aqueous solutions may have the geometry of a tetragonally distorted octahedron, with two water molecules coordinated to copper. Similar structures have been found in the solid state for $CuCl_2 \cdot 2H_2O$ made of $[CuCl_4(H_2O)_2]^{2-}$ units[22] (λ_{max} 280 nm[40]) and for $LiCuCl_3 \cdot 2H_2O$ made of $[CuCl_5(H_2O)]^{3-}$ units (λ_{max} 270, 380, 485 nm[40]).

Registry No. $CuCl^+$, 15697-17-3; $CuCl_2$, 7447-39-4; $CuCl_3^-$, 15697-18-4; $CuCl_4^{2-}$, 15489-36-8.

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Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana

Studies on Metal Carboxylates. 12.[1] Reactions of Molybdenum(II), Rhodium(II), and Rhenium(III) Acetates with Gaseous Hydrogen Chloride and Hydrogen Bromide

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Molybdenum(II) acetate ($Mo_2(O_2CCH_3)_4$) reacts with gaseous hydrogen chloride and hydrogen bromide at 300 °C to afford the phases β-MoX_2, where X = Cl or Br. Reaction of these halides with pyridine and monodentate tertiary phosphines to produce metal–metal bonded dimers of the type $Mo_2X_4L_4$ suggests that they are best formulated as $[Mo_2X_4]_n$ and are accordingly the parent halides of haloanions $Mo_2X_8^{4-}$. In contrast to this behavior, the rhenium(III) acetates, $Re_2(O_2CCH_3)_4X_2$, where X = Cl or Br, react with HCl and HBr to yield the trinuclear halides Re_3X_9. This is the first instance where a dinuclear rhenium halide containing a quadruple metal–metal bond has been converted to a trinuclear cluster. The related reaction of dinuclear rhodium(II) acetate with HCl and HBr differs from those involving $Mo_2(O_2CCH_3)_4$ and $Re_2(O_2CCH_3)_4X_2$ in that disproportionation to RhX_3 and rhodium metal occurs.

During a study of the x-ray photoelectron spectra of transition metal chloride clusters,[2] we showed that the β form of molybdenum(II) chloride[3-5] is not structurally related to the α form, in which a hexanuclear cluster of molybdenum atoms is known to be present,[6] and which may, using Schäfer's notation,[6] be written as $[Mo_6Cl_8]Cl_{4/2}Cl_2$. In view of the absence of any detailed information concerning the structure of β-$MoCl_2$ and the paucity of studies dealing with its chemical reactivity, we decided to explore its chemistry in more detail. In particular, since this phase is prepared by the reaction of molybdenum(II) acetate with hydrogen chloride, we were interested in establishing whether metal–metal bonded Mo_2 units, as present in $Mo_2(O_2CCH_3)_4$,[7] are preserved in this phase. During the course of this work we extended the preparative procedure which has been used[3,4] to prepare β-$MoCl_2$ to include the reactions of $Mo_2(O_2CCH_3)_4$, $Rh_2(O_2CCH_3)_4$, and $Re_2(O_2CCH_3)_4Cl_2$ with both hydrogen chloride and hydrogen bromide. The results of these studies are now reported in detail.[8]

Experimental Section

Starting Materials. Molybdenum hexacarbonyl, hydrated rhodium(III) chloride, potassium perrhenate, tertiary phosphines and pyridine, together with all reagent-grade solvents and gases, were obtained from commercial sources. All solvents were deoxygenated by purging with nitrogen gas for at least 1 h prior to use.

The following compounds were prepared by standard literature procedures: $Mo_2(O_2CCH_3)_4$,[3] $K_4Mo_2Cl_8$,[9] $Cs_3Mo_2Br_8H$,[10,11] Rh_2-

$(O_2CCH_3)_4 \cdot n CH_3OH$,[12] $Re_2(O_2CCH_3)_4X_2$ (X = Cl or Br),[13] and $ReOCl_3(PPh_3)_2$.[14]

Synthetic Procedures. All Reactions Were Carried out in a Nitrogen Atmosphere Unless Otherwise Stated. (A). Reactions of Metal Acetates with Hydrogen Chloride and Hydrogen Bromide. (i) $Mo_2(O_2CCH_3)_4$. β-$MoCl_2$ was prepared by a slight modification of the procedure described by Sheldon et al.[4] Finely ground molybdenum(II) acetate (1.0 g) was placed in a porcelain boat which was then inserted into a dry open-ended glass tube. The tube was placed in a horizontal tube furnace and dry hydrogen chloride gas was passed over the $Mo_2(O_2CCH_3)_4$ for 1 h at room temperature. The temperature of the furnace was raised to 300 °C and the passage of HCl continued for 6 h. The resulting brown powder was reground and reheated at 300 °C in a flow of HCl gas for a further 3 h. The final product (0.76 g) was analytically pure. Anal. Calcd for $MoCl_2$: Cl, 42.5. Found: Cl, 42.6. Yield: 90%.

