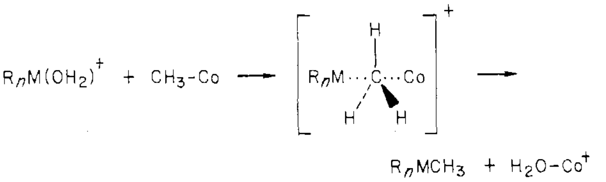
$[CH_3B_{12}] = 7.6 \times 10^{-5}$ M. The highest $[CH_3HgOAc]$ we used was 0.0178 M which, using the dissociation constant of 2.8×10^{-4} reported by Maguire et al.,[10] should give $[CH_3Hg^+] = 5.0 \times 10^5$ M. Under these conditions, no "base-off" complex would be expected.

Methylmercuric and methylplatinum compounds were reported in the reaction with mercuric salts[2] and hexachloroplatinate(IV) ion.[4] An unstable $CH_3PdCl_3^{2-}$ intermediate was postulated in the tetrachloropalladate reaction,[5] decomposing to give the detected products CH_3Cl and palladium metal. Wood et al. reported that treatment of CH_3HgOAc with $^{14}CH_3B_{12}$, followed by extraction with toluene, caused much of the label to pass into the toluene layer, presumably through formation of $^{14}CH_3HgCH_3$.[7] When we reacted CH_3HgOAc and CH_3B_{12} in a sealed vessel and subsequently evacuated the gaseous layer into a NaCl gas cell, we found infrared peaks at 2900, 1440, 1195, 781, and 700 cm^{-1}, very close to values assigned for the vibrational spectrum of dimethylmercury.[11] The Hg–C stretching vibration at 540 cm^{-1} could not be detected with any certainty, due to cell end absorption. Reaction between $(CH_3)_4AsI$ and CH_3B_{12} gave the characteristic, unpleasant odor of $(CH_3)_3As$. The corresponding reaction of $(CH_3)_3TeI$ gave $(CH_3)_2Te$, also detectable by its odor, and some elemental Te, presumably by decomposition of the initially formed $(CH_3)_4Te$.[12] Neither $(CH_3)_4AsI$ nor $(CH_3)_3TeI$ gave an odor in the absence of methylcobalamin.

DeSimone et al.[2] have proposed that transmethylation of mercuric salts occurs through electrophilic attack on the carbanionic methyl group, followed by cleavage of the Co–C bond. Our observations are consistent with this mechanism, which is represented in eq 2. Since the methyl group bonds



(2)

to the metal as an electron-donating carbanion, methylmetal compounds should be less electrophilic than inorganic analogues and thereby react more slowly with methylcobalamin. This indeed is observed for Hg(II),[2] Tl(III),[13] and Pb(IV).[13]

Methylmercuric ion[2] and trimethyllead ion[14,15] are known to undergo methylation through biological processes. The volatile products play an important role in the movement of these metals through the environment. Our work indicates that this might also happen for other methylmetal compounds, including the previously unsuspected "onium" salts of group 5 and 6 elements. Preliminary observations further suggest that similar reactions occur with other organometals, particularly ones of mercury, lead, and tin that have numerous biocidal applications, with the implication that unexpected and undesired reactions of these compounds may occur under environmental conditions. We are currently investigating these possibilities.

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Registry No. Methylcobalamin, 13422-55-4; CH_3HgOAc, 108-07-6; $(CH_3)_2TlOAc$, 18000-46-9; $(CH_3)_3PbOAc$, 5711-19-3; $(CH_3)_3SnOAc$, 1118-14-5; $(CH_3)_3TeI$, 18987-26-3; $(CH_3)_4PI$, 993-11-3; $(CH_3)_4AsI$, 5814-20-0; $(CH_3)_4SbI$, 2185-78-6.

