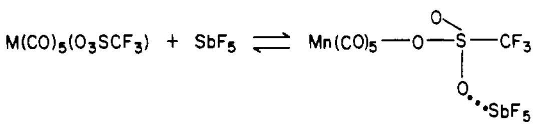
dissociation from $Re(CO)_5(O_3SCF_3)$, since the Re-triflate separation must be greater than in the Mn complex. Differing crystal field activation energy barriers[32] may [Re(I) is expected to show larger splittings than Mn(I)] account for the difference.

The enhanced kinetic lability in superacid solvents as well as the shifts in spectroscopic parameters suggest that the metal-triflate bond is seriously weakened in acidic solvent systems. For the case of CF_3SO_3H/SbF_5 the equilibria of eq 15 and/or 16 may

$$M(CO)_5(O_3SCF_3) + SbF_5 \rightleftharpoons M(CO)_5^+ + CF_3SO_3{\cdot}SbF_5^- \tag{15}$$



$$M(CO)_5(O_3SCF_3) + SbF_5 \rightleftharpoons Mn(CO)_5{-}O{-}S(O)(O{\cdots}SbF_5){-}CF_3 \tag{16}$$

be important. Either type of complexation would lead to labilization of the triflate complex. The surprising finding on addition of $[PPN][O_3SCF_3]$ (in place of SbF_5) to CF_3SO_3H implies that a cation, $[PPN]^+$, may aid in the dissociation of bound $O_3SCF_3^-$. Because of the poor nucleophilicity of CO it is likely that the enhanced rate of reaction between $M(CO)_5(O_3SCF_3)$ and carbon monoxide in superacid solvents results from increased triflate dissociation. The premise[88] that one can stabilize coordinatively unsaturated complexes (or molecules that behave as such) in highly acidic media seems justified.

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Reactions of Chloro Complexes of Dimolybdenum(II) Containing Quadruple Metal-Metal Bonds with Bidentate Tertiary Phosphines $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ (n = 1-3) and $(C_6H_5)_2P(CH_2)_2As(C_6H_5)_2$ in Alcohol Media. Effect of Ligand Hydrocarbon Chain Length and Solvent on Product Formation and Isomerization

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The reactions of $K_4Mo_2Cl_8$ with the bidentate tertiary phosphines bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1-(diphenylphosphino)-2-(diphenylarsino)ethane (arphos), and 1,3-bis(diphenylphosphino)propane (dppp) in methanol, ethanol, and 1-propanol produce complexes of the type $Mo_2Cl_4(LL)_2$. The reactions of $Mo_2Cl_4(py)_4$ and $Mo_2Cl_4(P(n\text{-}Pr)_3)_4$ with dppe and dppp have also been explored. The only form of $Mo_2Cl_4(dppm)_2$ isolated from the three alcoholic solvents is the species known to have a bridging dppm structure. In refluxing methanol both $Mo_2Cl_8^{4-}$ and $Mo_2Cl_4(py)_4$ yield α-$Mo_2Cl_4(LL)_2$ complexes (LL = dppe, dppp), whose spectral properties are consistent with structures containing chelating phosphine ligands. In 1-propanol these reactants lead to β-$Mo_2Cl_4(LL)_2$ complexes (LL = dppe, dppp), which are believed to exhibit structures with a trans disposition of donor atoms in the $MoCl_2P_2$ moiety and with the phosphine bridging the Mo_2 unit. Reaction in ethanol gives rise to mixtures. Under refluxing conditions only β-$Mo_2Cl_4(arphos)_2$ is produced in pure or nearly pure form from $K_4Mo_2Cl_8$ and arphos, whereas in methanol at lower temperatures mixtures of α and β isomers result from reaction with $(NH_4)_5[Mo_2Cl_8]Cl{\cdot}H_2O$. The chelating isomers are converted to the bridging forms on reflux in 1-propanol or prolonged reflux in methanol (arphos, dppp). These results indicate a thermodynamic stabilization of the β-$Mo_2Cl_4(LL)_2$ species in the higher alcohols while the α isomers are the kinetically favored products in methanol. Although the reaction of $Mo_2Cl_4(P(n\text{-}Pr)_3)_4$ and dppe in methanol yields a mixture of α- and β-$Mo_2Cl_4(dppe)_2$, the reaction with dppp produces $Mo_2Cl_4(P(n\text{-}Pr)_3)_2(dppp)$, whose spectral properties are similar to those of the known $Mo_2Cl_4(PR_3)_4$ species.

Introduction

Hundreds of complexes containing quadruple bonds between transition-metal atoms are known, and the essential features of this multiple-bonding type are now well established.[1] In recent years there has been considerable interest in understanding geometric factors affecting the δ component of such bonds.[2] Although maximum overlap in the δ bond is achieved in an M_2L_8 framework when the donor atoms are in an eclipsed configuration, several examples exist of crystallographically characterized species in which substantial movement toward a staggered array of pendant atoms occurs.[3-5] In an earlier study we prepared a number of tetrahalodimolybdenum(II) complexes containing bidentate tertiary phosphines and arsines.[6] On the basis of interpretation of spectroscopic and other physical measurements, we proposed structures for certain of these $Mo_2X_4(LL)_2$ compounds (X = Cl, Br) in which bridging of two molybdenum atoms by the organic ligands is accompanied by such staggering of ligand atoms about the Mo-Mo axis.