The related reaction of $Mo_2(O_2CCH_3)_4$ (1.0 g) with hydrogen bromide afforded a dark brown product when a procedure similar to that used to prepare β-$MoCl_2$ was employed. Reaction at 300 °C for a total of 4 h produced 0.77 g of β-$MoBr_2$. Anal. Calcd for $MoBr_2$: Br, 62.5. Found: Br, 62.2. Yield: 65%.

(ii) $Rh_2(O_2CCH_3)_4$. The methanolate of $Rh_2(O_2CCH_3)_4$,[12] when reacted with dry HCl or HBr gas at 340 °C for 3 h, produced very dark brown-black materials in almost quantitative yield. Microanalytical data were consistent with the stoichiometry RhX_2, where X = Cl or Br. Anal. Calcd for $RhCl_2$: Cl, 40.8. Found (for separate preparative samples): Cl, 41.0; 41.0; 39.65. Calcd for $RhBr_2$: Br, 61.0. Found: Br, 61.1. These products appeared to be insoluble in most common organic solvents at room temperature and magnetic susceptibility measurements showed them to be essentially diamagnetic ($\chi_g = +0.06 \times 10^{-6}$ and -0.12×10^{-6} cgs units for $RhCl_2$ and $RhBr_2$, respectively).

However, x-ray powder measurements on these materials showed that they were not authentic rhodium(II) halides. Only lines characteristic of rhodium(III) halide[15] and rhodium metal[16] were discernible in the x-ray powder patterns.[17] This conclusion was supported by the x-ray photoelectron spectrum of the material analyzing as $RhCl_2$. While the chlorine 2p binding energy spectrum showed a well resolved spin–orbit doublet at 199.9 ($2p_{1/2}$) and 198.4 ($2p_{3/2}$) eV, the rhodium 3d peaks at 314.1 ($3d_{3/2}$) and 309.4 ($3d_{5/2}$) eV exhibited low binding energy tails which clearly arose from the presence of an additional rhodium containing component in this material.

It was found possible to separate the rhodium(III) halide from rhodium metal by extraction of the former into pyridine. A quantity of "$RhCl_2$" (0.3 g) was added to 50 ml of ethanol and 10 ml of dry pyridine and the reaction mixture was refluxed for 20 h and then filtered. The filtrate was evaporated to dryness to afford the salt $[RhCl_2py_4]Cl$ (identified by a comparison of its infrared spectrum with that reported[18] in the literature). The insoluble black residue was shown to be rhodium metal by x-ray powder measurements. When this reaction was repeated using pyridine in place of the ethanol–pyridine mixture, the rhodium(III) chloride was converted to *trans*-$RhCl_3py_3$. Once again its identity was established by infrared spectroscopy.[18]

(iii) $Re_2(O_2CCH_3)_4X_2$ (X = Cl or Br). Using a procedure similar to that described in (Aii), the reaction of $Re_2(O_2CCH_3)_4X_2$ with HX afforded the trihalides Re_3X_9 in ~95% yield. Anal. Calcd for Re_3Cl_9: Cl, 36.35. Found (for separate preparative samples): Cl, 36.1; 36.2. Calcd for Re_3Br_9: Br, 56.3. Found (for separate preparative samples): Br, 56.0; 56.5.

It was subsequently found that Re_3Br_9 could be prepared by the reaction of $Re_2(O_2CCH_3)_4Cl_2$ with hydrogen bromide. Consequently, in the synthesis of Re_3X_9 by this procedure, $Re_2(O_2CCH_3)_4Cl_2$ is the only rhenium starting material which is necessary.

The identity of these trihalides as the authentic trinuclear phases Re_3X_9 was based upon a variety of evidence. Re_3Cl_9 was readily converted to the complexes $[Ph_4As]_2Re_3Cl_{11}$ and $Re_3Cl_9(PPh_3)_3$ which had identical electronic absorption spectral properties and/or x-ray diffraction patterns to those described in the literature.[17,24,25] Also, the electronic absorption spectra of both methanol–HX and acetone solutions of these halides were identical with the corresponding literature data.[24] Both phases had x-ray photoelectron spectra which were consistent with their structural formulation. Rhenium $4f_{5/2,7/2}$ binding energies of 44.9 and 42.6 eV for Re_3Cl_9 and of 45.0 and 42.6 eV for Re_3Br_9 are in good agreement with literature data[2] and furthermore, these measurements showed the absence of perrhenate contaminants.[26] The chlorine 2p spectrum of Re_3Cl_9 exhibited a broad unresolved band envelope centered at ~199.1 eV. This feature is very characteristic of this phase[2] and arises from overlapping chlorine $2p_{1/2,3/2}$ doublets due to different chlorine environments in terminal and bridging Re–Cl bonds.[27]

