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Complex Halides of the Transition Metals. 24.[1] Reactions of Dimeric Molybdenum(II) Halide Complexes Containing Strong Metal–Metal Bonds with Bidentate Tertiary Phosphines and Arsines. Evidence for the Staggered Configuration in Dimers of Molybdenum(II)

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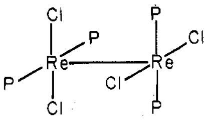
Received June 22, 1977

The reactions of $K_4Mo_2Cl_8$ and $Mo_2X_4(PR_3)_4$, where X = Cl or Br and R = Et or *n*-Bu, with the bidentate phosphine and arsine donors bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1-diphenylphosphino-2-diphenylarsinoethane (arphos), 1,2-bis(diphenylarsino)ethane (dpae), and *o*-phenylenebis(dimethylarsine) (diars) produce metal–metal bonded complexes of the type $Mo_2X_4(LL)_2$. The dimeric complex $Mo_2Cl_4(dppm)_2$ shows spectral similarities to $Mo_2Cl_4(PR_3)_4$ and the rhenium analogue $Re_2Cl_4(dppm)_2$ and it is believed to possess a similar structure to the latter complex with an eclipsed ligand configuration and bridging dppm molecules. The dppe complex $Mo_2Cl_4(dppe)_2$ exists in both α and β forms, which are believed to exhibit quite different structures. α-$Mo_2Cl_4(dppe)_2$ possesses a $\sigma^2\pi^4\delta^2$ ground-state configuration and available evidence indicates that it contains chelating dppe molecules and a cis disposition of Mo–Cl bonds within the individual $[MoCl_2P_2]$ units. β-$Mo_2Cl_4(dppe)_2$ exhibits very similar infrared and electronic absorption spectral properties to $Mo_2Cl_4(arphos)_2$ and $Mo_2Cl_4(dpae)_2$ implying that this group of complexes possesses closely related structures. Since β-$Mo_2Cl_4(dppe)_2$, $Mo_2Cl_4(arphos)_2$, $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(arphos)_2$ are isomorphous, it seems likely that these molybdenum complexes have the same structure as their rhenium analogues, namely, a staggered noncentrosymmetric structure, wherein the dppe, arphos, and dpae ligands assume a novel bonding mode in which they bridge the rhenium atoms within the dimer. This is the first instance where a metal–metal quadruple bond ($\sigma^2\pi^4\delta^2$) has been modified to a triple bond ($\sigma^2\pi^4$) without an accompanying change in the metal oxidation state. $Mo_2Br_4(dppe)_2$ is probably related structurally to β-$Mo_2Cl_4(dppe)_2$ rather than to the α isomer. The diars complexes $Mo_2Cl_4(diars)_2$ and $Re_2Cl_4(diars)_2$ do not appear to be isostructural. The electronic absorption spectrum of $Re_2Cl_4(diars)_2$ provides evidence for the oxidation of this complex by O_2 to form $[Re_2Cl_4(diars)_2]^+$ of some electronically related species. The x-ray photoelectron spectra of the new molybdenum complexes are in accord with their formulation as derivatives of the molybdenum(II) chlorides.

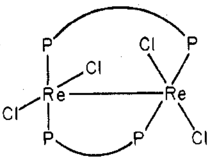
Introduction

In exploring the factors which influence the electronic structures of low oxidation state halide complexes of molybdenum and rhenium which contain strong metal–metal bonds (double, triple, or quadruple),[2] we recently established[3] that the metal–metal bonded dimers $Re_2Cl_4(LL)_2$, where LL = 1,2-bis(diphenylphosphino)ethane (dppe) or 1-diphenylphosphino-2-diphenylarsinoethane (arphos), differ structurally from the related complexes with monodentate tertiary phosphines, $Re_2Cl_4(PR_3)_4$.[4,5] In contrast to the latter systems, which possess an eclipsed noncentrosymmetric D_{2d} structure I,[5] the complexes with dppe and arphos were suggested to have



I

the staggered structure II,[3] wherein the dppe and arphos



II

ligands assume a novel bonding mode in which they bridge the rhenium atoms *within* the dimer. The latter structure formulation was based upon differences between the electronic absorption spectra and magnetic properties of $Re_2Cl_4(PR_3)_4$ and $Re_2Cl_4(LL)_2$ and experiments with scaled molecular models which were constructed to minimize unfavorable steric interactions. Earlier attempts to solve the crystal structure of either $Re_2Cl_4(dppe)_2$ or $Re_2Cl_4(arphos)_2$ were thwarted by a disorder problem and small crystal size. Accordingly, as an alternative approach to aid us in establishing whether our structural conclusions were correct, we set out to synthesize and characterize the related molybdenum(II) complexes of this type. This investigation has led us to study the reactions of the complexes $K_4Mo_2Cl_8$ and $Mo_2X_4(PR_3)_4$, where X = Cl or Br and R = Et or *n*-Bu, with the bidentate ligands dppe, arphos, bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylarsino)ethane (dpae), and *o*-phenylenebis(dimethylarsine) (diars), the results of which are reported herein. Since the completion of this study, our original suggestion[3] concerning the structures of $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(arphos)_2$ has been confirmed by a single-crystal x-ray structural analysis of $Re_2Cl_4(dppe)_2$.[6]

Experimental Section

Starting Materials. The following compounds were prepared by standard literature procedures: $K_4Mo_2Cl_8$,[7] $Mo_2Cl_4(PEt_3)_4$,[8] $Mo_2Cl_4(P\text{-}n\text{-}Bu_3)_4$,[9] and $Mo_2Br_4(PEt_3)_4$.[8] Commercial reagents and

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solvents were used as received. All arsine and phosphine ligands were obtained from Strem Chemicals, Inc.

Reactions Procedures. All reactions were carried out in a nitrogen atmosphere and solvents were deoxygenated by purging with N_2 gas for several hours prior to use.

