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Dimolybdenum(II) Complexes That Contain the Ligand *cis*-$Ph_2PCH{=}CHPPh_2$ (dppee). Synthesis and Characterization of the α- and β-Isomers of $Mo_2X_4(dppee)_2$ (X = Cl, Br)

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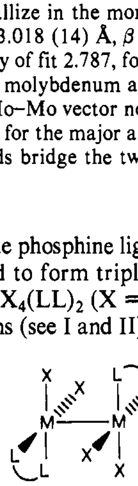
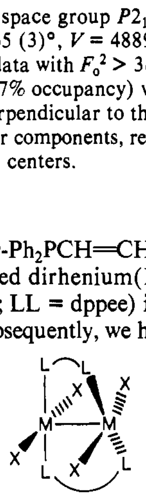
The α- and β-isomers of $Mo_2X_4(dppee)_2$ (X = Cl, Br, I; dppee = *cis*-$Ph_2PCH{=}CHPPh_2$) have been synthesized by utilizing several synthetic strategies: the reactions of salts of $[Mo_2X_8]^{4-}$ (X = Cl, Br) with dppee in alcohol solvents, the reactions of $Mo_2Cl_4(PR_3)_4$ (PR_3 = $PMePh_2$, PEt_2Ph) with dppee in acetone, or the reactions of $Mo_2(O_2CCH_3)_4$ with dppee and Me_3SiX (X = Cl, Br, I) in a variety of solvents. The kinetic products α-$Mo_2X_4(dppee)_2$, which are formed under mild (room-temperature) conditions, isomerize to the more thermodynamically stable β-isomers at elevated temperatures. Differences in the electrochemical (cyclic voltammetric) properties and electronic absorption spectra of the α- and β-isomers have been examined. The α-isomers possess an eclipsed rotational geometry and chelating phosphine ligands, while for the β-isomers the rotational geometry is staggered and the phosphine ligands bridge the dimolybdenum unit. The X-ray crystal structure of β-$Mo_2Cl_4(dppee)_2$ has been determined. Crystals of β-$Mo_2Cl_4(dppee)_2$, which were obtained directly from the reaction of $Mo_2(O_2CCH_3)_4$ with dppee in the presence of Me_3SiCl, crystallize in the monoclinic space group $P2_1/n$ with the following unit cell dimensions: a = 16.911 (4) Å, b = 13.110 (5) Å, c = 23.018 (14) Å, β = 106.65 (3)°, V = 4889 (7) Å^3, and Z = 4. The structure was refined to R = 0.0796 (R_w = 0.0886), with quality of fit 2.787, for 4784 data with $F_o^2 > 3\sigma(F_o^2)$. Refinement of the structure was complicated by a disorder in which a second set of molybdenum atoms (17% occupancy) was found, centered at the same point as the principal pair (83% occupancy), with the Mo–Mo vector nearly perpendicular to that of the primary Mo_2 unit. The Mo–Mo distances refined to 2.163 (2) and 2.142 (7) Å for the major and minor components, respectively. The molecules possess an overall staggered geometry in which the dppee ligands bridge the two metal centers.

Introduction

The bidentate phosphine ligand *cis*-$Ph_2PCH{=}CHPPh_2$ (dppee) has been found to form triply bonded dirhenium(II) complexes of the type $Re_2X_4(LL)_2$ (X = Cl, Br; LL = dppee) in both α- and β-isomeric forms (see I and II).[2] Subsequently, we have succeeded in determining the crystal structures of α- and β-$Re_2Cl_4(dppee)_2$,[3] the first time that such isomers of dirhenium(II) have been structurally characterized. In order to investigate further how the presence of a "rigid" –CH=CH– backbone in dppee, as compared to the more flexible backbone in the $Ph_2PCH_2CH_2PPh_2$ ligand (abbreviated dppe), might affect the chemistry of complexes of types I and II (vide supra), we have examined the chemistry of their related quadruply bonded dimolybdenum(II) analogues α- and β-$Mo_2X_4(dppee)_2$.