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Conversion of the Molybdenum(III) Halides to Metal–Metal Bonded Dimers of the Type $Mo_2X_4L_4$ by Dimethylamine and Tertiary Phosphines[1]

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Access to the chemistry of those molybdenum(II) halides and their derivatives, which contain the metal–metal bonded Mo_2^{4+} core, invariably utilizes molybdenum(II) acetate, $Mo_2(O_2CCH_3)_4$, as the initial synthetic starting material.[3-15] An important class of such complexes are those of the type $Mo_2X_4L_4$ (X = Cl, Br, I; L = neutral donor) which are prepared via the molybdenum(II) complexes $K_4Mo_2Cl_8$,[3] $(NH_4)_5Mo_2Cl_9 \cdot H_2O$,[6,7,12] β-MoX_2 (X = Cl, Br, I),[3,4] and $(picH)_2[Mo_2X_6(H_2O)_2]$ (pic = 4-methylpyridine; X = Br, I),[14,15] or the molybdenum(III) derivatives $Cs_3Mo_2X_8H$ (X = Cl, Br).[7] The use of $Cs_3Mo_2X_8H$ in the synthesis of the pyridine complexes $Mo_2X_4(py)_4$ is of particular interest,[7] since upon reaction of pyridine with the corresponding enneahalodimolybdenum(III) derivatives $Cs_3Mo_2X_9$ or by use of much more forcing conditions in its reaction with $Cs_3Mo_2X_8H$, only the monomeric molybdenum(III) species *mer*-$MoX_3(py)_3$ can be isolated.[8] While the transformation of $Mo_2X_8H^{3-}$ to *mer*-$MoX_3(py)_3$ is believed to proceed, *at least in part*, through the intermediacy of the molybdenum(II) derivatives $Mo_2X_4(py)_4$, there is no evidence to support such a mechanism in the case of the conversion of $Mo_2X_9^{3-}$ to *mer*-$MoX_3(py)_3$. Likewise, the reactions of $Cr_2Cl_9^{3-}$ and $W_2Cl_9^{3-}$ to produce *mer*-$CrCl_3(py)_3$[16,17] and $W_2Cl_6(py)_4$,[18] respectively, do not appear to involve the formation of chromium(II) or tungsten(II) intermediates. The surprising differences which exist between the reactions of $Mo_2X_8H^{3-}$ and $Mo_2X_9^{3-}$ have led us to investigate certain aspects of the reactivity of the parent trihalides MoX_3 (X = Cl, Br). We now report details of the

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conversion of MoX_3, by single-step reductive pathways, to derivatives of the type $Mo_2X_4L_4$.

Experimental Section

Starting Materials. The samples of $MoCl_3$ used in the reaction with aliphatic amines were prepared by the method of Mallock.[19] A sample of this halide was also supplied by the Climax Molybdenum Co. and this was used in the reactions with tertiary phosphines. $MoBr_3$ was prepared by the direct bromination of molybdenum metal powder at 400 °C.[20]

Aliphatic amines, tertiary phosphines, and all reagent grade solvents were obtained from commercial sources. The amines were dried by distillation from freshly crushed barium oxide and then from $MoCl_5$. The solvents which were used in the reactions between MoX_3 and tertiary phosphines were deoxygenated by purging with nitrogen gas prior to use.

Synthetic Procedures. Reactions were carried out using one of two procedures. An all-glass vacuum line system[21] was used for the reactions between the halides MoX_3 (X = Cl, Br) and the amines R_2NH (R = Me, Et). Reactants were mixed and then sealed, under vacuum, in glass ampules. The reactions of MoX_3 with PR_3 (R = Et, *n*-Pr) were carried out in a nitrogen atmosphere using conventional glassware.

(A) Reactions of Molybdenum Halides with Dimethylamine and Diethylamine. (i) $MoBr_3 + Me_2NH$. A large excess of dry dimethylamine (25 mL) was reacted with $MoBr_3$ (0.76 g) at room temperature for 7 days in a sealed ampule. The violet amine-insoluble complex $Mo_2Br_4(NHMe_2)_4$ was obtained by filtration of the contents of the ampule in a vacuum line at −78 °C. This product (0.36 g) was washed six times with anhydrous dimethylamine before being dried in vacuo at room temperature for several hours. Yield: 46%. Anal. Calcd for $C_8H_{28}Br_4Mo_4N_4$: Br, 46.2; Mo, 27.7; N, 8.10. Found: Br, 46.1; Mo, 28.1; N, 8.11. This amine-insoluble complex (mp 208 °C dec) was also insoluble in benzene, chloroform, cyclohexane, chlorobenzene, and ethanol and slowly decomposed in moist air.

A heterogeneous, dark brown, amine-soluble product (0.61 g) was obtained by distillation of the dimethylamine from the combined filtrates, followed by vacuum drying.