(A) Reactions with Bis(diphenylphosphino)methane (dppm). (i) $K_4Mo_2Cl_8$ in Methanol. A suspension of $K_4Mo_2Cl_8$ (0.40 g) and dppm (0.48 g) in anhydrous methanol (40 mL) rapidly darkened upon heating. After a reflux period of 2 h, a green precipitate had formed. This was isolated (0.57 g), washed with water (to remove any excess $K_4Mo_2Cl_8$), methanol, and diethyl ether, and dried in vacuo. Anal. Calcd for $MoCl_2[(C_6H_5)_2PCH_2P(C_6H_5)_2]$: C, 54.5; H, 4.0; Cl, 12.9. Found: C, 54.5; H, 4.1; Cl, 13.6. Yield 82%. The blue-green powder was stable in air and slightly soluble in acetone, dichloromethane, and chloroform but insufficiently so to permit a molecular weight determination.

A mixture of this complex (0.07 g) and tetraethylammonium chloride (0.16 g) was dissolved in 15 mL of carbon tetrachloride–methylene chloride (1:1 by volume) to produce a deep red solution. A pink suspension resulted upon refluxing this solution for 0.5 h; reflux was continued overnight to ensure complete reaction. A pink powder (0.04 g) was isolated, washed with ethanol and diethyl ether, and dried. Anal. Calcd for $[(C_2H_5)_4N]_3Mo_2Cl_9$: C, 32.0; H, 6.7; Cl, 35.4. Found: C, 32.2; H, 6.6; Cl, 35.4. Yield 72%.

(ii) $Mo_2Cl_4(PEt_3)_4$ in Methanol. Upon heating a suspension of $Mo_2Cl_4(PEt_3)_4$ (0.11 g) and dppm (0.10 g) in methanol (15 mL), a deep turquoise colored solution resulted. After refluxing the reaction mixture for 5 days, the solution had turned a dark olive green. Filtration afforded a mixture of dark green and deep blue crystals and a dark brown solution. The deep blue crystals were dissolved in a large volume of diethyl ether, leaving behind a small quantity of green powder (0.02 g) which was then dried. Yield 13%. Infrared spectroscopy showed that it was the same complex as that isolated from the $K_4Mo_2Cl_8$ reaction A(i).

(iii) $Mo_2Cl_4(PEt_3)_4$ in Benzene. An opaque deep blue solution formed upon refluxing a mixture of $Mo_2Cl_4(PEt_3)_4$ (0.10 g) and dppm (0.20 g) in benzene (20 mL). Following 11 days of reflux, the solution was kept at room temperature for 1 day and then filtered. The small quantity of tiny, feathery green crystals (0.02 g) was washed with methanol and dried. Yield 13%. The identity of this complex as $[MoCl_2(dppm)]_n$ was demonstrated by infrared spectroscopy.

Evaporation of the initial blue reaction filtrate gave a blue solid (0.02 g), the infrared spectrum of which revealed the presence of both PEt_3 (1266 (s) cm^{-1}) and dppm (700 (s) and 503 (s) cm^{-1}), together with phosphine oxide (1099 (s, br) cm^{-1}) and possibly molybdenum oxide (~800 and 396 (s, br) cm^{-1}) contaminants.

(iv) $Mo_2Br_4(PEt_3)_4$ in Methanol. A suspension of $Mo_2Br_4(PEt_3)_4$ (0.10 g) and dppm (0.17 g) in methanol was refluxed for 24 h. A dark blue-green precipitate (0.04 g) was isolated, washed with methanol and diethyl ether (small volume), and dried in vacuo. Anal. Calcd for $MoBr_2[(C_6H_5)_2PCH_2P(C_6H_5)_2]$: C, 46.9; H, 3.5; Br, 25.0. Found: C, 46.9; H, 3.5; Br, 25.2. Yield 31%. The physical properties and infrared spectrum of this complex in the region above 400 cm^{-1} were identical with those of the samples of $[MoCl_2(dppm)]_n$ which were prepared in reactions A(i–iii).

(B) Reactions with 1,2-Bis(diphenylphosphino)ethane (dppe). (i) $K_4Mo_2Cl_8$ in Methanol. A green suspension quickly developed on refluxing a mixture of $K_4Mo_2Cl_8$ (0.21 g) and dppe (0.27 g) in anhydrous methanol (25 mL). After 3 h a light green powder (0.30 g) was isolated, washed with methanol and diethyl ether, and dried. Anal. Calcd for $MoCl_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$: C, 55.2; H, 4.3; Cl, 12.5. Found: C, 54.2; H, 4.7; Cl, 13.0. Yield 91%. This material is stable toward air and insoluble in most organic solvents. It is hereafter referred to as α-$Mo_2Cl_4(dppe)_2$.

Oxidation of this species (0.05 g) with refluxing carbon tetrachloride–dichloromethane (10 mL) in the presence of an excess of tetraethylammonium chloride (0.15 g) required 6 days for the reaction to go to completion. The resulting pink powder (0.03 g) was filtered off, washed with ethanol and diethyl ether, and dried. Anal. Calcd for $[(C_2H_5)_4N]_3Mo_2Cl_9$: C, 32.0; H, 6.7. Found: C, 33.0; H, 6.6. Yield 75%. Its infrared spectrum was similar to that of the product obtained upon the related oxidation of $[MoCl_2(dppm)]_n$ (see A(i)).

(ii) $K_4Mo_2Cl_8$ in Ethanol. A suspension of $K_4Mo_2Cl_8$ (0.40 g) and dppe (0.40 g) in absolute ethanol (40 mL) was refluxed for a period of 4 days to afford a crop of very small shiny brown crystals and a pale brown solution. The insoluble product was first washed with ethanol and water, the latter giving a red solution (indicative of the presence of unreacted $K_4Mo_2Cl_8$). The resulting olive green solid (0.41 g) was further washed with water until the washings were colorless, followed by ethanol and diethyl ether and then dried. Anal. Calcd for $MoCl_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$: C, 55.2; H, 4.3; Cl, 12.5. Found: C, 55.5; H, 4.2; Cl, 12.4. Yield 57%. This product exhibited the same lack of solubility as α-$Mo_2Cl_4(dppe)_2$ but its spectral properties and x-ray powder diffraction pattern are consistent with it being a mixture of α and β isomers (see B(i) and B(iii)).

Chlorocarbon oxidation of the olive green product (0.05 g) in the presence of tetraethylammonium chloride (0.15 g) gave a pink powder (0.04 g) which was isolated after 2 days. A small amount of unreacted starting material was evident in this product. Anal. Calcd for $[(C_2H_5)_4N]_3Mo_2Cl_9$: C, 32.0; H, 6.7. Found: C, 34.4; H, 5.8.

