantially with the nature of the halogen. Thus, optimum conversions of $Mo_2Br_8H^{3-}$ to *mer*-$MoBr_3(py)_3$ required only 2 and 8 h, respectively. Under similar conditions, comparable conversions of $Mo_2Cl_8H^{3-}$ and $Mo_2Cl_9^{3-}$ to *mer*-$MoCl_3(py)_3$ required 18 h. Finally, it should be noted that our efforts to extend the reactions outlined in Scheme I to tertiary phosphines were uniformly unsuccessful.

The reactions of $Cr_2Cl_9^{3-}$, $Mo_2Cl_9^{3-}$, and $W_2Cl_9^{3-}$ with pyridine permit a comparison of the relative reactivities of these related ions which merits brief attention. Salts of $Cr_2Cl_9^{3-}$ react readily with refluxing pyridine, producing the mononuclear chromium(III) complex *mer*-$CrCl_3(py)_3$.[12,13] In contrast, the reaction of $W_2Cl_9^{3-}$ with pyridine under similar conditions yields the dinuclear complex $W_2Cl_6(py)_4$,[4a] a substance whose diamagnetism and short metal–metal distance suggest the presence of a significant tungsten–tungsten bond[4b] and which is unaffected by extended treatment with pyridine at elevated temperatures (see Experimental Section).

The dinuclear molybdenum complexes $Mo_2Cl_9^{3-}$ and $Mo_2Cl_8H^{3-}$ undergo reactions with pyridine which seem to

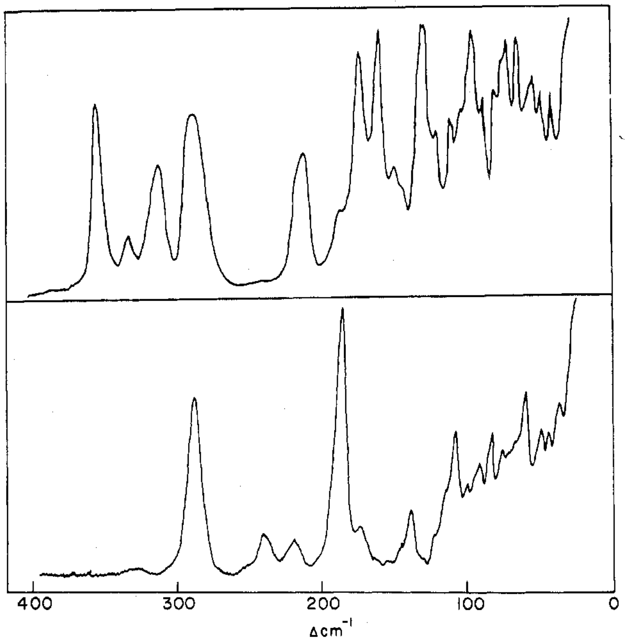


Figure 1. Solid-state Raman spectra of $Cs_3Mo_2Cl_8H$ (top) and $Cs_3Mo_2Br_8H$ (bottom) recorded using 5145-Å radiation.

Table I. Low-Frequency Solid-State Raman Bands[a] Observed for $Cs_3Mo_2Cl_8H$ and $Cs_3Mo_2Br_8H$

$Cs_3Mo_2Cl_8H$		$Cs_3Mo_2Br_8H$	
351 s	184 sh	330 w	188 vs
329 m-w	169 s	289 s	173 m
309 m	155 s	240 m	139 m
284 s	144 w	209 m	108 s
208 s	124 s		

[a] Recorded using 5145-Å exciting radiation.

Table II. Summary of Selected Low-Frequency Infrared Data Observed for *mer*-Tribromo- and *mer*-Trichlorotris(pyridine)molybdenum(III)[a]

mer-$MoCl_3(py)_3$		*mer*-$MoBr_3(py)_3$	
457 sh	277 sh	460 m	245 s
443 s	251 s	440 s	188 sh
435 sh	222 w-m	394 m	175 s
415 w-m	207 s	375 w	160 s
375 w-m	155 sh	309 m	155 sh
318 vs	146 s	*269* vs	115 m
307 vs		*260* vs	

[a] Frequencies in italic type denote bands which, based on position and intensity, are assigned as metal-halogen stretching vibrations.