I (α)



II (β)

Experimental Section

Starting Materials. Samples of the complexes $Mo_2(O_2CCH_3)_4$,[4] $K_4Mo_2Cl_8$,[5] $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$,[6] $Mo_2Cl_4(PMePh_2)_4$,[7] $Mo_2Cl_4(PEt_2Ph)_4$,[7] and $(NH_4)_4Mo_2Br_8$[8] were obtained by using procedures similar to those described in the literature. The ligand *cis*-$Ph_2PCH{=}CHPPh_2$ was purchased from the Pressure Chemical Co., and Me_3SiX (X = Cl, Br, I) was obtained from the Aldrich Chemical Co. Solvents used in the preparation of the complexes were of commercial grade and were thoroughly deoxygenated prior to use.

Reaction Procedures. All reactions were performed in a nitrogen atmosphere by using standard vacuum line techniques. Chromatographic separations were performed on a silica gel column (60–200 mesh, Davidson Grade 62).

A. Preparation of α-$Mo_2Cl_4(dppee)_2$. (i) Reaction of $K_4Mo_2Cl_8$ with dppee in Methanol. A mixture of $K_4Mo_2Cl_8$ (0.07 g, 0.11 mmol), dppee (0.12 g, 0.303 mmol), and methanol (10 mL) was stirred at room temperature for 4 h. A green solid was filtered off, washed with water, methanol, hexanes, dichloromethane, and diethyl ether, and then dried; yield 0.048 g (58%). The product was found to be the monohydrate. Anal. Calcd for $C_{52}H_{46}Cl_4Mo_2OP_4$: C, 54.57; H, 4.05; Cl, 12.39. Found: C, 54.25; H, 3.87; Cl, 11.88. The presence of H_2O was confirmed by IR spectroscopy (Nujol mull), which showed ν(OH) at 3400 cm^{-1}.

When the reaction mixture was refluxed for 1 h, or the reaction carried out at room temperature for 1 day, a mixture of α- and β-$Mo_2Cl_4(dppee)_2$ was isolated. The components (present in approximately equal proportions) could be separated by extracting the β-isomer into acetone.

(ii) Reaction of $K_4Mo_2Cl_8$ with dppee in Ethanol. A mixture of $K_4Mo_2Cl_8$ (0.07 g, 0.11 mmol), dppee (0.12 g, 0.303 mmol), and ethanol (10 mL) was refluxed for 2.5 days. The reaction mixture was cooled to room temperature. A green-brown solid (0.12 g) was filtered off, washed with water, benzene, toluene, hexanes, and diethyl ether, and then dried. This material was identified as a mixture of α- and β-$Mo_2Cl_4(dppee)_2$ from its electrochemical properties. The product was washed with acetone and dichloromethane to leave a dark green solid, which was washed with diethyl ether and dried; yield 0.03 g (24%). This product was identified as α-$Mo_2Cl_4(dppee)_2$. The combined acetone and dichloromethane washings were set aside (see preparation B(i)).

(iii) Reaction of $Mo_2(O_2CCH_3)_4$ with dppee and Me_3SiCl in Acetone. A mixture of $Mo_2(O_2CCH_3)_4$ (0.1 g, 0.23 mmol), dppee (0.22 g, 0.56 mmol), and acetone (10 mL) was treated with an excess of Me_3SiCl (0.2 mL), and the resultant mixture was stirred at room temperature for 2 h. The green solid was filtered off, washed with acetone, dichloromethane (until the washings were clear), hexanes, and diethyl ether, and then dried; yield 0.04 g (15%).

B. Preparation of β-$Mo_2Cl_4(dppee)_2$. (i) Reaction of $K_4Mo_2Cl_8$ with dppee in Ethanol. Diethyl ether was added to the washings obtained from preparation A(ii). A brown solid was filtered off and dried. It was purified by chromatography (silica gel column with CH_2Cl_2 as eluent) and recrystallized from CH_2Cl_2/diethyl ether; yield 0.04 g (32%).