(ii) $MoCl_3 + Me_2NH$. A procedure analogous to that described in part A(i) afforded an amine-insoluble purple powder. Anal. Calcd for $C_8H_{28}Cl_4Mo_2N_4$: Mo, 37.4. Found: Mo, 40.2. Although the elemental microanalyses of this material were in poor agreement with the formulation $Mo_2Cl_4(NHMe_2)_4$, its spectral properties were in accord with this dimer being the major component but with contamination by higher oxidation state molybdenum oxides (see Results and Discussion).

(B) Reactions of Molybdenum(III) Chloride and Bromide with Triethylphosphine and Tri-*n*-propylphosphine. (i) $MoBr_3 + PEt_3$. $MoBr_3$ (0.2 g) was treated with 1.0 mL of triethylphosphine in 10 mL of ethanol (200 proof). The reaction mixture was refluxed for 24 h and then filtered hot to remove any unreacted $MoBr_3$. The filtrate was cooled in an ice bath, and the resulting dark blue crystals of $Mo_2Br_4(PEt_3)_4$ (0.08 g) were filtered off, washed with ethanol, and dried. Yield: 30%. Anal. Calcd for $C_{24}H_{60}Br_4P_4Mo_2$: C, 29.3; H, 6.2. Found: C, 29.1; H, 6.1. The infrared and electronic absorption spectra [λ_{max} (diffuse reflectance) at 605 (s) and 475 (m–w) nm] of this product were identical with those for the complex of this same stoichiometry prepared by an alternative procedure.[3] Use of 1-propanol as the reaction solvent did not give a significantly higher yield of $Mo_2Br_4(PEt_3)_4$.

(ii) $MoBr_3$ + P-*n*-Pr_3. An analogous procedure to that described in B(i) produces 0.14 g of Mo_2Br_4(P-*n*-$Pr_3)_4$ from 0.2 g of $MoBr_3$. Yield: 38%. The identity of this product was confirmed by a comparison of its infrared and electronic absorption spectral properties [λ_{max} (diffuse reflectance) at 610 (s) and 480 (m–w) nm] with those of an authentic sample of this complex.[3]

(iii) $MoCl_3 + PEt_3$. The reaction between $MoCl_3$ (0.6 g) and triethylphosphine (2.0 mL) in ethanol (15 mL) was extremely slow. Even after a reflux period of 48 h most of the starting chloride (~85%) had not reacted. The reaction mixture was filtered, the dark blue solution was chilled in an ice bath, and the resulting crystals (0.03 g) of $Mo_2Cl_4(PEt_3)_4$ were filtered off, washed with ethanol, and dried in vacuo. The reaction filtrate was evaporated to dryness and extracted with diethyl ether to afford a further quantity (~0.06 g) of $Mo_2Cl_4(PEt_3)_4$. Yield: 10%. The spectral properties of this product [λ_{max} (diffuse reflectance) at 590 (s) and 460 (m–w) nm] were identical with those of an authentic sample of this complex.[3]

(iv) $MoCl_3$ + P-*n*-Pr_3. The dark blue-purple complex Mo_2Cl_4(P-*n*-$Pr_3)_4$ was obtained in low yield by using a similar procedure to that described in part B(iii). Its spectral properties [λ_{max} (diffuse reflectance) at 595 (s) and 460 (m–w) nm] confirmed its identity.[3]

(C) Reaction of $Mo_2X_4(NHMe_2)_4$ with Tri-*n*-propylphosphine. (i) $MoBr_3$. A quantity of $Mo_2Br_4(NHMe_2)_4$ (0.1 g) was mixed with 1.0 mL of tri-*n*-propylphosphine and 10 mL of ethanol and then warmed for 4 h. The reaction mixture was cooled in ice water and then filtered, and the dark blue insoluble product was washed with ethanol and then vacuum dried. IR spectroscopy revealed the presence of "contaminant" bands at ~3400 (s), ~3200 (s), and 1640 (m) cm^{-1}, consistent with the presence of water-containing impurities. Extraction of the product with deoxygenated diethyl ether (2 × 25 mL) produced a blue solution and left a light brown solid which was discarded. The blue filtrate was evaporated to dryness to afford a crop of dark blue crystals of Mo_2Br_4(P-*n*-$Pr_3)_4$ which were dried in vacuo. Yield: 65%. Anal. Calcd for $C_{36}H_{84}Br_4P_4Mo_2$: C, 37.5; H, 7.4; Br, 27.7. Found: C, 37.6; H, 7.4; Br, 27.8. Its spectral properties (IR and electronic absorption) were identical with literature data for Mo_2Br_4(P-*n*-$Pr_3)_4$.[3]