An intriguing observation resulting from our investigation was the isolation of two isomers of $Mo_2Cl_4(dppe)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) depending upon reaction conditions. One of these was assigned a molecular structure in which each dppe binds to a molybdenum atom in a chelating mode while in the other dppe appeared to bridge the Mo_2 moiety. In an effort to further examine the effect of the length of the hydrocarbon chain of these organic ligands and solvent on isomer formation of $Mo_2Cl_4(LL)_2$ complexes, we recently explored the reactions of chloro complexes of Mo^{II}_2 with the bidentate ligands $Ph_2P(CH_2)_nPPh_2$ (n = 1-3) and $Ph_2P(CH_2)_2AsPh_2$. The results reported here indicate that the occurrence of structural isomers is a common feature among $Mo_2Cl_4(LL)_2$ systems.

While this study was in progress, Professor Malcolm Chisholm informed us of the results of a similar investigation in his laboratory.

Experimental Section

Starting Materials. $K_4Mo_2Cl_8$ and $(NH_4)_5[Mo_2Cl_8]Cl{\cdot}H_2O$ were prepared by established procedures.[7,8] $Mo_2Cl_4(py)_4$ and $Mo_2Cl_4(P(n\text{-}$

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Pr)$_3$)$_4$ were prepared from $K_4Mo_2Cl_8$ in 1-propanol by following previously reported methods.[9] All organic ligands and $Mo(CO)_6$ were obtained from Strem Chemical Co.

Reaction Procedures. All reactions were performed under a nitrogen atmosphere, and reagent-grade solvents were deoxygenated by purging with nitrogen for 15–30 min prior to use.

(A) Reactions with Bis(diphenylphosphino)methane (dppm). (1) $K_4Mo_2Cl_8$ in Methanol. By the method of Best, Smith, and Walton a dark blue-green material was isolated after a 2-h reflux, washed with deionized water, absolute ethanol, and diethyl ether, and dried under vacuum;[6] yield 84%.

(2) $K_4Mo_2Cl_8$ in Ethanol and 1-Propanol. A similar procedure was followed in these solvents for a reflux period of 1 day to yield dark blue-green powders.

(3) Conversion Reaction of Methanol Product in 1-Propanol. The product of the methanol reaction was refluxed in 1-propanol (15 mL) for 22 h. The suspension was cooled to room temperature, filtered, and washed to obtain a dark blue-green product.

(B) Reactions with 1,2-Bis(diphenylphosphino)ethane (dppe). (1) $K_4Mo_2Cl_8$ in Methanol. As previously reported, a light green powder was obtained form a 3-h reflux followed by cooling, washing with water, ethanol, toluene, and diethyl ether, and drying under vacuum;[6] yield 46%. This species is designated α-$Mo_2Cl_4(dppe)_2$.

(2) $Mo_2Cl_4(py)_4$ in Methanol. A mixture of $Mo_2Cl_4(py)_4$ (0.06 g, 0.09 mmol) and dppe (0.07 g, 0.18 mmol) was refluxed in methanol (20 mL) to give an aqua-colored suspension within 10 min. After 3 h the reaction mixture was cooled, filtered, washed with water, ethanol, and diethyl ether, and dried to yield an aqua-colored powder (0.10 g, 98%). IR spectroscopy revealed that the product was α-$Mo_2Cl_4(dppe)_2$, and the presence of lattice methanol was indicated by two weak bands at 3650 and 3530 cm^{-1} and an enhanced absorption at 1022 cm^{-1}.[10]

(3) $Mo_2Cl_4(P(n\text{-}Pr)_3)_4$ in Methanol. A suspension of $Mo_2Cl_4(P(n\text{-}Pr)_3)_4$ (0.07 g, 0.07 mmol) and dppe (0.12 g, 0.30 mmol) in methanol (15 mL) was refluxed for 4 h. The resulting gray suspension was cooled and filtered, and the solid was washed with water, ethanol, toluene, and diethyl ether and dried, giving a gray powder (0.05 g, 64%).

(4) $K_4Mo_2Cl_8$ in Ethanol. The previously reported procedure was used (4-day reflux) to isolate an olive green powder;[6] yield 72%.

(5) $Mo_2Cl_4(py)_4$ in Ethanol. $Mo_2Cl_4(py)_4$ (0.05 g, 0.08 mmol) and dppe (0.06 g, 0.15 mmol) were refluxed in ethanol (20 mL) to produce a green suspension within 10 min. An olive green solid (0.07 g, 79%) was isolated after 1 h, which was found upon examination under a microscope to contain a small amount of $Mo_2Cl_4(py)_4$.

(6) $K_4Mo_2Cl_8$ in 1-Propanol. When a suspension of $K_4Mo_2Cl_8$ (0.21 g, 0.33 mmol) and dppe (0.25 g, 0.63 mmol) in 1-propanol (25 mL) was heated, a light brown solution developed. After the solution was refluxed for 1 day, a light brown solid had precipitated. This was isolated, rinsed with water, ethanol, and diethyl ether, and dried to yield a light brown powder (0.15 g, 40%). This product will be designated β-$Mo_2Cl_4(dppe)_2$. Anal. Calcd for $C_{26}H_{24}Cl_2MoP_2$: C, 55.25; H, 4.30; Cl, 12.54. Found: C, 54.84; H, 4.24; Cl, 12.98.

(7) $Mo_2Cl_4(py)_4$ in 1-Propanol. $Mo_2Cl_4(py)_4$ (0.06 g, 0.09 mmol) and dppe (0.07 g, 0.18 mmol) in 1-propanol (20 mL) were refluxed for 3 h. The resulting brown suspension was cooled and filtered, and a brown powder (0.10 g, 98%) was recovered after washing with water, ethanol, and diethyl ether and drying. IR spectroscopy indicated that the product was β-$Mo_2Cl_4(dppe)_2$.