(iii) $Mo_2Cl_4(PEt_3)_4$ in Methanol. A gray precipitate formed upon refluxing a mixture of $Mo_2Cl_4(PEt_3)_4$ (0.30 g) and dppe (0.60 g) in methanol (25 mL). The reaction was stopped after 3 days, and the gray product (0.17 g) filtered off and washed with benzene and diethyl ether to dissolve a blue contaminant (presumably unreacted $Mo_2Cl_4(PEt_3)_4$). Anal. Calcd for $MoCl_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$: C, 55.2; H, 4.3. Found: C, 53.3; H, 4.4. Yield 40%. This species is stable toward air and insoluble in a variety of organic solvents. It will be referred to as β-$Mo_2Cl_4(dppe)_2$.

Although oxidation by refluxing carbon tetrachloride appeared to occur within minutes, the resulting brownish pink product was not pure $(Et_4N)_3Mo_2Cl_9$ as revealed by its infrared spectrum.

(iv) $Mo_2Cl_4(P\text{-}n\text{-}Bu_3)_4$ in Methanol. Overnight reflux of a suspension of $Mo_2Cl_4(P\text{-}n\text{-}Bu_3)_4$ (0.50 g) and dppe (0.50 g) in methanol (40 mL) gave a gray powder (0.34 g) whose infrared spectrum was identical with that of β-$Mo_2Cl_4(dppe)_2$ prepared from the PEt_3 derivative. Anal. Calcd for $MoCl_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$: C, 55.2; H, 4.3; Cl, 12.5. Found: C, 53.8; H, 4.5; Cl, 12.2. Yield 69%.

(v) $Mo_2Cl_4(PEt_3)_4$ in Benzene. A mixture of $Mo_2Cl_4(PEt_3)_4$ (0.10 g) and dppe (0.20 g) was dissolved in benzene (20 mL) to form a deep blue solution. After an 11-day reflux period the only solid that had formed was a very small number of brown crystals which had deposited on the boiling stick. A lilac solid (0.10 g) was recovered by evaporation of solvent; its infrared spectrum revealed the presence of triethylphosphine, dppe, and a phosphine oxide contaminant.

(vi) $Mo_2Br_4(PEt_3)_4$ in Methanol. A suspension of $Mo_2Br_4(PEt_3)_4$ (0.10 g) and dppe (0.24 g) in methanol (30 mL) quickly turned brown upon heating. After 20 h of reflux, the resulting brown solid (0.05 g) was filtered off, washed with methanol and diethyl ether, and dried. Anal. Calcd for $MoBr_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$: C, 47.7; H, 3.7; Br, 24.4. Found: C, 46.4; H, 3.6; Br, 24.2. Yield 38%. This product is stable toward air and displays the typical insolubility of other dppe complexes. Its infrared spectrum above 400 cm^{-1} is identical with that of β-$Mo_2Cl_4(dppe)_2$.

(C) Reactions with 1-Diphenylphosphino-2-diphenylarsinoethane (arphos). (i) $K_4Mo_2Cl_8$ in Methanol. A suspension of $K_4Mo_2Cl_8$ (0.20 g) and arphos (0.39 g) in methanol (25 mL) turned gray-brown upon refluxing for 4 h. The gray-brown powder (0.35 g) was filtered off and washed with methanol and diethyl ether. Anal. Calcd for $MoCl_2[(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2]$: C, 51.3; H, 4.0. Found: C, 51.2; H, 4.3. Yield 91%. Occasionally a small quantity of green contaminant was evident in these reactions.

(ii) $K_4Mo_2Cl_8$ in Ethanol. A rose-colored suspension of $K_4Mo_2Cl_8$ (0.51 g) and arphos (0.72 g) in ethanol (50 mL) was filtered after a 6-day reflux period. The light red precipitate was washed with water to dissolve any unreacted $K_4Mo_2Cl_8$. This left behind a red-brown powder which was further rinsed with ethanol and diethyl ether and dried (0.69 g). Anal. Calcd for $MoCl_2[(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2]$: C, 51.3; H, 4.0; Cl, 11.6. Found: C, 50.2; H, 4.1; Cl, 11.9. Yield 69%. The infrared spectrum of this product was identical with that of the product of this same stoichiometry which was isolated from methanol. None of the green material which was seen in the previous reaction C(i) was observed in this system.

(D) Reactions of 1,2-Bis(diphenylarsino)ethane (dpae). (i) $K_4Mo_2Cl_8$ in Methanol. A methanol (25 mL) suspension of $K_4Mo_2Cl_8$ (0.30 g) and dpae (0.45 g) was refluxed for 15 min. The dark brown solution was filtered leaving a mixture of a red powder and large colorless needles. Washing with benzene removed the latter, and the remaining pink powder (0.08 g) was washed with acetone and water (to remove any $K_4Mo_2Cl_8$) followed by acetone and diethyl ether and then dried. Anal. Calcd for $MoCl_2[(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2]$: C, 47.8; H, 3.7; Cl, 10.9. Found: C, 48.0; H, 3.9; Cl, 11.0. Yield

Table I. Spectral Properties of Molybdenum Complexes Containing Bidentate Ligands[a]

Complex	Electronic absorption maxima, nm	Infrared spectra (400–200 cm^{-1})[b]
$Mo_2Cl_4(dppm)_2$	615 s, 475 sh, 445 m	*340* s, *289* m
$Mo_2Br_4(dppm)_2$	785 w?, 640 m, br, 480 w, 400 w	260 w
α-$Mo_2Cl_4(dppe)_2$	675 s, 475 w, 390 sh, 345 vs	347 w, *307* s, *290* m–s
β-$Mo_2Cl_4(dppe)_2$	780 s, 675 m,[c] 565 vw, sh, 470 s, 345 vs	*340* s, 306 sh,[c] *291* s
$Mo_2Br_4(dppe)_2$	840 s, ~600 vw, sh, 495 s, 375 s	~270 w
$Mo_2Cl_4(arphos)_2$	760 s, 560 vw, sh, 480 s, 345 vs	*346* vs, 307 m–s,[d] *293* m–s
$Mo_2Cl_4(dpae)_2$	740 s, ~550 vw, sh, 480 s, 345 vs	391 m, *352* vs, 304 sh, *295* s, 282 w
$Mo_2Cl_4(diars)_2$	650 vs, 465 s, 400 s	365 s, sh, 360 s, 310 vs, 295 vs, sh, 275 s
$Re_2Cl_4(diars)_2$	1300 m, vbr,[e] 630 sh, 480 s	378 w, 368 m, 355 s, 346 m, sh, 335 m, sh, 279 m, 244 w, br