(B) The Synthesis of $Re_2(O_2CCH_3)_4Cl_2$. The highest yield synthesis for $Re_2(O_2CCH_3)_4Cl_2$ is that described by Rouschias and Wilkinson[19] in which *trans*-$ReOCl_3(PPh_3)_2$ is refluxed with acetic anhydride in a nitrogen atmosphere for 12 h or more. Since *trans*-$ReOCl_3(PPh_3)_2$ can be produced from rhenium metal in 85% yield[20] and converted to $Re_2(O_2CCH_3)_4Cl_2$ in 61% yield,[19] this method is preferred over the alternative sequence $KReO_4 \rightarrow [(C_4H_9)_4N]_2Re_2Cl_8 \rightarrow Re_2(O_2CCH_3)_4Cl_2$ which affords the acetate in an overall yield no better than ~38%.[21-23]

We have managed to improve the yield of $Re_2(O_2CCH_3)_4Cl_2$ over that reported by Rouschias and Wilkinson.[19] $ReOCl_3(PPh_3)_2$ was prepared by the method of Chatt and Rowe,[14] using $NaReO_4$ as starting material, in yields as high as ~90%. $ReOCl_3(PPh_3)_2$ (0.5 g) was then added to 50 ml of acetic anhydride and the reaction mixture was refluxed for 48 h. The resulting orange precipitate of $Re_2(O_2CCH_3)_4Cl_2$ (0.16 g) was filtered off, washed with ethanol and diethyl ether, and dried in vacuo. Anal. Calcd for $C_8H_{12}Cl_2O_8Re$: C, 7.6; H, 0.95; Cl, 22.4. Found: C, 7.9; H, 0.9; Cl, 22.6. Yield: 77%.

(C) Reactions of β-MoX_2 with Pyridine and Tertiary Phosphines. (i) Pyridine. β-$MoCl_2$ (0.10 g) and 15 ml of pure dry pyridine were refluxed together for 3 days. The resulting red-brown precipitate (0.05 g) was filtered off, washed with pyridine, and dried in vacuo. Anal. Calcd for $C_{20}H_{20}Cl_4N_4Mo_2$: C, 37.0; H, 3.1. Found: C, 34.6; H, 2.8. Yield: 26%.

The identity of this product as the dinuclear species $Mo_2Cl_4(py)_4$ was confirmed by the striking similarity of its low-frequency infrared spectrum (343 s [ν(Mo–Cl)], 283 m-w [ν(Mo–Cl)], 247 m-w, 214 w cm^{-1}) and electronic absorption spectrum (λ_{max} (Nujol mull) 560 s, 405 vs nm) to those of an authentic sample of this complex prepared[28] by the reaction of $Cs_3Mo_2Cl_8H$[11] with pyridine. In keeping with the results of San Filippo et al.,[28] we were unable to obtain a satisfactory carbon microanalysis for this complex. There is no obvious reason for this behavior.

Occasionally, the reaction between β-$MoCl_2$ and pyridine was found to produce a small quantity of the mononuclear molybdenum(III) complex $MoCl_3(py)_3$. While we were unable to ascertain the reaction conditions which would reproducibly afford this product, the following conditions are those which on one occasion did produce this complex in reasonably good yield. A quantity of β-$MoCl_2$ (3.50 g) was subjected to Soxhlet extraction using 50 ml of dry pyridine in a nitrogen atmosphere. After a period of 4 days, this extraction had produced a dark brown pyridine solution while 0.4 g of β-$MoCl_2$ was left unreacted in the thimble. The pyridine solution was evaporated to 10 ml on a vacuum line and then cooled to −10 °C for 48 h. Yellow crystals (0.5 g) were filtered off, washed with 5 ml of cold deaerated ethanol followed by 10 ml of ether, and then dried in vacuo. Recrystallization was effected by dissolving the product in chloroform followed by the slow addition of benzene. Anal. Calcd for $C_{15}H_{15}Cl_3N_3Mo$: C, 41.0; H, 3.5; N, 9.5; Cl, 24.2. Found: C, 43.1; H, 3.7; N, 9.0; Cl, 24.0. The high carbon microanalysis probably arises from the presence of a small amount of "lattice" benzene in the recrystallized product. The low-frequency infrared spectrum (400–200 cm^{-1}) of this complex exhibited the following absorptions: 322 vs, 279 w, 254 and 247 m doublet, 228 w, 213 w cm^{-1}.

The reaction between β-$MoBr_2$ (0.11 g) and pyridine was carried out in an analogous fashion to that described for β-$MoCl_2$, to afford 0.05 g of the dark green crystalline complex $Mo_2Br_4(py)_4$. Anal. Calcd for $C_{20}H_{20}Br_4N_4Mo_2$: C, 29.0; H, 2.4; Br, 38.6. Found: C, 29.0; H, 2.6; Br, 38.9. Yield: 26%. As was the case with the analogous chloride, a comparison of the low-frequency infrared spectrum (266 and 261 s doublet [ν(Mo–Br)], 240 m, 212 w cm^{-1}) and electronic absorption spectrum (λ_{max} (Nujol mull) 680 s, ~460 and 425 s nm doublet) of this product with those for the complex of this same stoichiometry prepared by an alternative procedure[28] confirmed its identity.