(ii) $MoCl_3$. A similar reaction between $Mo_2Cl_4(NHMe_2)_4$ and tri-*n*-propylphosphine afforded dark blue crystals of Mo_2Cl_4(P-*n*-$Pr_3)_4$ which were identified by electronic absorption spectroscopy.[3]

Physical Measurements and Analytical Procedures. These were carried out as described previously.[3]

Results and Discussion

Some years ago, one of us reported[22,23] the results of studies on the reactions of molybdenum(III) chloride and bromide with liquid ammonia, methylamine, and dimethylamine. In each instance, it was believed that solvolysis occurred to afford amine-insoluble products whose stoichiometries approximated to $MoX_2(NH_2)\cdot 3NH_3$, $MoBr(NHMe)_2\cdot 0.66NH_2Me$, and $MoBr_2(NMe_2)\cdot NHMe_2$.[22,23] Their formulation as derivatives of molybdenum(III) was based (in part) upon the results of oxidation state titrations. These reports appeared 7 years before the structural characterization of the $Mo_2Cl_8{}^{4-}$ anion[24] and 10 years before the first report[6] of $Mo_2X_4L_4$ complexes.

A more complete characterization has enabled us to reformulate the dimethylamine product, $MoBr_2(NMe_2)\cdot NHMe_2$, as the molybdenum(II) complex $Mo_2Br_4(NHMe_2)_4$, a new member of the class of molybdenum(II) derivatives $Mo_2X_4L_4$ which contain quadruple Mo–Mo bonds. This bromide complex is essentially diamagnetic at 20 °C ($\chi_M' = 70 \times 10^{-6}$ cgsu) and exhibits two absorption bands with maxima at 581 and 488 nm in its diffuse reflectance electronic absorption spectrum, which are typical of dinuclear molybdenum(II) complexes of the type $Mo_2X_4L_4$.[3-7] A comparison of the infrared spectrum of this complex (4000–500 cm^{-1}) with those of the complex *fac*-$Mo(CO)_3(NHMe_2)_3$[25] and several transition-metal dimethylamides $M(NMe_2)_x$[26] shows the presence of bands which are assignable to coordinated dimethylamine modes and the absence of corresponding absorptions due to $Mo-NMe_2$ groups. Characteristic absorptions are at 3210 (N–H stretch) and 1470 (N–H bend) cm^{-1}. Bands at 286 and 264 cm^{-1} in the low-frequency IR spectrum of this complex are comparable to the ν(Mo–Br) modes (270–260 cm^{-1}) in the related spectra of the complexes $Mo_2Br_4(PR_3)_4$ and $Mo_2Br_4(py)_4$.[3,7]

The conversion of $Mo_2Br_4(NHMe_2)_4$ to the complex Mo_2Br_4(P-*n*-$Pr_3)_4$, upon its reaction with tri-*n*-propylphosphine under mild reaction conditions, is further support for our structural formulation. Such ligand-substitution reactions are characteristic of dimers of the type $Mo_2X_4L_4$.[7]

The X-ray photoelectron spectrum (XPS) of the complex shows that the Mo 3d binding energies [$3d_{3/2}$, 232.1 eV; $3d_{5/2}$, 228.9 eV] fall in the range which is characteristic of the molybdenum(II) halides and their derivatives.[3-5,27] The Br $3p_{1/2,3/2}$ binding energies of 188.7 and 182.0 eV, respectively, are consistent with the presence of terminal metal–bromine bonds.[28]

The complex $Mo_2Cl_4(NHMe_2)_4$ may be prepared in an impure state from $MoCl_3$. Its diamagnetism ($\chi_M' \sim 140 \times 10^{-6}$ cgsu), diffuse reflectance electronic absorption spectrum (λ_{max} at 555 and 472 nm), and infrared spectrum (4000–500 cm^{-1}) show that it possesses properties very similar to those of the analogous bromide complex. This is further supported by its conversion to pure $Mo_2Cl_4(P\text{-}n\text{-}Pr_3)_4$.