[a] All spectra were recorded as Nujol mulls. [b] ν(Mo–Cl) modes are given in italics. [c] This absorption is probably due to the presence of a small amount of the α isomer. [d] This band is assigned to a ligand mode. The free arphos ligand has a band at 306 cm^{-1} which is observed at a similar frequency in complexes such as $Re_2Br_4(arphos)_2$ and $ReBr_4(arphos)$ where it is not obscured by ν(Re–X) modes. [e] Impurity band arising from oxidation (see Results and Discussion).

Table II. X-Ray Photoelectron Spectra of Metal–Metal Bonded Complexes of Molybdenum(II)[a]

	Mo		Cl			
Complex	$3d_{3/2}$	$3d_{5/2}$	$2p_{1/2}$	$2p_{3/2}$	P 2p	C 1s
$K_4Mo_2Cl_8$	232.1	229.0 (1.3)	200.2	198.6 (1.4)		284.8 (1.8)[e]
$(NH_4)_5Mo_2Cl_9 \cdot H_2O$[b]	232.2	229.2 (1.1)	~199.8	198.6 (1.3)		284.9 (1.6)[e]
$Mo_2Cl_4(PEt_3)_4$[c]	231.8	228.7 (1.4)	199.6	198.2 (1.5)		284.8 (1.4)
$Mo_2Cl_4(PPr_3)_4$[c]	232.0	228.8 (1.5)				284.8 (1.8)
$Mo_2Cl_4py_4$[b]	231.7	228.7 (1.3)	199.9	198.5 (1.2)		284.8 (1.8)
$Mo_2Cl_4(dppm)_2$	231.8	228.7 (1.7)	199.4	198.0 (1.3)	131.4 (2.0)	284.7 (1.6)
α-$Mo_2Cl_4(dppe)_2$	231.5	228.5 (1.2)	199.6	198.1 (1.2)		284.7 (1.3)
β-$Mo_2Cl_4(dppe)_2$	232.2	229.0 (1.5)	199.9	198.4 (1.4)	131.5 (2.1)	285.0 (1.6)
$Mo_2Br_4(dppe)_2$	232.0	228.8 (1.4)	189.0[d]	182.5 (2.2)[d]	131.4 (2.0)	285.0 (1.6)
$Mo_2Cl_4(arphos)_2$	231.9	228.9 (1.4)	199.9	198.4 (1.3)		284.7 (1.3)
$Mo_2Cl_4(dpae)_2$	231.7	228.7 (1.4)	199.6	198.1 (1.4)		284.7 (1.5)

[a] All spectra are referenced to the carbon 1s binding energy of graphite taken as 284.0 eV; full-width half-maximum values (fwhm) are given in parentheses. [b] Present data in good agreement with that reported previously in ref 26. [c] Data taken from ref 26. [d] Br $3p_{1/2,3/2}$ binding energies. [e] C 1s binding energy of carbon contaminant.

13%. This complex is quite insoluble in methanol, acetone, dichloromethane, benzene, and diethyl ether and is stable toward air.

(E) Reactions with *o*-Phenylenebis(dimethylarsine) (diars). (i) $K_4Mo_2Cl_8$ in Methanol. A deep purple suspension developed within 15 min of refluxing a mixture of $K_4Mo_2Cl_8$ (0.10 g) and diars (1 mL) in methanol (10 mL). Filtration of the reaction mixture after 5 h separated a green precipitate from a deep red solution. The solid (0.09 g) was rinsed with water, methanol, ethanol, and diethyl ether to yield a dark green microcrystalline product. Anal. Calcd for $MoCl_2[C_6H_4(As(CH_3)_2)_2]$: C, 26.5; H, 3.6; Cl, 15.7. Found: C, 26.0; H, 3.7; Cl, 15.4. Yield 63%. This product is unreactive toward air and insoluble in common organic solvents.

(ii) $(Bu_4N)_2Re_2Cl_8$ in Ethanol. $(Bu_4N)_2Re_2Cl_8$ (0.31 g) and diars (1.2 mL) were refluxed together in ethanol (20 mL). After 7 h the opaque dark brown suspension was filtered off and the resulting gray-brown solid (0.05 g) was washed with ethanol and diethyl ether and dried. Anal. Calcd for $ReCl_2[C_6H_4(As(CH_3)_2)_2]$: C, 22.1; H, 2.3; Cl, 13.1. Found: C, 22.6; H, 3.4; Cl, 12.9. Yield 17%.

Physical Measurements. Infrared spectra in the region 4000–200 cm^{-1} were recorded as Nujol mulls using a Beckman IR-12 spectrophotometer. Electronic absorption spectra were recorded on a Cary 14 spectrophotometer. Magnetic susceptibilities were determined by the Gouy technique using $Hg[Co(SCN)_4]$ as the calibrant. The measurements were made at only one temperature, approximately 25 °C. 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 excitation source. Full details of the experimental procedures are described elsewhere.[10,11] X-ray powder patterns were recorded using a General Electric recording diffractometer with a Cu Kα (1.5405 Å) radiation source. The sample was deposited on an adhesive tape attached to a microscope slide. Measured diffraction angles (2θ) were converted to interplanar spacings (d) by use of published tables.

Analytical Procedures. Elemental microanalyses were performed by Dr. C. S. Yeh of the Purdue University microanalytical laboratory.

Results and Discussion

The only previous studies on complexes of the type $Mo_2X_4(LL)_2$, where LL represents a bidentate donor, are those described by San Filippo[12] and Brencic[13–15] who isolated derivatives with several sulfur ligands (2,5-dithiahexane, 4,7-dithiadecane, and 5,8-dithiadodecane for X = Cl and/or Br),[12] 1,2-bis(dimethylphosphino)ethane (X = Cl),[12] 2,2′-bipyridyl (X = Cl, Br, or I)[12–15] and 1,10-phenanthroline (X = Cl).[13] However, only in the case of the work of San Filippo[12] were these species subjected to a detailed spectroscopic characterization and in no instance has the structure of any of the complexes yet been determined crystallographically.