(8) $Mo_2Cl_4(P(n\text{-}Pr_3)_4$ in 1-Propanol. An initially blue suspension of $Mo_2Cl_4(P(n\text{-}Pr)_3)_4$ (0.05 g, 0.05 mmol) and dppe (0.10 g, 0.25 mmol) in 1-propanol (15 mL) turned brown within 10 min of refluxing. After 1 h a brown solid was isolated, washed with ethanol and diethyl ether, and dried to yield a brown powder (0.04 g, 71%), which was found to be β-$Mo_2Cl_4(dppe)_2$ by IR spectroscopy.

(9) Isomerization Reactions. α-$Mo_2Cl_4(dppe)_2$ and the gray- and olive-colored dppe materials were all converted to brown products upon 1-day reflux in 1-propanol. The isolated species were shown to be β-$Mo_2Cl_4(dppe)_2$ by their IR spectra.

(C) Reactions with 1-(Diphenylphosphino)-2-(diphenylarsino)ethane (arphos). (1) $K_4Mo_2Cl_8$ in Methanol (Reflux). $K_4Mo_2Cl_8$ (0.10 g, 0.16 mmol) and arphos (0.18 g, 0.41 mmol) in methanol (15 mL) were refluxed for 4 h. The suspension was cooled to room temperature and filtered, and the solid was washed with water, ethanol, toluene, ethanol, and diethyl ether. The product (0.09 g, 49%), a mixture of a brown powder, β-$Mo_2Cl_4(arphos)_2$, and a small amount of a green powder, was dried by vacuum.

(2) $K_4Mo_2Cl_8$ in Methanol (Room Temperature). $K_4Mo_2Cl_8$ (0.10 g, 0.16 mmol) and arphos (0.18 g, 0.41 mmol) in methanol (15 mL) were stirred at room temperature for 1 day. The gray-green product (0.17 g, 87%) was filtered, washed with water, ethanol, and ether, and dried. Anal. Calcd for $C_{26}H_{24}AsCl_2MoP$: C, 51.3; H, 4.0; Cl, 11.6. Found: C, 51.2; H, 4.2; Cl, 11.8.

(3) $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$ in Methanol. $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$ (0.05 g, 0.08 mmol) and arphos (0.07 g, 0.16 mmol) in methanol (15 mL) were stirred for 15 min at −10 °C, resulting in a purple suspension. Additional stirring for 5 min at 0 °C led to a green suspension, which was filtered, and the product was washed with water, methanol, toluene, methanol, and diethyl ether and dried to yield a gray-green powder (0.04 g, 37%.

(4) $K_4Mo_2Cl_8$ in Ethanol. $K_4Mo_2Cl_8$ (0.10 g, 0.16 mmol) and arphos (0.18 g, 0.41 mmol) in ethanol (15 mL) were refluxed under nitrogen for 3 days, giving a magenta suspension. The suspension was cooled to room temperature and filtered, and the product was washed with water, ethanol, toluene, ethanol, and diethyl ether and dried. The product (0.04 g, 21%) was a rust-colored powder. IR spectroscopy revealed that this species was β-$Mo_2Cl_4(arphos)_2$.

(5) $K_4Mo_2Cl_8$ in 1-Propanol. $K_4Mo_2Cl_8$ (0.10 g, 0.16 mmol) and arphos (0.18 g, 0.41 mmol) in 1-propanol (15 mL) were refluxed for 3 days. The system was cooled, and filtered, and the product was washed and dried. The product was a dark brown powder and shown by IR spectroscopy to be β-$Mo_2Cl_4(arphos)_2$.

(6) Isomerization Reactions. Reflux of the gray-green product resulted in complete conversion to β-$Mo_2Cl_4(arphos)_2$ in methanol (3 days) and 1-propanol (40 min).

(D) Reactions with 1,3-Bis(diphenylphosphino)propane (dppp). (1) $K_4Mo_2Cl_8$ in Methanol. Within 15 min of refluxing, a suspension of $K_4Mo_2Cl_8$ (0.20 g, 0.32 mmol) and dppp (0.26 g, 0.63 mmol) in methanol (25 mL) turned green. After 1 h a light green powder (0.28 g, 76%) was isolated, washed with water, ethanol, and diethyl ether, and dried. This product is designated α-$Mo_2Cl_4(dppp)_2$. Anal. Calcd for $C_{27}H_{26}Cl_2MoP_2$: C, 55.98; H, 4.52; Cl, 12.24. Found: C, 56.16; H, 4.86; Cl, 12.82.

(2) $Mo_2Cl_4(py)_4$ in Methanol. By a similar procedure $Mo_2Cl_4(py)_4$ (0.10 g, 0.15 mmol) and dppp (0.12 g, 0.29 mmol) in methanol (20 mL) afforded α-$Mo_2Cl_4(dppp)_2$ (0.16 g, 95%) (by IR spectroscopy) within 10 min.