XPS measurements on $Mo_2Cl_4(NHMe_2)_4$ show a well-resolved Cl $2p_{1/2,3/2}$ doublet at 199.4 and 198.0 eV, but the Mo $3d_{3/2,5/2}$ spectrum reveals that this complex [Mo $3d_{5/2}$ energy at 229.0 eV] is contaminated by appreciable amounts of a high-oxidation-state molybdenum species [Mo $3d_{5/2}$ energy at ~231.5 eV], most likely Mo(IV) or Mo(VI).[27] We believe that this contaminant is present in the $MoCl_3$ starting material and remains mixed in with the amine-insoluble $Mo_2Cl_4(NHMe_2)_4$ after reaction with dimethylamine.

These trihalide–amine reactions are undoubtedly complex since the yields of the amine-insoluble $Mo_2X_4(NHMe_2)_4$ do not exceed 50% on the basis of the weight of MoX_3 used. The remaining molybdenum is found as an amine-soluble product mixed with dimethylammonium halide (the presence of the latter being shown by IR spectroscopy). While we have not identified all of the possible organic oxidation byproducts of these reactions, studies on other amine-induced reductions of metal halides[29] show that the amine hydrohalide is formed.

Our demonstration that the complex previously formulated as $MoBr_2(NMe_2)\cdot NHMe_2$[22] is in reality $Mo_2Br_4(NHMe_2)_4$ clearly casts doubt on the reliability of the oxidation state titrations used[22,23] to characterize the insoluble products arising from the reaction between MoX_3 and ammonia, methylamine, and dimethylamine as derivatives of molybdenum(III).

The reduction of MoX_3 to $Mo_2X_4L_4$ can also be accomplished by reaction of these halides with the tertiary phosphines PEt_3 and $P\text{-}n\text{-}Pr_3$, although the reactions are slow and, accordingly, the yields of $Mo_2X_4(PR_3)_4$ are low. The sluggish nature of these reactions, particularly in the case of $MoCl_3$, presumably reflects the difficulty of breaking the strong metal–halogen bridges in these highly insoluble trihalides. The reactions of $K_4Mo_2Cl_8$, $(NH_4)_5Mo_2Cl_9\cdot H_2O$, or $Cs_3Mo_2X_8H$ with tertiary phosphines remain the preferred method for preparing $Mo_2X_4(PR_3)_4$.[3,6,7]

The solid-state structures of $MoCl_3$[30] and $MoBr_3$[31] are based on face-shared MoX_6 octahedra with adjacent metal atoms drawn together in pairs (Mo–Mo = 2.76 Å in $MoCl_3$; Mo–Mo = 2.92 Å in $MoBr_3$). The formation of $Mo_2X_4L_4$ must involve cleavage of the halide bridges but retention and enhancement of the metal–metal interactions of the trihalides. Although diamagnetic complexes of the type $Mo_2Cl_6(PR_3)_3$ have been prepared,[32] there is no evidence to suggest that they are intermediates in the formation of $Mo_2Cl_4(PR_3)_4$.

In contrast to the preceding results, MoX_3 complexes have been found to react quite differently with pyridine, to produce monomeric $MoX_3(py)_3$,[22] and with 2,2′-bipyridyl, to afford the molybdenum(III) ionic dimers $[MoX_2(bpy)_2]^+$ $[MoX_4(bpy)]^-$.[33] Accordingly, the molybdenum(III) halides resemble the reactivity patterns of both $Mo_2X_8H^{3-}$ and $Mo_2X_9^{3-}$, in their tendency to produce either Mo(II) complexes (upon reaction with dimethylamine and tertiary phosphines) or unreduced Mo(III) derivatives (upon reaction with pyridine and 2,2′-bipyridyl).

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Registry No. $Mo_2Br_4(NHMe_2)_4$, 65863-81-2; $Mo_2Cl_4(NHMe_2)_4$, 65863-82-3; $Mo_2Br_4(PEt_3)_4$, 59752-94-2; $Mo_2Br_4(P\text{-}n\text{-}Pr_3)_4$, 59752-95-3; $Mo_2Cl_4(PEt_3)_4$, 59780-36-8; $Mo_2Cl_4(P\text{-}n\text{-}Pr_3)_4$, 59780-37-9; $MoBr_3$, 13446-57-6; $MoCl_3$, 13478-18-7.

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