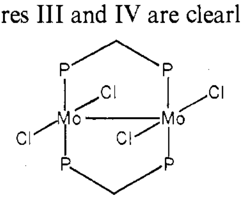
Using the complexes $K_4Mo_2Cl_8$, $Mo_2Cl_4(PEt_3)_4$, $Mo_2Cl_4(P\text{-}n\text{-}Bu_3)_4$, and $Mo_2Br_4(PEt_3)_4$[7–9] as starting materials, we have isolated the new complexes listed in Table I. In some systems, the products which are obtained depend on both the nature of the molybdenum starting material and the solvent. While some of the results augment those previously obtained on the related rhenium systems,[3] others yield products which differ structurally from their rhenium analogues. Because the behavior of these ligands appears to fall into three distinct categories, each class of donor system will be considered separately. The results of studies on the low-frequency infrared and electronic absorption spectral studies on these complexes and their x-ray photoelectron spectra are summarized in Tables I and II.

(a) Bis(diphenylphosphino)methane. The reaction of $K_4Mo_2Cl_8$ or $Mo_2Cl_4(PEt_3)_4$ with dppm yields a blue-green product of stoichiometry $[MoCl_2(dppm)]$. The bromide complex $[MoBr_2(dppm)]$ was obtained from $Mo_2Br_4(PEt_3)_4$ by an analogous procedure. The related rhenium(II) systems[3] are rather more complicated. The rhenium(II) dimer $Re_2Cl_4(dppm)_2$ could only be prepared[3] from $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ since reaction of dppm with $Re_2Cl_4(PEt_3)_4$ afforded the mixed-ligand complex $Re_2Cl_4(PEt_3)_2(dppm)$. It was proposed[3] that these diamagnetic rhenium(II) species possess a structure with bridging rather than chelating dppm ligands, thereby retaining the strong Re–Re bond of the parent $Re_2Cl_4(PR_3)_4$ complexes. This conclusion is supported by the recent crystal structure determination of $[Re_2Cl_4(dppm)_2]Cl$,[16] a species which is formally a one-electron oxidation product of $Re_2Cl_4(dppm)_2$. Two different rhenium(II) bromide complexes have been prepared.[3] α-$[ReBr_2(dppm)]_n$ is a reduction product which is obtained upon reacting $(Bu_4N)_2Re_2Br_8$ with dppm in acetonitrile. The reaction of dppm with $Re_2Br_4(P\text{-}n\text{-}Pr_3)_4$ in benzene produces β-$[ReBr_2(dppm)]_n$. The spectroscopic properties of these two bromide phases do not indicate[3] a close structural relationship to one another or to $Re_2Cl_4(dppm)_2$.

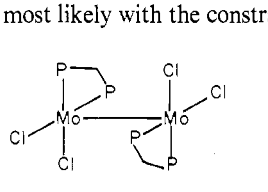
Evidence for the dimeric nature of $[MoCl_2(dppm)]_n$ follows from several lines of reasoning. The magnetic susceptibility of this complex ($\chi_g = -0.37 \times 10^{-6}$ cgsu at 299 K) is inconsistent with magnetically dilute Mo(II) centers (d^4) and favors the existence of Mo–Mo bonds. The rapid oxidation of this complex by CCl_4 in the presence of excess Et_4NCl to form $(Et_4N)_3Mo_2Cl_9$ supports a dimeric metal–metal bonded structure since a similar reactivity pattern is displayed by $Mo_2Cl_4(PEt_3)_4$ and $Mo_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ in their oxidation to the molybdenum(III) salts $(R_3PCl)_3Mo_2Cl_9$.[8] The identification of the oxidation product as $(Et_4N)_3Mo_2Cl_9$ was based upon microanalytical data and the similarity of its low-frequency infrared spectrum (ν(Mo–Cl) modes at 325 (s), 308 (s), 271 (m–w), and 255 (w) cm^{-1}) to that expected for a salt of the $Mo_2Cl_9^{3-}$ anion.[17]

Additional similarities between $Mo_2Cl_4(dppm)_2$ and $Mo_2Cl_4(PR_3)_4$ are apparent in a comparison of their respective electronic absorption spectra. The absorption maxima and relative intensities of these complexes show a very close resemblance to one another. The lowest energy absorption of $Mo_2Cl_4(dppm)_2$ is at 615 nm, similar to that encountered in the related spectra of $Mo_2Cl_4(PR_3)_4$ (580–600 nm)[8,12] and quite different from the spectra of related complexes of other bidentate phosphine donors (Table I). Although $Mo_2Cl_4(dppm)_2$ and $Re_2Cl_4(dppm)_2$ are not isomorphous, as determined by the lack of coincidence between the stronger lines of their x-ray powder patterns,[18] this does not necessarily mean that they are not isostructural. Possible differences in molecular packing can be inferred from the infrared spectra of the two species in the region 600–800 cm^{-1}, where out-of-plane C–H deformation modes of the aromatic rings occur. It is likely that these vibrational modes are sensitive to intermolecular interactions in the crystalline state. In $Re_2Cl_4(dppm)_2$ these absorptions occur with considerable complexity while in the related spectra of $Mo_2X_4(dppm)_2$ there are only three intense sharp bands in this spectral region.