(ii) Triethylphosphine and Tri-*n*-propylphosphine. The following procedure is fairly typical of that used in the reactions between β-MoX_2 and these two phosphines. A suspension of β-$MoBr_2$ (0.50 g) in 40 ml of absolute ethanol was treated with 2.5 ml of triethylphosphine

and the reaction mixture was refluxed for 3 days. The resulting deep purple crystals (0.58 g) were filtered off, washed with ethanol, and dried. Anal. Calcd for $C_{24}H_{60}Br_4P_4Mo_2$: C, 29.3; H, 6.2; Br, 32.5. Found: C, 29.1, H, 6.1; Br, 32.3. Yield: 60%. This complex appeared to be reasonably stable toward dry air but its solutions in diethyl ether and dichloromethane rapidly decomposed.

The related tri-*n*-propylphosphine complex $Mo_2Br_4[P(n\text{-}Pr)_3]_4$, which like $Mo_2Br_4(PEt_3)_4$ is a new complex, was prepared by an analogous procedure using *n*-propyl alcohol as the reaction solvent. However, it proved necessary to purify the purple precipitate of $Mo_2Br_4[P(n\text{-}Pr)_3]_4$ since it was contaminated with an unidentified brown solid. This was accomplished by extracting the desired complex into dry deoxygenated diethyl ether, filtering, and evaporating the filtrate to dryness *without heating*. The resulting dark blue residue was washed with ethanol and then dried. 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, 7.7; Br, 27.0. Yield: 51%.

The reactions between β-$MoCl_2$ and triethylphosphine and tri-*n*-propylphosphine likewise afforded the dark blue dinuclear species $Mo_2Cl_4(PEt_3)_4$ and $Mo_2Cl_4[P(n\text{-}Pr)_3]_4$, respectively. However, much longer reflux reaction times were necessary to produce yields of complex comparable to those experienced with the related reactions involving β-$MoBr_2$. Anal. Calcd for $C_{24}H_{60}Cl_4P_4Mo_2$: C, 35.75; H, 7.5; Cl, 17.6. Found: C, 35.4; H, 7.3; Cl, 17.4. Calcd for $C_{36}H_{84}Cl_4P_4Mo_2$: C, 44.3; H, 8.7; Cl, 14.6. Found: C, 44.3; H, 8.7; Cl, 14.4.

The complexes $Mo_2Cl_4(PR_3)_4$, where R = Et or *n*-Pr, and $Mo_2X_4[P(n\text{-}Bu)_3]_4$, where X = Cl or Br, have previously been prepared by San Filippo et al.[28,29] using $(NH_4)_5Mo_2Cl_9\cdot H_2O$ or $Cs_3Mo_2Br_8H$[11] as starting materials. The electronic absorption spectra of the dinuclear phosphine complexes prepared from β-MoX_2 agree closely with the literature data,[29] thereby confirming their identity (see Results and Discussion section).

(D) Reactions of $K_4Mo_2Cl_8$ with Tertiary Phosphines. The reactions of the salt $K_4Mo_2Cl_8$ with triethylphosphine, diethylphenylphosphine, ethyldiphenylphosphine, and methyldiphenylphosphine afforded a route to complexes of the type $Mo_2Cl_4(PR_3)_4$ in yields in excess of 70%. The following procedure is typical of that used. $K_4Mo_2Cl_8$ (0.30 g) was mixed with 1.5 ml of triethylphosphine and 25 ml of dry methanol and the reaction mixture was refluxed for 4 h. The complex $Mo_2Cl_4(PEt_3)_4$ precipitated as a purple powder (0.32 g) during this time and was filtered off, washed with water (to remove any excess $K_4Mo_2Cl_8$) and methanol, and then dried in vacuo. Yield: 82%. Its identity was confirmed by a comparison of both its low-frequency infrared and electronic absorption spectra with those reported in the literature.[28,29]

The complexes $Mo_2Cl_4(PEt_2Ph)_4$, $Mo_2Cl_4(PEtPh_2)_4$, and $Mo_2Cl_4(PMePh_2)_4$ which were also prepared by this method are all new complexes. They were isolated in yields of 72, 45, and 78%, respectively, and were characterized by elemental microanalyses and/or infrared and electronic absorption spectroscopy (see Results and Discussion section). Anal. Calcd for $C_{40}H_{60}Cl_4P_4Mo_2$: C, 48.1; H, 6.1; Cl, 14.2. Found: C, 47.7; H, 6.35; Cl, 14.5. Calcd for $C_{52}H_{52}Cl_4P_4Mo_2$: C, 55.0; H, 4.6; Cl, 12.5. Found: C, 55.3; H, 4.5; Cl, 12.31.