Table III. Solid-State Raman Frequencies and Relative Intensities Observed for *mer*-$MoX_3(py)_3$[a]

mer-$MoCl_3(py)_3$			*mer*-$MoBr_3(py)_3$		
ν, cm^{-1}	λ_0,[b] Å	R[c]	ν, cm^{-1}	λ_0,[b] Å	R[c]
282	5682	0.19	264	6471	0.12
	5309	0.21		5682	0.14
	5145	0.25		5309	0.16
	4965	0.25		5145	0.20
	4880	0.31		4965	0.26
	4765	0.37		4880	0.30
307	5682	0.15		4762	0.35
	5309	0.16	1013, 1018	6471	0.27
	5145	0.17		5682	0.33
	4965	0.17		5309	0.39
	4880	0.21		5145	0.39
	4765	0.24		4965	0.42
1013, 1018	6471	0.49		4880	0.46
	5682	0.57		4762	0.48
	5309	0.70	1605	6471	0.06
	5145	0.66		5682	0.09
	4965	0.82		5309	0.15
	4880	0.81		5145	0.15
	4762	1.09		4965	0.20
1606	6471	0.12		4880	0.24
	5682	0.17		4762	0.30
	5309	0.28			
	5145	0.27			
	4965	0.43			
	4880	0.46			
	4762	0.77			

[a] See Experimental Section for description of sample preparation. [b] Exciting wavelength. [c] Intensity of indicated band, relative to the ν_1 band of $KReO_4$ or the δ band of $NaNO_2$. $R = I_2M_2/I_1M_1$; I = intensity, M = moles; 1 = standard, 2 = $MoX_3(py)_3$.

reflect a reactivity that is transitional between the two extremes provided by $Cr_2Cl_9^{3-}$ and $W_2Cl_9^{3-}$. Thus, the initial reaction of $Mo_2Cl_8H^{3-}$ with pyridine occurs with retention of the dinuclear framework. However, extended treatment of both $Mo_2Cl_8H^{3-}$ and $Mo_2Cl_9^{3-}$ with pyridine leads to a destruction of the dinuclear unit that results in the production of pyridine-coordinated mononuclear complexes of molybdenum(III).

An obvious correlation suggested by these results is that the reactivity of the participating complexes parallels the purported strength of the metal-metal interaction. Thus $Cr_2Cl_9^{3-}$, whose magnetic behavior and intermetallic distance suggest essentially no direct metal-metal interaction,[13,14] is readily cleaved to mononuclear $CrCl_3(py)_3$ while the basic dinuclear framework or $W_2Cl_9^{3-}$, which is presumed to involve a strong tungsten-tungsten bond, is preserved in $W_2Cl_6(py)_4$. The reactivity of $Mo_2Cl_8H^{3-}$ and $Mo_2Cl_9^{3-}$, both of which are believed to involve weak to moderate molybdenum-molybdenum bonding,[15] falls between these two extremes. However, these observations may also reflect kinetic factors.[16] In the absence of specific knowledge of such factors, a definitive interpretation of the origins of these differences in the relative reactivities cannot be made.

Spectroscopic Work. The low-frequency Raman spectra of $Cs_3Mo_2Cl_8H$ and $Cs_3Mo_2Br_8H$ (Figure 1) are tabulated in Table I. Because of the complexity imposed by the presence of both terminal and bridging halogens, neither of these spectra are readily interpretable although both are rich in detail.

A single-crystal x-ray study has established that $MoCl_3(py)_3$ has C_{2v} symmetry;[12] $MoBr_3(py)_3$ appears to be isostructural.[12] Group theory considerations predict a maximum of three ir- and Raman-active (A_1, B_1, B_2) metal-halogen stretching vibrations for *mer*-$MoX_3(py)_3$.

The low-frequency infrared data for *mer*-$MoCl_3(py)_3$ and *mer*-$MoBr_3(py)_3$ are collected in Table II. The intense bands at 318 and 307 cm^{-1} are assigned as molybdenum-chlorine stretching vibrations. Unfortunately, metal-nitrogen stretching vibrations also occur in this region of the spectrum.[17] Because of this overlap, the critical band at 277 cm^{-1} cannot be unambiguously assigned as either ν(Mo-Cl) or ν(Mo-N). Corresponding Raman data are also ambiguous (vide infra) and the interpretation of the vibrational data for *mer*-$MoBr_3(py)_3$ is even more uncertain. In the absence of isotopic substitution studies, these facts make it impossible to obtain a complete assignment of the metal-halogen vibrations in *mer*-$MoX_3(py)_3$.