(3) $Mo_2Cl_4(P(n\text{-}Pr)_3)_4$ in Methanol. $Mo_2Cl_4(P(n\text{-}Pr)_3)_4$ (0.15 g, 0.15 mmol) and dppp (0.40 g, 0.97 mmol) were refluxed in methanol (25 mL). After 1 day a solid was isolated, washed with ethanol and diethyl ether, and dried to give a dark blue powder (0.08 g, 50%). Anal. Calcd for $C_{45}H_{68}Cl_4Mo_2P_4$ ($Mo_2Cl_4(P(n\text{-}Pr)_3)_2(dppp)$): C, 50.67; H, 6.43; Cl, 13.29. Found: C, 51.75; H, 6.48; Cl, 14.42.

(4) $K_4Mo_2Cl_8$ in Ethanol. A brown suspension resulted upon refluxing for 30 min a mixture of $K_4Mo_2Cl_8$ (0.21 g, 0.33 mmol) and dppp (0.27 g, 0.65 mmol) in ethanol (25 mL). After 1 day of reflux this suspension was cooled and filtered and the product was washed with water, ethanol, and diethyl ether and dried. The resulting green solid was revealed by examination under a microscope to be a mixture of a light green powder and dark green crystals. These species were separated by hand and shown by IR spectroscopy to be α- and β-$Mo_2Cl_4(dppp)_2$, respectively.

(5) $Mo_2Cl_4(py)_4$ in Ethanol. $Mo_2Cl_4(py)_4$ (0.05 g, 0.08 mmol) and dppp (0.07 g, 0.17 mmol) were refluxed together in ethanol (15 mL) for 1 day during which time the suspension turned green (within 15 min). The solid was filtered off, washed with ethanol and diethyl ether, and dried, affording a green powder (0.08 g, 88%). The IR spectrum identified this material as α-$Mo_2Cl_4(dppp)_2$. Shorter reaction times invariably result in contamination of the product with $Mo_2Cl_4(py)_4$.

(6) $K_4Mo_2Cl_8$ in 1-Propanol. A mixture of $K_4Mo_2Cl_8$ (0.41 g, 0.65 mmol) and dppp (0.53 g, 1.3 mmol) in 1-propanol (25 mL) was refluxed for 3 days. The resulting dark green suspension was cooled and filtered, and the deep green solid, β-$Mo_2Cl_4(dppp)_2$ (0.23 g, 31%), was washed with water, ethanol, and diethyl ether and dried. Anal. Calcd for $C_{27}H_{26}Cl_2MoP_2$: C, 55.98; H, 4.52; Cl, 12.24. Found: C, 55.06; H, 4.72; Cl, 12.53.

(7) $Mo_2Cl_4(py)_4$ in 1-Propanol. A similar procedure was followed with this reagent (0.10 g, 0.15 mmol). Since the color change occurred within 10 min, the product (0.14 g, 82%) was isolated after only 4 h of refluxing. IR spectroscopy confirmed it as β-$Mo_2Cl_4(dppp)_2$.

(8) Isomerization Reactions. α-$Mo_2Cl_4(dppp)_2$ was refluxed in methanol and 1-propanol for 2.5 days and 6 h, respectively. The products obtained were found to be a mixture of α and β phases for methanol and β only in propanol.

Physical Measurements. Infrared spectra from 4000 to 200 cm^{-1} were recorded as Nujol mulls with a Pye Unicam SP3-300 spectrophotometer. Electronic spectra were obtained also with mulls and with solutions in

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dichloromethane in 1-cm quartz cells on a Perkin-Elmer Model 559 UV–visible spectrophotometer. Magnetic measurements were done with a Cahn Instruments Faraday magnetic susceptibility balance utilizing $HgCo(SCN)_4$ as a calibrant. X-ray diffraction powder patterns were recorded for selected compounds on a General Electric recording diffractometer with a Cu Kα (λ = 1.5405 Å) radiation source at the Purdue University Chemical Engineering Department. Samples were deposited on adhesive tape attached to microscope slides.

Analytical Determinations. Microanalyses were performed by Galbraith Laboratories of Knoxville, TN.

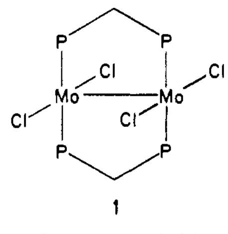
Results and Discussion

We have studied the reactions in alcohol media of $K_4Mo_2Cl_8$ with three bidentate tertiary phosphines and a mixed phosphine–arsine and of $Mo_2Cl_4(py)_4$ and $Mo_2Cl_4(P(n\text{-}Pr)_3)_4$ with two of these ligands. The choice of different molybdenum starting materials arose from our prior observation that reactions of $Mo_2Cl_8^{4-}$ and $Mo_2Cl_4(PR_3)_4$ lead to different products for certain of these ligands.[6] The reactivity of the pyridine complex parallels that of the anionic species nearly exactly, rather than that of the monodentate phosphine complex. The bidentate ligands included bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1-(diphenylphosphino)-2-(diphenylarsino)ethane (arphos), and 1,3-bis(diphenylphosphino)propane (dppp). These reactions have been carried out in methanol, ethanol, and 1-propanol with the solvent clearly determining the product(s) obtained.

The compounds produced in this study along with their infrared and electronic spectra are presented in Table I. These materials are stable toward air and moisture, at least during normal laboratory operations. They are insoluble in most common organic solvents with the exception of dichloromethane; in the latter solvent, the slight solubility enabled our recording of solution electronic spectra. Magnetic measurements were done on all compounds. Although most were found to be diamagnetic, consistent with metal–metal bonding, a few displayed weak paramagnetism. Because detailed studies have not been conducted on complexes of this type, their magnetic properties will not be discussed further.

Because the results for each ligand system differed, the following discussion is organized by treating each phosphine separately except dppe and arphos, which show some similarities.