(E) The Carbon Tetrachloride Oxidation of $Mo_2Cl_4(PR_3)_4$, where R = Et or *n*-Pr. $Mo_2Cl_4(PEt_3)_4$ (0.10 g) was suspended in 5 ml of carbon tetrachloride and 5 ml of methylene chloride. Upon heating this reaction mixture, a deep red color was quickly generated and after 3–5 min a precipitate of the complex $(Et_3PCl)_3Mo_2Cl_9$ had formed. It redissolved as the reaction was continued, but upon cooling the reaction flask in ice, this red product again precipitated. This product (0.03 g) was filtered off, washed with diethyl ether, and dried in vacuo. Anal. Calcd for $C_{18}H_{45}Cl_{12}P_3Mo_2$: C, 22.2; H, 4.7; Cl, 43.8. Found: C, 21.3; H, 4.4; Cl, 44.1. Yield: 29%.

The related reaction between $Mo_2Cl_4[P(n\text{-}Pr)_3]_4$ and CCl_4/CH_2Cl_2 likewise produced a pink colored product. Although this was not subjected to elemental microanalysis, its diffuse reflectance and Nujol mull electronic absorption spectra and low-frequency infrared spectrum so closely resemble the related spectra of $(Et_3PCl)_3Mo_2Cl_9$ (see Results and Discussion section) that it is almost certainly the complex $[(n\text{-}Pr)_3PCl]_3Mo_2Cl_9$.

Physical Measurements. Infrared spectra in the region 4000–200 cm^{-1} were recorded as Nujol mulls using Beckman and Acculab 6 spectrophotometers. Electronic absorption spectra were recorded on Beckman DU-2 and Cary 14 spectrophotometers. Magnetic moments were measured by the Gouy method using $Hg[Co(SCN)_4]$ as the calibrant. X-ray photoelectron spectra were recorded using a Hewlett-Packard 5950A ESCA spectrometer. The aluminum $K\alpha_{1,2}$ line (1486.6 eV) was used as the x-ray excitation source. Full details of the experimental procedure are described elsewhere.[2,30]

Analytical Procedures. Elemental microanalyses were performed by Dr. C. S. Yeh of the Purdue University microanalytical laboratory or by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results and Discussion

Using a similar procedure to that used to prepare the halide known as β-$MoCl_2$,[4] the related bromide phase can be generated in good yield by the reaction of molybdenum(II) acetate ($Mo_2(O_2CCH_3)_4$) with hydrogen bromide at 300 °C. Both phases exhibit very low magnetic susceptibilities at room temperature (μ_{eff} = 0.49[4] and 0.60 BM for β-$MoCl_2$ and β-$MoBr_2$, respectively) and their solid-state electronic absorption spectra were poorly defined, revealing no dominant absorption maxima in the visible region. Like β-$MoCl_2$, the bromide did produce a characteristic x-ray powder diffraction pattern.[17] By monitoring the powder pattern over a period of several days, it was apparent that this phase decomposes fairly rapidly upon exposure to the atmosphere. This was also shown by the appearance of several molybdenum–oxygen stretching frequencies (e.g., 975 cm^{-1}) in the infrared spectra of "aged" samples and by the molybdenum 3d binding energy spectra of these same materials. The presence of three molybdenum peaks (234.4, 231.4, and 228.6 eV) arises from the overlap of the molybdenum $3d_{3/2,5/2}$ peaks of pure β-$MoBr_2$ at 231.4 and 228.6 eV with those due to the presence of some higher oxidation state molybdenum oxide contaminant.

Since none of the preceding information provides any direct insight into the detailed structures of these phases we felt it was important to investigate their chemical reactivity. In particular, we thought that it was not unreasonable to expect that the structure of β-MoX_2 might contain pairs of strongly metal–metal bonded molybdenum atoms, for in dinuclear molybdenum(II) acetate,[7] from which these halides are prepared, there is a strong metal–metal bond. We have found that the reactions of these phases with pyridine, triethylphosphine, and tri-*n*-propylphosphine lead to the formation of dinuclear metal–metal bonded species of the type $Mo_2X_4L_4$. These complexes are identical with products of this same stoichiometry which have previously been prepared[28,29] from the molybdenum complexes $(NH_4)_5Mo_2Cl_9\cdot H_2O$ (containing the $Mo_2Cl_8^{4-}$ anion) and $Cs_3Mo_2Br_8H$. The spectral properties of these complexes are presented in Table I. Since β-MoX_2 react in this fashion, there is little doubt that they are best represented as $[Mo_2X_4]_n$ and accordingly are the parent halides of the $Mo_2X_8^{4-}$ anions.