(ii) Reaction of $K_4Mo_2Cl_8$ with dppee in 1-Propanol. A mixture of $K_4Mo_2Cl_8$ (0.2 g, 0.316 mmol), dppee (0.50 g, 1.26 mmol), and 1-propanol (10 mL) was refluxed for 2 days. The resulting reaction mixture was cooled to room temperature. A brown-orange solid was filtered off, washed with water, methanol, hexanes, and diethyl ether, and then dried. A cyclic voltammogram of this product indicated that it was a mixture of β-$Mo_2Cl_4(dppee)_2$ and *trans*-$MoCl_2(dppee)_2$. Accordingly, the product was washed with acetone and dichloromethane and the resultant brown extract was treated the same as in preparation B(i) to give β-$Mo_2Cl_4(dppee)_2$ (0.05 g, 14%). Anal. Calcd for $C_{52}H_{46}Cl_4Mo_2OP_4$ (i.e. $Mo_2Cl_4(dppee)_2{\cdot}H_2O$): C, 54.57; H, 4.05. Found: C, 54.61; H, 4.32. Its IR spectrum (Nujol mull) showed ν(OH) at ca. 3350 w cm^{-1}.

The remaining orange solid was shown to be *trans*-$MoCl_2(dppee)_2$ on the basis of its spectroscopic and electrochemical properties; yield 0.1 g (32%). Anal. Calcd for $C_{52}H_{44}Cl_2MoP_4$: C, 65.08; H, 4.62. Found: C, 64.17; H, 4.78.

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(iii) Reaction of $Mo_2Cl_4(PMePh_2)_4$ or $Mo_2Cl_4(PEt_2Ph)_4$ with dppee in Acetone. A mixture of $Mo_2Cl_4(PMePh_2)_4$ (0.045 g, 0.04 mmol), dppee (0.044 g, 0.11 mmol), and acetone (10 mL) was refluxed for 1 h. The reaction mixture was cooled to room temperature. A brown solid was filtered off, washed with acetone, hexanes, and diethyl ether, and then dried; yield 0.03 g (69%).

When $Mo_2Cl_4(PEt_2Ph)_4$ was used in place of $Mo_2Cl_4(PMePh_2)_4$ with a reaction time of 20 h, β-Mo_2Cl_4(dppee)$_2$ was isolated in 63% yield.

(iv) Reaction of $Mo_2(O_2CCH_3)_4$ with dppee in the Presence of Me_3SiCl. A mixture of $Mo_2(O_2CCH_3)_4$ (0.05 g, 0.117 mmol), dppee (0.12 g, 0.303 mmol), THF (10 mL), and an excess of Me_3SiCl (0.35 mL) was stirred at room temperature for 20 h. The brown solid was filtered off, washed with THF, methanol, hexanes, and diethyl ether, and then dried; yield 0.125 g (95%).

When dichloromethane was used as a solvent with a reflux period of 2 days, β-Mo_2Cl_4(dppee)$_2$ was isolated in 68% yield.

C. Preparation of α-Mo_2Br_4(dppee)$_2$. (i) Reaction of $(NH_4)_4Mo_2Br_8$ with dppee in Methanol. A mixture of $(NH_4)_4Mo_2Br_8$ (0.20 g, 0.221 mmol), dppee (0.22 g, 0.555 mmol), and methanol (10 mL) was stirred at room temperature for 5 min. The green solid was filtered off, washed with water, methanol, hexanes, dichloromethane, and diethyl ether, and then dried; yield 0.09 g (31%).

When the reaction was carried out at room temperature for 15 min or 1 h, a mixture of α- and β-Mo_2Br_4(dppee)$_2$ was isolated.