Bis(diphenylphosphino)methane. In our earlier study we noted that the reaction of dppm with either $K_4Mo_2Cl_8$ in methanol or $Mo_2Cl_4(PEt_3)_4$ in methanol or benzene led to the isolation of $Mo_2Cl_4(dppm)_2$.[6] A structure based upon bridging dppm ligands and eclipsed configuration about the Mo–Mo axis, 1 was proposed.

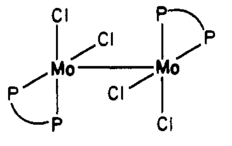


1

Cotton and co-workers also prepared this complex as well as its thiocyanate analogue from $Mo_2Cl_4(P(n\text{-}Bu)_3)_4$ in toluene, and their structure determination revealed that the bridging dppm geometry is correct.[11]

The reaction of $K_4Mo_2Cl_8$ with dppm in any of the three alcohols appears to generate only $Mo_2Cl_4(dppm)_2$ with bridging phosphine. This conclusion is derived from the close similarities of the infrared and electronic spectra of these species. However, there are solid-state spectral differences between the methanol product and those resulting from the other solvents. In particular, the IR spectra for the ethanol and 1-propanol products show new or enhanced splittings of several peaks (1095, 755, 370, 300, and 275 cm^{-1}), and for these products the electronic spectra display a single band (450 nm) intermediate between the two absorptions (442 and 472 nm) for the methanol product while the $\delta \rightarrow \delta^*$ band positions differ by 8 nm. However, the solution electronic spectra are identical for the methanol and ethanol materials. Finally, reflux of the methanol-derived complex in 1-propanol leads to conversion to a material with spectra identical with those of the synthetic products from the higher alcohols. These results suggest that in the latter solvents a different crystalline packing arrangement is produced, which is consistent with the quite distinct X-ray powder patterns exhibited by the methanol and ethanol products.

1,2-Bis(diphenylphosphino)ethane and 1-(Diphenylphosphino)-2-(diphenylarsino)ethane. We have reexamined the dppe and arphos systems and now revise and extend our original interpretation. In the initial report we observed that $K_4Mo_2Cl_8$ and dppe react in methanol to quickly form a green compound, which we formulated as α-$Mo_2Cl_4(dppe)_2$, while $Mo_2Cl_4(PR_3)_4$ (R = Et, *n*-Bu) leads to the gray species then designated β-$Mo_2Cl_4(dppe)_2$.[6] Inspection of the low-frequency infrared and solid-state electronic spectra and the X-ray powder patterns of the olive green materials isolated from the reaction with $K_4Mo_2Cl_8$ in ethanol indicated that this product was mixture of these. We suggested that α-$Mo_2Cl_4(dppe)_2$ possesses the structure 2, in which dppe served as a chelating ligand, that the phosphine bridged both molybdenum atoms in the structure of the β complex 3, and that a staggered configuration resulted from steric constraints imposed by the ethane portion of dppe.



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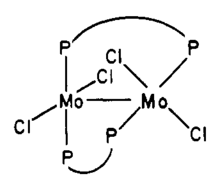

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Two structure determinations are relevant to the discussion of the dppe system. Cotton and co-workers carried out the reaction of $W_2Cl_4(P(n\text{-}Bu)_3)_4$ with dppe in toluene, which afforded two crystalline forms of $W_2Cl_4(dppe)_2$.[4] The green crystals were shown to have a chelated structure analogous to that of 2 with the ligand array effectively eclipsed. The brown materials manifests a structure analogous to that of 3 with bridging dppe and a twist angle of 31.3°.

In our earlier report we noted that reaction of $K_4Mo_2Cl_8$ and arphos in refluxing methanol or ethanol yields a brown material, which was formulated as $Mo_2Cl_4(arphos)_2$ and presumed to have a molecular structure analogous to that of 3.[6] Subsequent confirmation of the latter proposal was obtained from the crystal structure determination of the brown compound $Mo_2Br_4(arphos)_2$, prepared by Walton et al., which does indeed possess a geometry with bridging arphos and staggered configuration.[3] Spectral comparison of the infrared (4000–400 cm^{-1}) and the electronic spectra for these $Mo_2X_4(arphos)_2$ species indicates a close structural relationship.[12]

In the present study the reactions of dppe with either $K_4Mo_2Cl_8$ or $Mo_2Cl_4(py)_4$ in refluxing methanol rapidly yielded the green α-$Mo_2Cl_4(dppe)_2$. Use of the same reactants in ethanol produces more slowly the olive green material originally proposed as a mixture of the α and β phases. However, reaction in 1-propanol with either molybdenum reactant gives a brown product that we now designate as β-$Mo_2Cl_4(dppe)_2$ in pure form. It will be seen that the phosphine-exchange reaction with $Mo_2Cl_4(PR_3)_4$ (R = Et, *n*-Pr, *n*-Bu) in methanol, which results in a gray powder, also produces a mixture of the α and β complexes.