The Raman spectra of *mer*-$MoCl_3(py)_3$ and *mer*-$MoBr_3(py)_3$ exhibit significant resonance effects (cf. Figure 2). Thus, the failure to observe a band (such as, for example, a particular Mo-Cl stretching vibration) does not necessarily reflect its absence since preferred intensity enhancement of certain modes

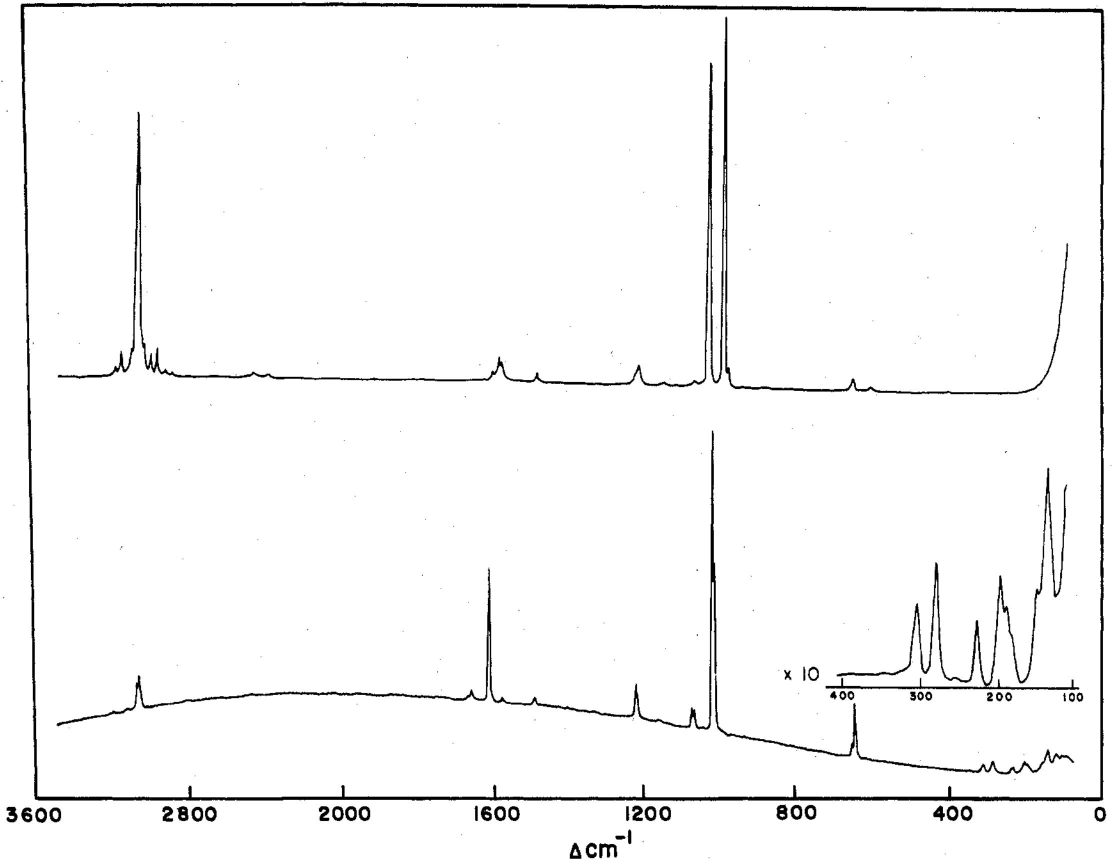


Figure 2. Raman spectra of pyridine (top, neat liquid) and *mer*-$MoCl_3(py)_3$ (bottom, solid) recorded using 5145-Å radiation.

(e.g. totally symmetric modes[18]) and/or, of course, accidental degeneracy, may affect the number of apparent fundamentals. By far the most intense bands in the Raman spectra of *mer*-$MoX_3(py)_3$ are the ligand-localized modes. It is also the intensities of these bands which exhibit the greatest dependence on excitation frequency.