(ii) Reaction of $Mo_2(O_2CCH_3)_4$ with dppee and Me_3SiBr. A mixture of $Mo_2(O_2CCH_3)_4$ (0.03 g, 0.070 mmol), dppee (0.07 g, 0.176 mmol), and dichloromethane (10 mL) was cooled to 0 °C, and an excess of Me_3SiBr (0.14 mL) was added. The reaction was stirred for 10 min. The green solid was filtered off, washed with dichloromethane, THF, hexanes, and diethyl ether, and then dried; yield 0.045 g (49%). Anal. Calcd for $C_{52}H_{44}Br_4Mo_2P_4$: C, 47.89; H, 3.40. Found: C, 47.23; H, 3.50.

D. Preparation of β-Mo_2Br_4(dppee)$_2$. (i) Reaction of $(NH_4)_4Mo_2Br_8$ with dppee in 1-Propanol. A mixture of $(NH_4)_4Mo_2Br_8$ (0.05 g, 0.055 mmol), dppee (0.07 g, 0.17 mmol), and 1-propanol (10 mL) was refluxed for 17 h and the reaction mixture then allowed to cool to room temperature. The resulting purple solid was filtered off, washed with THF, hexanes, and diethyl ether, and then dried; yield 0.055 g (76%). Anal. Calcd for $C_{52}H_{44}Br_4Mo_2P_4$: C, 47.89; H, 3.40. Found: C, 47.66; H, 3.47.

When the reaction mixture was carried out in refluxing 1-propanol for 4 days, a mixture of β-Mo_2Br_4(dppee)$_2$ and *trans*-$MoBr_2$(dppee)$_2$ was isolated.

(ii) Reaction of $Mo_2(O_2CCH_3)_4$ with dppee and Me_3SiBr. A mixture of $Mo_2(O_2CCH_3)_4$ (0.05 g, 0.117 mmol), dppee (0.11 g, 0.278 mmol), and THF (10 mL) was treated with an excess of Me_3SiBr (0.15 mL). The reaction mixture was refluxed for 8 h and cooled to room temperature, and the dark purple solid was filtered off, washed with THF, methanol, hexanes, and diethyl ether, and then dried; yield 0.105 g (69%).

E. Preparation of Mo_2I_4(dppee)$_2$. A mixture of $Mo_2(O_2CCH_3)_4$ (0.03 g, 0.07 mmol), dppee (0.07 g, 0.18 mmol), THF (10 mL), and an excess of Me_3SiI (1 mL) was stirred at room temperature for 5 min. A yellow-green solid was filtered off, washed with THF, hexanes, and diethyl ether, and then dried; yield 0.08 g (76%). Anal. Calcd for $C_{52}H_{44}I_4Mo_2P_4$: C, 41.85; H, 2.97. Found: C, 40.81; H, 3.24. This product is stable as a solid, but its solutions decompose quite quickly in many nonaqueous solvents.

F. Isomerization Reactions. (i) α-Mo_2Cl_4(dppee)$_2$. A small quantity of α-Mo_2Cl_4(dppee)$_2$ (0.03 g, 0.03 mmol) was refluxed in dichloromethane (10 mL) for 2 days. A brown solution was formed. The volume of solvent was reduced to ~2 mL, and diethyl ether was added to precipitate the brown β-isomer. This product was filtered off, washed with carbon tetrachloride, hexanes, and diethyl ether, and then dried; yield 0.026 g (87%). Its identity was confirmed by its spectroscopic and electrochemical properties.

(ii) α-Mo_2Br_4(dppee)$_2$. A quantity of α-Mo_2Br_4(dppee)$_2$ (0.1 g, 0.077 mmol) was refluxed in THF (10 mL) for 3 days and the reaction mixture cooled to room temperature. The purple solid, which was identified as β-Mo_2Br_4(dppee)$_2$ on the basis of its spectroscopic and electrochemical properties, was filtered off, washed with hexanes and diethyl ether, and then dried; yield 0.08 g (80%).