In view of the structural characterization of the green isomer of $W_2Cl_4(dppe)_2$, the original proposal, based on spectra correlations, of a chelating role for dppe in α-$Mo_2Cl_4(dppe)_2$ is thus more firmly established.[6]

That the new brown material and not the gray product is pure β-$Mo_2Cl_4(dppe)_2$ follows from an examination of their low-fre-

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Table I. Spectral Properties of $Mo_2Cl_4(LL)_2$ Complexes[a]

complex(es)	infrared spectra, cm^{-1} [b]	electronic spectra, nm[c]	
		solid state	soln[d]
$Mo_2Cl_4(dppm)_2$/MeOH	345 vs, 285 s	612 s, 472 w, 442 w, 375 sh	634 (2490), 462 (900), 364 sh (2040), 325 (5600)
$Mo_2Cl_4(dppm)_2$/EtOH	370 w, 300 (sh) w, 285 m, 275 (sh) w	620 s, 450 w, 380 sh	634 vs, 460 m, 368 sh, 325 vs
α-$Mo_2Cl_4(dppe)_2$	337 w, 300 m-s, 285 m-s	670 s, 470 w, 400 sh, 380 sh	676 (2460), 468 (460), 388 (1360), 344 (6180)
β-$Mo_2Cl_4(dppe)_2$	338 vs, 300 (sh), w, 287 s	780 s, 560 m, 473 m, 345 vs	762 (1030), 548 (210), 469 (780), 345 (8050)
$Mo_2Cl_8^{4-}$/dppe/EtOH[e]	334 vs, 300 s, 281 vs	776 s, 675 s, 472 m, 385 sh	760 m, 680 m, 542 m, 464 m, 344 vs
$Mo_2Cl_4(PR_3)_4$/dppe[e]	339 m-s, 302 (sh) w, 287 m-s	776 s, 672 s, 554 w, 473 s, 400 sh	754 s, 680 s, 540 w, 470 s
α-, β-$Mo_2Cl_4(arphos)_2$	276 (sh) m, 286 s, 299 s, 340 s	748 s, 672 s, 475 s, 390 vs	720 s, 672 s, 552 w, 476 s
β-$Mo_2Cl_4(arphos)_2$	276 (sh) m, 287 s, 301 m, 341 s	757 s, 552 sh, 478 s	738 (1090), 540 sh (290), 478 (910), 364 sh (2080), 342 (3540)
α-$Mo_2Cl_4(dppp)_2$	305 m-s, 281 m	656 s, 464 m, 398 s	644 (4060), 468 (700), 388 (1640), 350 (7090)
β-$Mo_2Cl_4(dppp)_2$	335 s, 289 s, 280 (sh) w	680 s, 544 vw, 465 m-s, 420 sh, 353 vs	680 (2680), 464 (1240), 420 (460), 355 (4780)
$Mo_2Cl_4(P(n\text{-}Pr)_3)_2(dppp)$	330 s, 280 m	590 vs, 460 w, 405 w-m	590 (2490), 460 (370), 395 (550)
$Mo_2Cl_4(P(n\text{-}Pr)_3)_4$	328 s, 285 m	585 vs, 445 w, 380 vw	

[a] All solid-state spectra recorded as mineral oil mulls. [b] ±2 cm^{-1}. [c] ±2 nm. [d] Molar absorptivities (M^{-1} cm^{-1}) in parentheses. [e] α-, β-$Mo_2Cl_4(dppe)_2$.

quency infrared (enhanced band at 300 cm^{-1} for the gray material, presumably due in part to the α complex) and electronic spectra (two absorption bands both in the solid state and in solution, arising from the $\delta \rightarrow \delta^*$ transition for the α and β species). Moreover, the X-ray powder patterns for both materials are quite similar, with several lines appearing in the brown solid with greater intensities. With the simplification of the spectra of β-$Mo_2Cl_4(dppe)_2$ attending the isolation of pure samples and the structural solution of the brown form of $W_2Cl_4(dppe)_2$, the molecular geometry assignment **3** is strengthened. The highest energy intense band in the Mo–Cl stretching region at 338 cm^{-1} (vs. 300 cm^{-1} for the α phase) supports a *trans*-$MoCl_2$ configuration and is thus in accord with the proposed bridging mode for dppe. Moreover, the pronounced red shift in the position of the $\delta \rightarrow \delta^*$ band for β-$Mo_2Cl_4(dppe)_2$ (λ_{max} 762 nm in dichloromethane solution) relative to that of α form (λ_{max} 676 nm) is in accord with reduced d-orbital overlap in the δ bond accompanying the staggered configuration.

We have isolated the brown compound now designated β-$Mo_2Cl_4(arphos)_2$ as the sole product from refluxing reactions in ethanol and 1-propanol. However, from reactions under reflux in methanol one can also obtain small quantities of a gray-green solid in addition to the brown major product; the former material is generated exclusively in this solvent at room temperature. Because we believed the gray-green powder to be a mixture of isomers analogous to $Mo_2Cl_4(dppe)_2$, we attempted to prepare a pure sample of α-$Mo_2Cl_4(arphos)_2$ by using the ammonium ion salt of $Mo_2Cl_8^{4-}$, which is appreciably more soluble in methanol than is $K_4Mo_2Cl_8$, and by conducting the reaction at low temperature (−10 to 0 °C) for short duration (15 min). These modifications led to a product that was seen by microscopic investigation to be largely the gray-green material but also containing small amounts of a light green species.

β-$Mo_2Cl_4(arphos)_2$ exhibits its most intense low-frequency infrared band at 341 cm^{-1}, consistent with *trans*-$MoCl_2$ stereochemistry, and a lowest energy electronic absorption band (due to a $\delta \rightarrow \delta^*$ transition) at 740 nm (solid state).[13] In the IR spectrum of the gray-green product two bands at 299 and 286 cm^{-1} are considerably enhanced in intensity relative to the 341-cm^{-1} absorption; at least one of these features arises from ν(Mo–Cl) occurring in the *cis*-$MoCl_2$ geometry.[13] Furthermore, in both solid-state and solution electronic spectra two bands attributable to $\delta \rightarrow \delta^*$ are found. These observations are in accord with the presence of two isomers of $Mo_2Cl_4(arphos)_2$, one of which contains chelating arphos (structure analogue of **2**). Examination of the spectra of a carefully separated small sample of the light green material revealed a substantial decrease in intensity of the 341-cm^{-1} IR band and the 740-nm visible band, indicating that this species was relatively pure α-$Mo_2Cl_4(arphos)_2$.