An understanding of resonance enhancement in a Raman spectrum rests on a proper interpretation of the electronic spectrum of the compound under investigation. The electronic spectrum of *mer*-$MoCl_3(py)_3$ exhibits two principal bands in the near-uv region [385 (ϵ 3000), 310 nm (ϵ 3300)].[19,20] These bands have been associated with metal–pyridine and metal–chlorine charge-transfer transitions, respectively.[20] Similar assignments, suitably red-shifted, can be reasonably made for *mer*-$MoBr_3(py)_3$. Conceivably, a complete excitation profile over these bands would allow a more definitive discussion of the nature of these maxima. Unfortunately, the appropriate range of excitation frequencies was unavailable. Nonetheless, it is apparent from the preresonance data shown in Table I that the greatest (ca. sevenfold) intensity enhancement is observed in the Raman band at 1606 cm^{-1}. This band is associated with the carbon–carbon stretching vibration of the coordinated pyridine ring and as such reflects the π character of the ring. It follows that the transition(s) responsible for resonance enhancement involves (involve) the electrons in the π orbitals of the coordinated pyridine, as might be anticipated to result, for example, from preresonance with a metal–pyridine charge-transfer band. This line of reasoning is consistent with the suggested[20] origin of the 385- and the 310-nm bands as metal–ligand charge-transfer transitions. What is not obvious is the detailed mechanism of the intensity enhancement. Thus, it is not apparent if the observed enhancement involves resonance with a single electronic band or if it is a consequence of vibronic coupling between one or more of the lower energy excited electronic states and one or more states of similar polarization in the middle to deep ultraviolet region.

Registry No. $Cs_3Mo_2Cl_8H$, 57719-40-1; $Cs_3Mo_2Br_8H$, 57719-38-7; $Cs_3Mo_2Cl_9$, 29013-02-3; *mer*-$MoCl_3(py)_3$, 39210-28-1; $Mo_2Cl_4(C_5H_5N)_4$, 51731-40-9; $Cs_3Mo_2Br_9$, 29013-06-7; *mer*-$MoBr_3(py)_3$, 39210-29-2.

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Mechanisms of Substitution of Ligand-Bridged Diiron Hexacarbonyl Complexes. $(OC)_3Fe(\mu\text{-}P(C_6H_5)_2)_2Fe(CO)_3$. Promotion of an SN1 Mechanism by a Bulky Bridging Ligand

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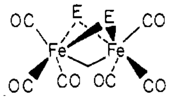
Phosphines and phosphites have been found to displace carbon monoxide from bis(μ-diphenylphosphido)-bis(tricarbonyliron), $(OC)_3Fe(\mu\text{-}P(C_6H_5)_2)_2Fe(CO)_3$, at about 150 °C. The kinetics of these reactions are reported. These results contribute to an integrated understanding of the substitution mechanism in a variety of diiron hexacarbonyl complexes containing different bridging groups. Previous papers in this series have described the kinetics and mechanisms of carbonyl displacement reactions of Lewis bases with mercapto-,[2] benzo[*c*]cinnoline-,[3] and ureylene-bridged[3] diiron hexacarbonyl complexes.

All of these complexes[4-8] have the same general structure I: two approximately octahedrally coordinated iron atoms



I

share an octahedral face; the vertices of the shared face are occupied by the two bridging atoms and an iron–iron bond. A variety of mechanistically interesting isomerization[8] and carbonyl-substitution[9] reactions have been observed for these complexes.

Substitution reactions of the organosulfur-[2] and organonitrogen-bridged[3] diiron hexacarbonyl complexes obey second-order rate laws, which are first order in the concentrations of both reactants and independent of the carbon monoxide concentration. The second-order rate constants are sensitive to both the electronic and the steric characteristics of the attacking nucleophiles. For these systems, the kinetic data imply a bimolecular substitution mechanism (SN2 or I_a).

The rate law and the thermal substitution mechanism of the organophosphorus-bridged complex are markedly different from those of the organosulfur- and organonitrogen-bridged systems.

Experimental Section

Materials. Ligands were obtained commercially. Diphenylphosphine was distilled and iron pentacarbonyl was filtered before use. Solvents were refluxed over calcium hydride or phosphorus pentoxide (dichloromethane) and then distilled in a nitrogen atmosphere. Carbon monoxide was passed through a trap at −78 °C before use.