Occasionally, in the reaction between β-$MoCl_2$ and pyridine, we isolated small quantities of the mononuclear molybdenum(III) complex $MoCl_3(py)_3$.[31] This reaction is reminiscent of that in which titanium(II) chloride reacts with pyridine to give $TiCl_3(py)_3$.[32] Apparently, Mo_2^{4+} is under certain circumstances a sufficiently powerful reducing agent to reduce pyridine. The fate of the reduced ligand is unknown.

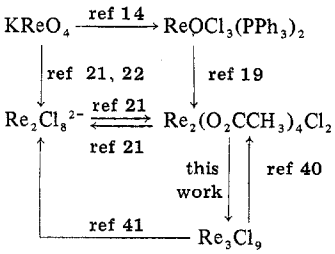
During the course of these studies, we took the opportunity to check whether the salt $K_4Mo_2Cl_8$ was as good a starting material for the synthesis of $Mo_2Cl_4(PR_3)_4$ as the complex $(NH_4)_5Mo_2Cl_9\cdot H_2O$. As expected, this proved to be the case. However, of more importance is the range of phosphine complexes which were isolated. These include the derivatives with diethylphenylphosphine, ethyldiphenylphosphine, and methyldiphenylphosphine. On the basis of their spectral properties (Table I), they are clearly identical structurally to the derivatives with triethylphosphine, tri-*n*-propylphosphine, and tri-*n*-butylphosphine. In a previous study, in which we investigated the ligand induced reductions of the $Re_2X_8^{2-}$ anions by these same tertiary phosphines,[33] we isolated two

Table I. Spectral Properties of Tertiary Phosphine Complexes of Molybdenum

Complex	Starting material	Medium[a]	Electronic absorption maxima, nm	Low-frequency infrared spectra, cm^{-1} [b]
$Mo_2Cl_4(PEt_3)_4$	β-$MoCl_2$	Petroleum ether	583 s, 465 m, 390 sh, 325 s	333 s, 284 m
	$K_4Mo_2Cl_8$			333 s, 309 w, 285 m
$Mo_2Cl_4[P(n\text{-}Pr)_3]_4$	β-$MoCl_2$	DR	590 s, 455 m-w, 325 s	328 s, 279 m
$Mo_2Cl_4[P(n\text{-}Bu)_3]_4$	$(NH_4)_5Mo_2Cl_9 \cdot H_2O$	CH_2Cl_2	590 s, ~465 w, 325 s	326 m, 278 m
$Mo_2Cl_4(PEt_2Ph)_4$	$K_4Mo_2Cl_8$	NM	600 s, 465 m-w, 335 s	335 s, 285 m, 225 m
$Mo_2Cl_4(PEtPh_2)_4$	$K_4Mo_2Cl_8$			343 s, 293 m, 225 m-w
$Mo_2Cl_4(PMePh_2)_4$	$K_4Mo_2Cl_8$	NM	600 s, ~470 w,br, ~425 w,br, 350 m	347 s, 295 m, 227 m-w
$Mo_2Br_4(PEt_3)_4$	β-$MoBr_2$	NM	610 s, ~475 w,br, ~425 w,br, 385 s	270 w,br
$Mo_2Br_4[P(n\text{-}Pr)_3]_4$	β-$MoBr_2$	NM	600 s, ~480 w,br, 370 s	266 w
$Mo_2Br_4[P(n\text{-}Bu)_3]_4$ [c]	$Cs_3Mo_2Br_8H$	*d*	600[e]	260 m
$(Et_3PCl)_3Mo_2Cl_9$	$Mo_2Cl_4(PEt_3)_4$	DR	750 w, ~650 sh, 530 s, 425 m	334 s, 307 s, 275 m, 250 w
$[(n\text{-}Pr)_3PCl]_3Mo_2Cl_9$	$Mo_2Cl_4[P(n\text{-}Pr)_3]_4$	DR	775 w, 670 w, 530 s, 420 m	335 s, 303 s, 277 m
$(Me_4N)_3Mo_2Cl_9$ [f]				325 vs, 308 m-s, 273 w, 250 w
$Cs_3Mo_2Cl_9$ [g]		Crystal	~760 w, ~660 w, 530 s, 422 s	

[a] DR = diffuse reflectance; NM = Nujol mull. [b] All spectra recorded as Nujol mulls. [c] Data taken from ref 28 and 29. [d] Medium not specified (see ref 28). [e] Only the most intense visible absorption band is reported (see ref 28). [f] Data taken from ref 35. [g] Data taken from ref 36.

Scheme I



series of complexes. These were the one-electron reduced species $Re_2X_5(PR_3)_3$, where PR_3 = $PMePh_2$ or $PEtPh_2$, and the two-electron reduction products $Re_2X_4(PR_3)_4$, where PR_3 = PMe_3, PEt_3, or $P(n\text{-}Pr)_3$. That this behavior is a consequence of the different basicities of the phosphines rather than differences in steric effects between the phosphine ligands is confirmed by our isolation of $Mo_2Cl_4(PEtPh_2)_4$ and $Mo_2Cl_4(PMePh_2)_4$ in the present work.