As far as the orientation of the ligands is concerned, structures III and IV are clearly most likely with the constraint of the eclipsed ligand configuration which is favored by systems possessing a $\sigma^2\pi^4\delta^2$ electronic configuration.[2] However, the close coincidence in position and relative intensity of the ν(Mo–Cl) modes of $Mo_2Cl_4(dppm)_2$ (Table I) with those present in the infrared spectra of $Mo_2Cl_4(PR_3)_4$,[8,12] complexes which have a trans arrangement of Mo–Cl bonds, strongly favors the bridging geometry III. A similar conclusion was previously arrived at from the resemblance between the spectra of $Re_2Cl_4(PR_3)_4$ and $Re_2Cl_4(dppm)_2$.[3]



III



IV

As was the case with $Mo_2Br_4(PR_3)_4$ complexes,[8] there is only one ν(Mo–Br) band at ~260 cm^{-1} in the spectrum of $Mo_2Br_4(dppm)_2$; additional ν(Mo–Br) vibrations occur below the limit of our measurements (<200 cm^{-1}). Above 400 cm^{-1}, the spectrum is identical with that of $Mo_2Cl_4(dppm)_2$ and quite different from the spectrum of the free ligand. There is no spectroscopic evidence to support a close structural relationship between $Mo_2Br_4(dppm)_2$ and either form of $[ReBr_2(dppm)]_n$.[3]

(b) 1,2-Bis(diphenylphosphino)ethane, 1-Diphenylphosphino-2-diphenylarsinoethane, and 1,2-Bis(diphenylarsino)ethane. The reactions of these ligands with $K_4Mo_2Cl_8$, $Mo_2X_4(PEt_3)_4$ (X = Cl or Br), and $Mo_2Cl_4(P\text{-}n\text{-}Bu_3)_4$ in methanol or ethanol afford complexes of the type $[MoX_2(LL)]_n$ (Table I) which are diamagnetic or very weakly paramagnetic.[19] In all cases except $Mo_2Cl_4(dppe)_2$, these reactions proceed to give a single isomeric product. In the reactions between dppe and $K_4Mo_2Cl_8$ or $Mo_2Cl_4(PR_3)_4$, where R = Et or *n*-Bu, either a light green (α) or gray (β) isomer was formed depending upon the choice of solvent and starting material. If $K_4Mo_2Cl_8$ is reacted with dppe in methanol and ethanol, the course of the reaction is solvent dependent. In methanol the reaction is rapid and apparently goes to completion within a few minutes yielding α-$[MoCl_2(dppe)]_n$. The dimeric nature of this species is indicated by its diamagnetism and its reaction with CCl_4 to give $Mo_2Cl_9^{3-}$. It appears to be essentially unreactive toward triethylphosphine. With ethanol as the solvent, this reaction is much slower, and considerable quantities of $K_4Mo_2Cl_8$ remain unreacted. The resulting olive green product, also analyzed as $[MoCl_2(dppe)]$, was diamagnetic and formed $Mo_2Cl_9^{3-}$ on chlorocarbon oxidation. As will be seen, this material is probably a mixture of two isomers of $Mo_2Cl_4(dppe)_2$.

A gray isomer, β-$[MoCl_2(dppe)]_n$, is obtained from the reaction of dppe with $Mo_2Cl_4(PEt_3)_4$ or $Mo_2Cl_4(P\text{-}n\text{-}Bu_3)_4$ in methanol. Although this species was only partially converted to $Mo_2Cl_9^{3-}$ in the same time period that the α phase was completely oxidized by CCl_4, its observed diamagnetism is consistent with retention of a Mo–Mo bond.

In contrast to the behavior of dppe, the reaction of $K_4Mo_2Cl_8$ and arphos in both methanol and ethanol gives the same product. As with the dppe system, the reaction in ethanol is much slower and unreacted $K_4Mo_2Cl_8$ is always present. The use of $Mo_2Cl_4(PEt_3)_4$ as a reactant failed to yield a pure product in either methanol or benzene. The synthesis of $Mo_2Cl_4(dpae)_2$ from $K_4Mo_2Cl_8$ in methanol closely resembles that of the related arphos complex.

Several related rhenium(II) complexes of this type, namely, $Re_2Cl_4(dppe)_2$, $Re_2Cl_4(arphos)_2$, and $Re_2Br_4(arphos)_2$, have been prepared[3] from $Re_2Cl_4(PEt_3)_4$, via ligand displacement reactions and/or by the ligand induced reductions of the $Re_2X_8^{2-}$ anions (X = Cl or Br). The only previous report of a molybdenum(II) dimer with bidentate phosphine or arsine donors is that which San Filippo and co-workers[12] isolated from the reaction of $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ with 1,2-bis(dimethylphosphino)ethane (dmpe) in methanol. They proposed that the resulting blue complex, $Mo_2Cl_4(dmpe)_2$, contains dmpe bonded in a chelating manner. Similar structural conclusions were made for complexes of other bidentate ligands.[12]

The low-frequency infrared spectra of β-$Mo_2Cl_4(dppe)_2$, $Mo_2Cl_4(arphos)_2$, and $Mo_2Cl_4(dpae)_2$ are very similar and each exhibits ν(Mo–Cl) modes at 350–340 (vs) and 295–290 (s) cm^{-1}, thereby resembling closely the related spectra of $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(arphos)_2$ (ν(Re–Cl) at ~330 (s) and ~300 (m–s), cm^{-1})[3] and $Mo_2Cl_4(PR_3)_4$ (ν(Mo–Cl) at ~330 (s) and ~280 (m) cm^{-1})[8] in which a trans disposition of M–Cl bonds are maintained within the individual $[MCl_2P_2]$ units. The electronic absorption spectra of β-$Mo_2Cl_4(dppe)_2$, $Mo_2Cl_4(arphos)_2$, and $Mo_2Cl_4(dpae)_2$ are likewise very similar (Table I and Figure 1) implying a similarity in electronic structure. The most prominent absorption band in the visible region is located between 740 and 780 nm (Table I), at a significantly lower energy than the lowest energy band in the related spectra of $Mo_2Cl_4(dppm)_2$ (Table I) and other halide

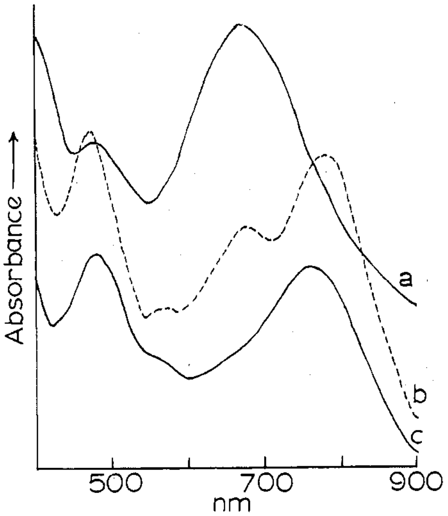


Figure 1. Electronic absorption spectra (Nujol mulls) of (a) α-$Mo_2Cl_4(dppe)_2$, (b) β-$Mo_2Cl_4(dppe)_2$, and (c) $Mo_2Cl_4(arphos)_2$.