X-ray Crystallography. A crystal of β-Mo_2Cl_4(dppee)$_2$, which had been obtained from preparation B(iv), was mounted on a glass fiber and covered with a thin layer of epoxy cement. Data were taken on a CAD-4 diffractometer, with procedures that have been described previously.[9] The unit cell parameters and Laue group were determined routinely; however, we observed that the diffraction maxima were quite broad, with an ω dispersion of over 1.5° for each of 25 selected reflections. Therefore, we used ω scans during intensity data collection, with a scan range of $(1.8 + 0.35 \tan \theta)°$ for each reflection. The data were reduced by standard algorithms.[10] An azimuthal scan of one reflection with setting angle χ near 90° indicated no need for an absorption correction. Important parameters are listed in Table I.

Table I. Crystallographic Data for β-Mo_2Cl_4(dppee)$_2$

formula	$Mo_2Cl_4P_4C_{52}H_{44}$	fw	1126.51
a, Å	16.911 (4)	space group	$P2_1/n$
b, Å	13.110 (5)	T, °C	22 ± 1
c, Å	23.018 (14)	λ(Mo Kα), Å	0.71073
β, deg	106.65 (3)	ρ_{calcd}, g cm^{-3}	1.530
V, Å^3	4889 (7)	μ(Mo Kα), cm^{-1}	8.85
Z	4	R^a	0.0796
		R_w^b	0.0886

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

The structure was solved by direct methods and developed in a sequence of least-squares refinements and difference Fourier maps. As was the case in the analogous dirhenium compound,[3] the structure of β-Mo_2Cl_4(dppee)$_2$ shows a disorder of the dimetal units. Two pairs of Mo atoms were found, with the Mo–Mo bonds centered at the same point and nearly perpendicular to each other. This is tantamount to essentially the same set of ligand atoms being shared by the two dimetal units, which represent the Δ and Λ conformers of β-Mo_2Cl_4(dppee)$_2$. In the early and middle stages of refinement, the multiplicities of the major and minor components were refined, with their sum fixed at 1.00. For the final refinement, the multiplicites were fixed at the values to which they had converged: 0.83 and 0.17.

One of the dppee ligands showed evidence, in the form of larger-than-expected displacement parameters, that the ligands were not strictly equivalent in the two site-sharing molecules. In order that static as well as dynamic displacement effects be properly represented, we used anisotropic displacement parameters for all atoms. The final refinement was blocked, with each block containing parameters for all of the Mo, Cl, and P atoms and half of the carbon atoms. Thus, the data-to-parameter ratio in each cycle was 13.9. The refinement converged with the residuals given in Table I.

Physical Measurements. IR spectra were recorded as Nujol mulls supported by KBr disks (4000–400 cm^{-1}) and polyethylene disks (400–200 cm^{-1}) with the use of a Perkin-Elmer 1800 or IBM Instruments IR/32 FTIR spectrometer. Electronic absorption spectra were recorded as CH_2Cl_2 solutions or Nujol mulls on an IBM Instruments 9420 (900–200 nm), HP 8451A (820–190 nm), or Cary 17 (2000–900 nm) spectrophotometer. Electrochemical measurements were made on CH_2Cl_2 solutions of the complexes that contained tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. The $E_{p,a}$, $E_{p,c}$, and $E_{1/2}$ $(=(E_{p,a} + E_{p,c})/2)$ values were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions $E_{1/2} = +0.47$ V vs Ag/AgCl for the Cp_2Fe^+/Cp_2Fe couple. Voltammetric experiments were peformed with the use of a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035 X-Y recorder. $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian XL-200 spectrometer operated as 80.98 MHz. An internal deuterium lock and an external reference, 85% H_3PO_4, were used. Positive chemical shifts were measured downfield from H_3PO_4. The ^1H NMR spectra were recorded with a 90-MHz Perkin-Elmer R-32 or a Varian XL-200 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuterated solvent. The X-band ESR spectrum of a frozen dichloromethane solution of $[MoCl_2(dppee)_2]PF_6$ was recorded at −160 °C with the use of a Varian E-109 spectrometer. Conductivity measurements were performed on 1×10^{-3} M acetonitrile solutions by using an Industrial Instruments Inc. Model RC 16B2 conductivity bridge.