During the characterization of these phosphine complexes, we also investigated the reactions of $Mo_2Cl_4(PEt_3)_4$ and $Mo_2Cl_4[P(n\text{-}Pr)_3]_4$ with carbon tetrachloride. We were prompted to do this because we had earlier found that treatment of $Re_2Cl_4(PEt_3)_4$ with refluxing CCl_4/CH_2Cl_2 mixtures results in oxidation to $(Et_3PCl)_2Re_2Cl_8$.[33] In the reaction between $Mo_2Cl_4(PEt_3)_4$ and CCl_4/CH_2Cl_2, the reaction product is the molybdenum(III) complex $(Et_3PCl)_3Mo_2Cl_9$. Thus the redox chemistries of isoelectronic molybdenum and rhenium dimers are strikingly similar in that oxidation of $Mo_2Cl_4(PEt_3)_4$ and $Re_2Cl_8^{2-}$ both proceed with retention of the metal–metal bonded dinuclear unit even though there is a structure change to a halogen-bridged nonachlorodimetallate type structure. In the case of $Re_2Cl_8^{2-}$, chlorine oxidation yields the $Re_2Cl_9^-$ anion[34] which is isoelectronic with $Mo_2Cl_9^{3-}$. Confirmation that $(Et_3PCl)_3Mo_2Cl_9$ is an authentic derivative of the $Mo_2Cl_9^{3-}$ anion is apparent from a comparison of its low-frequency infrared and electronic absorption spectra with those reported[35,36] for other salts of this anion (Table I).

Like the previously reported chlorine 2p binding energy spectrum of $(Et_3PCl)_2Re_2Cl_8$,[37] related measurements on $(Et_3PCl)_3Mo_2Cl_9$ revealed a three peak binding energy spectrum (201.6, 199.9, and 197.8 eV) arising from a near coincidence in the energy of a chlorine $2p_{1/2}$ component of one type of chlorine with the energy of a $2p_{3/2}$ component of another type. The deconvoluted spectrum[38] showed that there were two types of chlorine environments in the stoichiometric ratio 1:3. As with $(Et_3PCl)_2Re_2Cl_8$,[37] the higher binding energy doublet is assigned to the chlorine in the phosphonium cation. The related binding energies of the other elements present were as follows: Mo $3d_{3/2}$, 232.7; Mo $3d_{5/2}$, 229.5; C 1s, 284.7; P 2p, 132.5 eV.

In contrast to the behavior of $Mo_2(O_2CCH_3)_4$ toward the hydrogen halides, $Rh_2(O_2CCH_3)_4$ and $Re_2(O_2CCH_3)_4X_2$ react in quite different fashions. With $Rh_2(O_2CCH_3)_4$, disproportionation to RhX_3 and rhodium metal occurs and we have no evidence for the formation of rhodium(II) chloride by this route. In the case of $Re_2(O_2CCH_3)_4X_2$, we had hoped that a new structural form of rhenium(III) chloride would be formed, namely $[Re_2X_6]_n$, the parent halide of the $Re_2X_8^{2-}$ haloanions. Instead, the trinuclear phases Re_3X_9 are produced in very high yield. This reaction is particularly significant in that it is the first time that the quadruply bonded Re_2 unit (as present in $Re_2(O_2CCH_3)_4X_2$) has been transformed to the trinuclear Re_3 cluster. Previously, it has proved possible to convert trinuclear to dinuclear complexes, but not the reverse.[39] This new reaction now completes the sequence of conversions between mononuclear, dinuclear, and trinuclear rhenium species as outlined in Scheme I.

This new synthesis of Re_3Cl_9 and Re_3Br_9 offers advantages over the existing synthetic routes to these phases,[24,42,43] since the handling procedures are considerably simplified while good product yields are maintained.

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Registry No. $Mo_2Cl_4(PEt_3)_4$, 59780-36-8; $Mo_2Cl_4[P(n\text{-}Pr)_3]_4$, 59780-37-9; $Mo_2Cl_4(PEt_2Ph)_4$, 59752-91-9; $Mo_2Cl_4(PEtPh_2)_4$, 59752-92-0; $Mo_2Cl_4(PMePh_2)_4$, 59752-93-1; $Mo_2Br_4(PEt_3)_4$, 59752-94-2; $Mo_2Br_4[P(n\text{-}Pr)_3]_4$, 59752-95-3; $(Et_3PCl)_3Mo_2Cl_9$, 59752-98-6; $[(n\text{-}Pr)_3PCl]_3Mo_2Cl_9$, 59753-00-3; β-$MoCl_2$, 13478-17-6; β-$MoBr_2$, 13446-56-5; $K_4Mo_2Cl_8$, 25448-39-9; Re_3Cl_9, 14973-59-2; Re_3Br_9, 33517-16-7; $Re_2(O_2CCH_3)_4Cl_2$, 14126-96-6; $ReOCl_3(PPh_3)_2$, 17442-18-1; $Mo_2Cl_4(py)_4$, 51752-03-5; $MoCl_3(py)_3$, 13927-99-6; $Mo_2Br_4(py)_4$, 51731-40-9; pyridine, 110-86-1; triethylphosphine, 554-70-1; $Mo_2(O_2CCH_3)_4$, 14221-06-8; $Rh_2(O_2CCH_3)_4$, 15956-28-2; $Re_2(O_2CCH_3)_4Br_2$, 15654-27-0; HCl, 7647-01-0; HBr, 10035-10-6.