We suggested in the previous study that α-$Mo_2Cl_4(dppe)_2$ is the kinetic-product isomer because it forms quickly in methanol while the slower formation of the gray product (mixture of α and β phases) in this medium implied that the latter is the thermodynamically favored product.[6] We have now converted both of these materials to pure brown β-$Mo_2Cl_4(dppe)_2$ by refluxing them for extended periods in 1-propanol. These results indicate that at least in this solvent the brown β complex is the preferred equilibrium species. We recently isolated the corresponding green and brown forms of $Mo_2Br_4(dppe)_2$ and reported the first-order α-to-β isomerization in dichloromethane ($k = (7.6 \pm 1.1) \times 10^{-5}$ s^{-1} at 22 °C).[14] In contrast, α-$Mo_2Cl_4(dppe)_2$ has shown no such tendency to rearrange in this medium on the time scale of bromide-complex isomerization.

Further support for the identity of the gray-green arphos product as a mixture of isomers follows from reflux reactions in both methanol (3 days) and 1-propanol (40 min), which result in complete conversion to β-$Mo_2Cl_4(arphos)_2$. Moreover, in dichloromethane solution at room temperature (10^{-4} M) the electronic spectral band at 672 nm disappears essentially entirely in about 15 min, leaving a spectrum identical with that of pure β-$Mo_2Cl_4(arphos)_2$. No kinetic studies of this isomerization have been attempted due to our inability to isolate a pure sample of α-$Mo_2Cl_4(arphos)_2$. In any event it seems clear that the β isomer in this system is once again the thermodynamically favored species. The facile rearrangement in dichloromethane and the recovery of essentially only β-$Mo_2Cl_4(arphos)_2$ from refluxing synthetic reations suggest considerably greater lability for this α isomer relative to the α-$Mo_2X_4(dppe)_2$ complexes.

1,3-Bis(diphenylphosphino)propane. This system presents a similar variation in reactivity with molybdenum reactants and solvent as do the dppe and arphos reactions. $K_4Mo_2Cl_8$ and $Mo_2Cl_4(py)_4$ behave roughly the same in each solvent. Either reagent rapidly reacts with dppp in methanol to give a green compound formulated as α-$Mo_2Cl_4(dppp)_2$. In 1-propanol a forest green species, β-$Mo_2Cl_4(dppp)_2$, is produced after prolonged reflux. As with dppe the reaction in ethanol generates a mixture of these isomers. However, both components of this mixture could be separated by hand and easily identified by their infrared and electronic spectra. The exchange reaction utilizing $Mo_2Cl_4(P(n\text{-}Pr)_3)_4$ and carried out in methanol results in only partial displacement of monodentate phosphine, yeilding the deep blue material $Mo_2Cl_4(P(n\text{-}Pr)_3)_2(dppp)$.

α-$Mo_2Cl_4(dppp)_2$ exhibits a low-frequency infrared spectrum with two sharp bands at 281 and 305 cm^{-1} presumably due to

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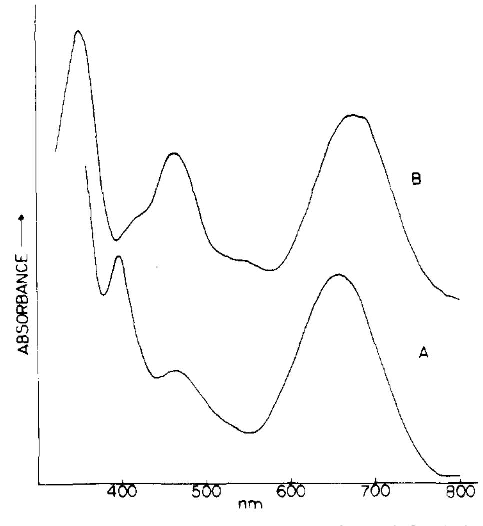
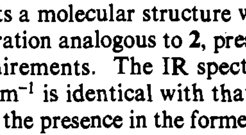


Figure 1. Electronic absorption spectra (solid state) for (A) α-$Mo_2Cl_4(dppp)_2$ and (B) β-$Mo_2Cl_4(dppp)_2$.