Elemental analyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

Results and Discussion

(1) Preparation and Properties of Mo_2X_4(dppee)$_2$ (X = Cl, Br). The reactions of the bidentate phosphine ligand *cis*-$Ph_2PCH{=}CHPPh_2$ (dppee) with salts of the octahalodimolybdate(II) anions $[Mo_2X_8]^{4-}$ (X = Cl, Br) in alcohol solvents afford complexes of the types α-Mo_2X_4(dppee)$_2$, β-Mo_2X_4(dppee)$_2$, and *trans*-MoX_2(dppee)$_2$. The product that is isolated depends upon the

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(10) Crystallographic calculations were done on a MicroVAX II (MicroVMS V4.5), with the program SHELX76 and the commercial package SDP/V V3.0.

Table II. Electrochemical Properties and Electronic Absorption Spectral Data for α- and β-$Mo_2X_4(L\text{-}L)_2$ (X = Cl, Br; L-L = dppee, dppe)

complex	voltammetric potentials[a] $E_{p,a}$	$E_{1/2}$(red)	electronic absorption spectra, nm[b]	ref
α-$Mo_2Cl_4(dppee)_2$	+0.58	−1.18	682 (2800), ~490 br, sh, 430 (670), 342 (5900)	*d*
α-$Mo_2Cl_4(dppe)_2$	+0.61	−1.26	676 (2460), 468 (460), 388 (1360), 344 (6180)	*e*
β-$Mo_2Cl_4(dppee)_2$	+0.75	−1.29	724 (980), −550 sh, 468 (730), −365 sh, 334 (3360)	*d*
β-$Mo_2Cl_4(dppe)_2$	+0.59[c]	−1.37	762 (1030), 548 (210), 469 (780), 345 (8050)	*e*
α-$Mo_2Br_4(dppee)_2$	+0.64	−1.04	696 (4300), 500 w, sh, 386 (5600)	*d*
α-$Mo_2Br_4(dppe)_2$	+0.65	−1.15	687 (2180), 480 (1060), 373 (5330)	*e*
β-$Mo_2Br_4(dppee)_2$	+0.77	−1.07	746 (1070), 630 (390), 492 (1010), 396 (1300), 360 (3320)	*d*
β-$Mo_2Br_4(dppe)_2$	+0.59[c]	−1.07	790 (1960), 636 (780), 477 (1480), 368 (5490)	*e*

[a] In volts vs Ag/AgCl. Recorded on solutions in 0.1 M TBAH–CH_2Cl_2 with use of a Pt-bead electrode. Data obtained at 200 mV s^{-1}. In the case of the reversible couples, the ΔE_p values ($=E_{p,a} - E_{p,c}$) are in the range 90–130 mV. [b] Spectra recorded on CH_2Cl_2 solutions. λ_{max} values are quoted with molar extinction coefficients in parentheses. [c] $E_{1/2}$ value. [d] This work. [e] Electronic absorption spectral data taken from ref 12 or 13. Cyclic voltammetric data recorded in the present study.

reaction conditions and the alcohol used. Reactions in methanol at room temperature with short reaction times give the green complexes α-$Mo_2X_4(dppee)_2$, in which the dppee ligands are chelating to individual metal atoms in the dimetal unit. However, reactions in methanol for an extended time or in refluxing ethanol produce a mixture of α- and β-$Mo_2X_4(dppee)_2$. When these same reactions are carried out in refluxing 1-propanol for a period of 2–4 days, a mixture of β-$Mo_2X_4(dppee)_2$ and *trans*-$MoX_2(dppee)_2$ is formed. However, a short reaction time in the case of X = Br (17 h) gave only β-$Mo_2Br_4(dppee)_2$.