complexes of molybdenum(II) containing Mo–Mo quadruple bonds.[12,20] The electronic absorption spectral properties of complexes of the latter type are also displayed by α-$Mo_2Cl_4(dppe)_2$, since its lowest energy band at 675 nm (Table I and Figure 1) is very close to that of $Mo_2Cl_4(dmpe)_2$ (666 nm).[12] Spectral differences between the α and β forms of $Mo_2Cl_4(dppe)_2$ are further seen in a comparison of their low-frequency infrared spectra. The highest energy ν(Mo–Cl) mode of α-$Mo_2Cl_4(dppe)_2$ is more than 30 cm^{-1} below that encountered in the spectra of β-$Mo_2Cl_4(dppe)_2$, $Mo_2Cl_4(arphos)_2$, $Mo_2Cl_4(dpae)_2$, and $Mo_2Cl_4(PR_3)_4$[8,12] in which a *trans*-$[MoCl_2(PR_3)_2]$ geometry is present. Moreover, the 307-cm^{-1} band of α-$Mo_2Cl_4(dppe)_2$ is roughly coincident with the most intense ν(Mo–Cl) band (300–312 cm^{-1}) in the infrared spectra of $Mo_2Cl_4(LL)_2$ complexes, where LL represents a bidentate donor, which San Filippo et at.[12] believe contain bidentate chelating donors. This evidence therefore supports both the presence of a chelating bidentate phosphine in α-$Mo_2Cl_4(dppe)_2$ and a *cis*-$[MoCl_2P_2]$ geometry. However, as pointed out by San Filippo et al.,[12] there are a minimum of three geometries possible for tetrahalodimolybdenum(II) complexes of the type $Mo_2X_4(LL)_2$ if an eclipsed configuration is maintained and the ligands (LL) are bidentate and chelating. We do not yet know which of these structures is appropriate to α-$Mo_2Cl_4(dppe)_2$.

The distinction between α- and β-$Mo_2Cl_4(dppe)_2$, and the similarity of the β isomer to $Mo_2Cl_4(arphos)_2$ and $Mo_2Cl_4(dpae)_2$ has been confirmed by x-ray powder diffraction measurements. The powder patterns of α- and β-$Mo_2Cl_4(dppe)_2$ are quite different.[18] While the quality of the powder pattern for β-$Mo_2Cl_4(dppe)_2$ was not as good as we had wished, nonetheless, all the stronger lines and many of the weaker ones coincide with those obtained for $Re_2Cl_4(dppe)_2$. This suggests that these complexes are isomorphous and further supports a dimeric structure for the molybdenum complex. Since there is also nearly flawless agreement between the x-ray powder patterns of $Mo_2Cl_4(arphos)_2$, $Re_2Cl_4(arphos)_2$, and $Re_2Cl_4(dppe)_2$[18] this also establishes the dimeric nature of $Mo_2Cl_4(arphos)_2$. Accordingly, we propose that β-$Mo_2Cl_4(dppe)_2$ and $Mo_2Cl_4(arphos)_2$ have the same ligand-bridged structure as the related rhenium(II) complexes (see structure II) in which the individual $[MoCl_2L_2]$ units assumed a staggered configuration with respect to one another. The similarity of the electronic and infrared spectra of $Mo_2Cl_4(dpae)_2$ to those of β-$Mo_2Cl_4(dppe)_2$ and $Mo_2Cl_4(arphos)_2$ is convincing evidence that it too has a structure closely related to that of II.

The method of preparation of $Mo_2Br_4(dppe)_2$ and the resemblance of its infrared spectrum in the region above 400 cm^{-1} to that of β-$Mo_2Cl_4(dppe)_2$ and between 400 and 200 cm^{-1} to that of $Mo_2Br_4(dppm)_2$ (ν(Mo–Br) at 270 cm^{-1}) all suggest that it is dimeric and contains bridging dppe ligands. The profile of its electronic absorption spectrum shows a close similarity to the spectrum of β-$Mo_2Cl_4(dppe)_2$.

It is tempting to conclude that for reactions of $K_4Mo_2Cl_8$ with dppe, the kinetically favored product is the one which contains a chelated ligand; hence it forms rapidly and exclusively in methanol. The differing solubilities of both reactants in ethanol could then result in a less rapid formation of the α isomer and also give rise to the thermodynamically more stable β isomer containing the bridging ligands. However, since the reaction of $K_4Mo_2Cl_8$ with arphos in both methanol and ethanol produces only that form of $Mo_2Cl_4(arphos)_2$ which is isostructural with β-$Mo_2Cl_4(dppe)_2$, it is clear that the mechanisms of these substitution reactions are not yet well understood and are deserving of a separate, detailed investigation.

A final point which should be made with regard to the unusual staggered structure, which is adopted by β-$Mo_2Cl_4(dppe)_2$, $Mo_2Br_4(dppe)_2$, $Mo_2Cl_4(arphos)_2$, $Mo_2Cl_4(dpae)_2$, $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(arphos)_2$, concerns differences in the electronic structures of these species. Like $Mo_2Cl_4(PR_3)_4$ and $Re_2Cl_4(PR_3)_4$, which possesses similar molecular structures but different electronic structures, the number of electrons available for metal–metal bonding within the dimers $M_2X_4(LL)_2$ are different for Mo_2^{4+} and Re_2^{4+}. In the complexes with monodentate phosphines, $M_2Cl_4(PR_3)_4$, the ground-state electronic configurations may be written $\sigma^2\pi^4\delta^2$ (for Mo) and $\sigma^2\pi^4\delta^2\delta^{*2}$ (for Re).[21] In spite of the population of the δ^* orbital of $Re_2Cl_4(PR_3)_4$ this does not result in the loss of an eclipsed configuration since this may still be favored over the staggered arrangement in these sterically crowded molecules.[22] Thus, in the formation of $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(arphos)_2$, the change to a staggered configuration does not involve any net change in metal–metal bond order since the δ bond will already have been lost upon addition of two electrons to the δ^* orbital.[23] In contrast to this situation, we note that for those molybdenum(II) dimers which are structural analogues of $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(arphos)_2$ the δ bond has been abolished (or at least drastically weakened) not as a result of oxidation or reduction of the Mo_2^{4+} moiety but because this particular bridging mode of dppe and arphos forces the two $[MoCl_2L_2]$ units to twist with respect to one another. If our conclusions are correct, then this is the first instance where a metal–metal quadruple bond ($\sigma^2\pi^4\delta^2$) has been modified to a triple bond ($\sigma^2\pi^4$) without an accompanying change in the metal oxidation state.