ν(Mo–Cl). The observation of two absorptions in these regions is consistent with predictions derived from the C_{2h} chelating structure **2** discussed in connection with α-$Mo_2Cl_4(dppe)_2$. Moreover, the occurrence of these bands in the vicinity of 300 cm^{-1} is in accord with the earlier report by San Filippo et al. on $Mo_2Cl_4(LL)_2$ complexes with potentially chelateing ligands.[13] In a related study we recently reported the preparation and structural characterization of $Re_2Cl_4(dppp)_2$, the product of the reduction of $Re_2Cl_8^{2-}$.[15] Although this species possesses a metal–metal triple bond (Re^{II}_2, $\sigma^2\pi^4\delta^2(\delta^*)^2$) and is thus free of electronic orientational constraints, it exhibits a molecular structure with chelating dppp and eclipsed configuration analogous to **2**, presumably as a result of ligand steric requirements. The IR spectrum of α-$Mo_2Cl_4(dppp)_2$ above 400 cm^{-1} is identical with that of $Re_2Cl_4(dppp)_2$ with the exception of the presence in the former of a weak doublet at 3520 and 3555 cm^{-1} and a moderately intense band at 1025 cm^{-1}, which may be assigned to lattice methanol.[10] This observation provides strong evidence for α-$Mo_2Cl_4(dppp)_2$ being isostructural with the rhenium complex. Additional support for a structural analogy between the α phases incorporating dppe and dppp comes from the quite close qualitative correspondence seen in their electronic spectra. Shifts in band maxima, e.g., 656 nm for the dppp complex and 670 nm for dppe for the intenses band most probably due to the $\delta \rightarrow \delta^*$ transition, likely arise from differences in ligand field splitting for the two phosphines. the solid-state electronic spectra for both α and β phases appear in Figure 1.

The low-frequency infrared spectrum of β-$Mo_2Cl_4(dppp)_2$ is characterized by two strong bands (289 and 335 cm^{-1}) that fall within the ranges expected for structures with a trans orientation of chlorine atoms around each metal atom.[13] The solid-state electronic spectrum for this compound is unlike that of the α isomer and is dissimilar to that of β-$Mo_2Cl_4(dppe)_2$. The most probable structure is one with intramolecular bridging dppp molecules and eclipsed configuration about the Mo–Mo bond, **4**.



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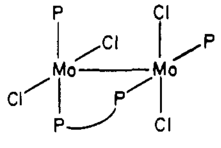
Examination of molecular models reveals that this geometry offers no obvious steric strain with dppp while with the ethane-derived ligands the now amply documented staggering in $M_2X_4(LL)_2$ can be seen to be a consequence of relieving such unfavorable interactions. Furthermore, the relatively close correspondence in the absorption maxima for the $\delta \rightarrow \delta^*$ transition for both α and β phases is consistent with a roughly eclipsed configuration for β-$Mo_2Cl_4(dppp)_2$. Available data do not enable us to dismiss intermolecular bridging modes, which would also be consistent with *trans*-$MoCl_2P_2$ and local D_{2h} symmetry. Yet the solubility of this material in dichloromethane would seem to preclude such a polymeric structure.

Prolonged reflux of α-$Mo_2Cl_4(dppp)_2$ in 1-propanol results in its complete conversion to the β isomer while the α-to-β transformation can be partially effected by extended reflux in methanol, the result being a mixture of these species. Hence, it appears that, analogous to the dppe system, the isomer with chelating dppp is rapidly produced by a favorable mechanistic route in methanol. The conversions in both alcoholic solvents indicate that β-$Mo_2Cl_4(dppp)_2$ is the thermodynamically preferred complex.

Contrary to our expectations based on the behavior of $Mo_2Cl_4(PR_3)_4$ toward dppm and dppe, the only product obtained from the reaction of $Mo_2Cl_4(P(n\text{-}Pr)_3)_4$ and dppp in methanol is $Mo_2Cl_4(P(n\text{-}Pr)_3)_2(dppp)$. With regard to the structural characterization of this material, the infrared spectrum shows two sharp ν(Mo–Cl) bands at 280 and 330 cm^{-1} indicative of a *trans*-$MoCl_2P_2$ geometry.[13] The electronic spectrum of this complex is very similar to that of its precursor, $Mo_2Cl_4(P(n\text{-}Pr)_3)_4$. These spectral results suggest the structure **5** with bridging dppp, which



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is based on that displayed by the crystallographically characterized $Mo_2Cl_4(PMe_3)_4$.[16] Examination of molecular models indicates that the bidentate phosphine is able to span the Mo_2 unit in the manner depicted although some strain is evident when the donor atoms are forced into a rigorously eclipsed orientation. Presumably some deviation from an eclipsed array would relieve this strain and still cause the propyl groups of the PPr_3 ligands to avoid one another. Again one must consider intermolecular bridging geometries although the limited solubility of this complex in dichloromethane makes such a polymeric linkage unattractive.

Conclusion

The results of this study in conjunction with our observations on $Mo_2Br_4(LL)_2$ complexes clearly indicate that chelating vs. bridging isomerism is a common feature of $Mo_2X_4(LL)_2$ species when LL is a bidentate tertiary phosphine or arsine. Moreover, in each case examined thus far the bridging complex appears to be the thermodynamically favored product in alcohol media. The mechanisms of such rearrangements are unclear at present and merit detailed kinetic investigation.

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Registry No. $Mo_2Cl_4(dppm)_2$, 64508-35-6; α-$Mo_2Cl_4(dppe)_2$, 64490-77-3; β-$Mo_2Cl_4(dppe)_2$, 64508-32-3; β-$Mo_2Cl_4(arphos)$, 64508-31-2; α-$Mo_2Cl_4(dppp)_2$, 96306-73-9; β-$Mo_2Cl_4(dppp)_2$, 96306-74-0; $Mo_2Cl_4(P(n\text{-}Pr)_3)_2(dppp)$, 96306-75-1; α-$Mo_2Cl_4(arphos)$, 96306-76-2; $K_4Mo_2Cl_8$, 25448-39-9; $Mo_2Cl_4(py)_4$, 51752-03-5; $Mo_2Cl_4(P(n\text{-}Pr)_3)_4$, 39043-51-1; $(NH_4)_5Mo_2Cl_9$, 61583-95-7.

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