Physical Measurements. Reaction rates were determined by monitoring the disappearance of the highest frequency, carbonyl-stretching absorption of the iron carbonyl substrate. Rate experiments were initiated by injection of a 1-ml aliquot of $Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$ stock solution into a previously thermostated solution of the desired ligand, which had been thoroughly purged with carbon monoxide. Pseudo-first-order conditions were ensured by use of a large excess of ligand. Reaction solutions were protected from light. At appropriate intervals, aliquots were transferred from the reaction mixture to a 1-mm path length infrared cell. A matched reference cell contained a solution of ligand at the same concentration as in the reaction mixture. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer and were calibrated against spectra of polystyrene and indene.[10]

Table I. First-Order Rate Constants for Carbonyl-Substitution Reactions of $Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$[a]

Ligand	[Ligand], M	$10^4 k_{obsd}$,[b] s^{-1}	T, °C
$P(C_6H_5)_3$	0.502	1.92 (16)	160
	0.167	1.80 (9)	160
	0.0488	2.01 (12)	160
	0.502	0.63 (4)	150
	0.167	0.59 (5)	150
	0.0488	0.64 (4)	150
	0.502	0.213 (14)	140
	0.167	0.215 (3)	140
	0.0488	0.200 (9)	140
$P(OC_6H_5)_3$	0.956	0.67 (6)	150
	0.0568	0.52 (2)	150
$P(n\text{-}C_4H_9)_3$	0.977	0.63 (1)	150
	0.0867	0.70 (5)	150

[a] In decalin solution; substrate concentration (2–3) × 10^{-3} M.
[b] Values in parentheses are the estimated standard deviation in the least significant digit.

Iron Carbonyl Complexes. Diiron nonacarbonyl was prepared from iron pentacarbonyl.[11] Reaction of $HP(C_6H_5)_2$ (11 g, 59 mmol) and $Fe_2(CO)_9$ (25 g, 69 mmol), followed by ultraviolet irradiation,[12] yielded 4.1 g of bis(μ-diphenylphosphido)-bis(tricarbonyliron) (6.3 mmol, 21% of theoretical yield), mp 179 °C (lit.[13] mp 178–179 °C). Infrared spectrum (cm^{-1}), ν_{CO}: 2055 (m), 2019 (vs), 1994 (m), 1968 (s).

Carbonyl-substituted derivatives of $Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$ were prepared by treating the substrate with a slight excess of the desired ligand in decalin solution at 150 °C. The reaction mixture was loaded onto a silica gel chromatography column and eluted with hexane to bring off decalin and unreacted starting materials. The derivative was then eluted with successively more benzene-rich hexane–benzene solutions. In each case, the orange derivative was recrystallized from dichloromethane–hexane.

Carbonyl-region infrared spectra were obtained in dichloromethane solutions and were very similar to those previously reported[14] for substitution at one or both of the positions trans to the iron–iron bond. Infrared spectra (cm^{-1}), ν_{CO}: for $Fe_2(CO)_5(\mu\text{-}P(C_6H_5)_2)_2P(C_6H_5)_3$ (mp 205 °C dec), 2026 (s), 1966 (vs), 1908 (w); for $Fe_2(CO)_5(\mu\text{-}P(C_6H_5)_2)_2P(OC_6H_5)_3$, 2028 (s), 1970 (vs), 1936 (vw), 1910 (w); for $Fe_2(CO)_5(\mu\text{-}P(C_6H_5)_2)_2P(n\text{-}C_4H_9)_3$, 2025 (s), 1957 (s), 1930 (vw), 1900 (w); for $Fe_2(CO)_4(\mu\text{-}P(C_6H_5)_2)_2(P(n\text{-}C_4H_9)_3)_2$, 1995 (s), 1956 (s), 1920 (s), 1900 (sh).

Results and Discussion

The photochemically initiated displacement of carbon monoxide from bis(μ-dimethylphosphido)-bis(tricarbonyliron), $(CO)_3Fe(\mu\text{-}P(CH_3)_2)_2Fe(CO)_3$, by phosphines has been shown[14] to give derivatives similar to those reported here. The infrared spectra of phosphine derivatives of phosphido-bridged complexes are closely similar whether the substitution is effected photochemically or thermally. These spectra are also very similar to those of derivatives in nitrogen-,[3] sulfur-,[2] and carbon-bridged[15] diiron hexacarbonyl systems. It appears that the carbonyl ligands trans to the iron–iron bond are the most readily displaced in all cases.[15-17]

Bis(μ-diphenylphosphido)-bis(tricarbonyliron) undergoes carbonyl substitution reactions much less readily than the organosulfur- and organonitrogen-bridged systems. Whereas the latter complexes react smoothly below 70 °C, the diphenylphosphido-bridged complex undergoes thermal substitution at a similar rate only above 140 °C. First-order rate