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Preparation and Characterization of Some Dimolybdenum(II) Carboxylates[1a]

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The reaction of $Mo_2X_4L_4$ [L = $(n\text{-}C_4H_9)_3P$] with benzoic acid produces either $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2X_2$, $(C_6H_5CO_2)_4Mo_2{\cdot}2P(n\text{-}C_4H_9)_3$, or $(C_6H_5CO_2)_4Mo_2$ depending on reaction conditions. Under similar conditions, alkylcarboxylic acids yield only the corresponding tetrakis-μ-(carboxylato) complex, $(RCO_2)_4Mo_2$. The near-uv–visible spectra of the tetrakis-μ-(arylcarboxylato) complexes are characterized by an intense, broad band, the position of which varies substantially with solvent donor nature. Spectral data indicate that the π framework of the aryl rings in these complexes is conjugated with the metal–metal chromophore. In addition, resonance Raman studies indicate that the intense, characteristic transition in the optical spectrum of $(4\text{-}NCC_6H_4CO_2)_4Mo_2$ (and presumably other tetrakis-μ-(arylcarboxylate) complexes of Mo_2^{4+}) involves significant and probably simultaneous change in the occupancy of both the metal–metal and the carboxylate orbitals, suggesting the involvement of a common molecular orbital. The chemical, spectroscopic, and structural relationships that exist between those complexes are discussed.

Introduction

The structural diversity and chemical reactivity of dinuclear complexes with strong metal-to-metal bonds have made them the focus of considerable current interest.[2] Such bonds are particularly prodigious in the chemistry of molybdenum(II). In an effort to determine the range of chemical reactivity of these complexes, we have undertaken an examination of their ligand substitution and redox behavior. Here, we report the preparation and characterization of a series of dinuclear molybdenum(II) carboxylates and the chemical, spectroscopic, and structural relationships that exist between them.

Experimental Section

Materials. Carboxylic acids and tri-*n*-butylphosphine were obtained commercially. The former were used without further purification; the latter was distilled under reduced pressure prior to use. All solvents were purchased as spectral quality or were purified according to standard procedures;[3] they were purged with dry nitrogen for 20–30 min prior to use to ensure oxygen removal.

Spectra and Analyses. Raman spectra were recorded on a Cary Model 82 laser Raman spectrometer equipped with a rotating-sample cell similar to that described elsewhere.[4] 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 krypton ion lasers. Reported frequencies are precise to ± 1 cm^{-1}. Infrared spectra were recorded on a Perkin-Elmer Model 225 spectrophotometer employing either KBr disks or Nujol mulls supported on polyethylene plates. Frequencies are precise to ± 1 cm^{-1}. Optical spectra were obtained on sealed samples using a Cary Model 14 spectrophotometer. Raman intensities were determined by adding a known amount of internal standard (KNO_3) to a predetermined quantity of the desired complex. 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 the 1049-cm^{-1} ν (A_1') band of the internal standard. All intensities were corrected for phototube response.

Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Tetrabromo- and tetrachlorotetrakis(tri-*n*-butylphosphine)dimolybdenum(II), $[(n\text{-}C_4H_9)_3P]_4Mo_2Br_4$ and $[(n\text{-}C_4H_9)_3P]_4Mo_2Cl_4$, were prepared as described previously.[5,6]

Bis-μ-(benzoato)-1,2-dichloro-1,2-bis(tri-*n*-butylphosphine)dimolybdenum(II), $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Cl_2$. $[(n\text{-}C_4H_9)_3P]_4Mo_2Cl_4$ (0.75 g, 0.66 mmol) was placed in a 100-ml flask equipped with a Teflon-coated stirrer bar and a condenser capped with a rubber septum. Benzoic acid (0.16 g, 1.3 mmol) was added and the condenser was attached. The system was flushed thoroughly with nitrogen before injecting benzene (10 ml) with a syringe. The resulting mixture was refluxed for 3 h and then concentrated by distillation to a volume of ~2 ml. Chilled (−15 °C) methanol (10 ml) was added to the cooled reaction mixture. The resulting orange precipitate was collected by suction filtration under nitrogen, rinsed