(c) *o*-Phenylenebis(dimethylarsine). This ligand is structurally different from the others considered thus far. Although the conformational variations of the ethane derivatives are now absent, nonetheless, like dppm, diars can bond in both chelating and bridging fashions.[24] Its reaction with $K_4Mo_2Cl_8$ in methanol is quite rapid, the resulting green product $[MoCl_2(diars)]_n$ being diamagnetic. The low-frequency infrared spectrum of this complex (Table I) exhibits as its most intense feature a band at 310 cm^{-1}. Such a feature is indicative of a *cis*-$MoCl_2L_2$ geometry and therefore the likely presence of chelating bidentate ligands.[12] Further support for this suggestion comes from the observation that the lowest energy band in the electronic absorption spectrum of this complex is at a similar frequency (650 nm) to that encountered in the spectra of the structurally related species α-$Mo_2Cl_4(dppe)_2$ and $Mo_2Cl_4(dmpe)_2$—675 and 666 nm, respectively.

Upon reacting $(Bu_4N)_2Re_2Cl_8$ with diars in ethanol, reduction occurs to afford the rhenium(II) complex $[ReCl_2$-

(diars)]$_n$. Its visible spectrum (Table I) shows a strong resemblance to that of $Re_2Cl_4(dppm)_2$.[3] Absorption bands at 630 (sh) and 480 nm in the spectrum of $[ReCl_2(diars)]_n$ correspond to those at 610 (sh) and 500 nm in the related Nujol mull spectrum of the dppm complex. Also, like $Re_2Cl_4(dppm)_2$ there is the appearance of a low-energy band in the region between 1300 and 1500 nm which is due to partial oxidation of the solid complex by O_2, thereby leading to the formation of $[Re_2Cl_4(diars)_2]^+$ or some electronically related species. In the case of $Re_2Cl_4(dppm)_2$, oxidation of the solid complex is extremely slow, and the growth of a band in this region only becomes apparent upon exposing solutions of this complex to oxygen for several hours.[3] In contrast to this, complexes of the type $Re_2Cl_4(PR_3)_4$ are oxidized to $[Re_2Cl_4(PR_3)_4]^+$, $Re_2Cl_5(PR_3)_3$, or some structurally related species very rapidly.[4,25] These observations suggest that $[ReCl_2(diars)]_n$ is correctly formulated as $Re_2Cl_4(diars)_2$ and bears a close structural relationship to $Re_2Cl_4(dppm)_2$ and $Re_2Cl_4(PR_3)_4$.

The low-frequency infrared spectrum of this complex is quite unlike that of $Mo_2Cl_4(diars)_2$, but its complexity precluded a definitive assignment of the ν(Re–Cl) modes. The x-ray powder patterns of $Mo_2Cl_4(diars)_2$ and $Re_2Cl_4(diars)_2$ are also quite different.[18] A structure containing bridging diars ligands seems most likely.

(d) X-Ray Photoelectron Spectra. This technique is potentially very helpful in the characterization of complexes of the type described in the present report. It has previously been shown[26,27] that the Mo 3d binding energies of complexes of the type $MoCl_4L_2$, $Mo_2Cl_9^{3-}$, $MoCl_6^{3-}$, $MoCl_3L_3$, $Mo_2Cl_8^{4-}$, and $Mo_2Cl_4L_4$, where L represents a neutral donor molecule such as a phosphine or amine, follow the sequence Mo(IV) > Mo(III) > Mo(II). XPS data for the new molybdenum complexes prepared in the present study, together with binding energy data for other relevant molybdenum(II) complexes are presented in Table II. The similarity of the Mo $3d_{3/2,5/2}$ binding energies of the complexes with dppm, dppe, and arphos to those of other structurally related molybdenum(II) dimers containing strong metal–metal bonds is strong support for our structural conclusions concerning these new complexes. Furthermore, the absence of higher oxidation state molybdenum-containing contaminants (including MoO^{3+} and MoO_2^{2+}) is clearly demonstrated by the absence of higher energy Mo $3d_{3/2,5/2}$ doublets which are characteristic of such species.[26,27]

The Cl 2p and Br 3p spectra of the phosphine complexes listed in Table II exhibited well-resolved $np_{1/2,3/2}$ spin–orbit doublets, features which are consistent with the presence of terminal metal–halogen bonds and the absence of metal–halogen bridging units.[28,29]

Acknowledgment. We thank the National Science Foundation (Grant CHE74-12788A02) for generous support of this work. Discussions with Professors F. A. Cotton and J. G. Norman, Jr., are gratefully acknowledged.

Registry No. $Mo_2Cl_4(dppm)_2$, 64508-35-6; $Mo_2Br_4(dppm)_2$, 64508-34-5; α-$Mo_2Cl_4(dppe)_2$, 64490-77-3; β-$Mo_2Cl_4(dppe)_2$, 64508-32-3; $Mo_2Br_4(dppe)_2$, 64508-29-8; $Mo_2Cl_4(arphos)_2$, 64508-31-2; $Mo_2Cl_4(dpae)_2$, 64521-03-5; $Mo_2Cl_4(diars)_2$, 64508-30-1; $Re_2Cl_4(diars)_2$, 64508-40-3; $K_4Mo_2Cl_8$, 25448-39-9; $(NH_4)_5Mo_2Cl_9$, 61583-95-7; $Mo_2Cl_4py_4$, 51752-03-5; $Mo_2Cl_4(PEt_3)_4$, 59780-36-8; $Mo_2Br_4(PEt_3)_4$, 59752-94-2; $Mo_2Cl_4(PBu_3)_4$, 38832-72-3; $(Bu_4N)_2Re_2Cl_8$, 14023-10-0; $[(C_2H_5)_4N]_3Mo_2Cl_9$, 25078-39-1.

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