Attempts to develop procedures that would afford exclusively β-$Mo_2X_4(dppee)_2$ led us to examine the reactions of *cis*-dppee with the mixed halo–phosphine complexes $Mo_2X_4(PR_3)_4$ (PR_3 = PEt_2Ph, $PMePh_2$) and with $Mo_2(O_2CCH_3)_4$. While the reactions between $Mo_2Cl_4(PR_3)_4$ and *cis*-dppee in refluxing acetone produced only β-$Mo_2Cl_4(dppee)_2$ (yield >60%), the reactions of $Mo_2(O_2CCH_3)_4$ with *cis*-dppee in the presence of Me_3SiX (X = Cl, Br) are more complicated and can afford either α- or β-$Mo_2X_4(dppee)_2$ depending upon the reaction conditions. Reactions in THF for an extended reaction period give the β-$Mo_2X_4(dppee)_2$ compounds in good yield, while reactions in acetone at room temperature (X = Cl) or CH_2Cl_2 at 0 °C (X = Br) afford the green α-isomers.

The isolation of the α-$Mo_2X_4(dppee)_2$ isomers, under mild reaction condition, accords with previous results, which showed that the α-isomers of the type $Mo_2X_4(L\text{-}L)_2$ (X = Cl, Br; L-L = bidentate phosphine ligands) are the kinetic products.[11] These α-isomers slowly isomerize in solution to form the thermodynamically favored β-isomers.[11-16] These observations have been substantiated here by the conversion of α-$Mo_2X_4(dppee)_2$ species in refluxing CH_2Cl_2 (X = Cl) or THF (X = Br) to their β-isomer analogues.

Table III. Low-frequency IR Spectral Data for α- and β-$Mo_2Cl_4(L\text{-}L)_2$ (L-L = dppee, dppe)[a]

complex	ν(Mo–Cl), cm^{-1}	complex	ν(Mo–Cl), cm^{-1}
α-$Mo_2Cl_4(dppee)_2$	333 vs, *307* s, *293* m–s	β-$Mo_2Cl_4(dppee)_2$	*347* s, *339* s, *295* s
α-$Mo_2Cl_4(dppe)_2$[b]	347 w, *307* s, *290* m–s	β-$Mo_2Cl_4(dppe)_2$[b]	*340* s, *306* sh, *291* sh

[a] Nujol mull spectra. ν(Mo–Cl) modes are given in italics. [b] Data taken from ref 11.

The characterization of α- and β-$Mo_2X_4(dppee)_2$ (X = Cl, Br) was based in part upon a comparison of their electrochemical and spectroscopic properties (Tables II and III) with the related properties of the previously characterized α- and β-$Mo_2X_4(dppe)_2$.[11-13,16,17]

Cyclic voltammograms (CV's) of these complexes in 0.1 M TBAH–CH_2Cl_2 revealed the presence of an irreversible one-electron oxidation and a reversible one-electron reduction (see Table II). These electrochemical properties are similar to those observed for α- and β-$Mo_2X_4(dppe)_2$ (Table II) and other dimolybdenum(II) species that contain the Mo_2^{4+} unit.[18]

The distinction between the α- and β-isomers of $Mo_2X_4(dppee)_2$ and their similarity to α- and β-$Mo_2X_4(dppe)_2$ are very evident from their electronic absorption spectra (Table II). The lowest energy absorption band (corresponding to the $\delta \rightarrow \delta^*$ transition) for β-$Mo_2X_4(dppee)_2$ is located at 722 nm (X = Cl) and 746 nm (X = Br); these absorptions are at significantly lower energies than the lowest energy bands in the spectra of α-$Mo_2X_4(dppee)_2$. A similar trend has been observed for the dppe analogues,[11-15] and is to be expected.[19]

The low-frequency IR spectra of α- and β-$Mo_2Cl_4(dppee)_2$ show ν(Mo–Cl) modes similar to those of α- and β-$Mo_2Cl_4(dppe)_2$ (Table III), thereby substantiating further the close structural relationship between these two sets of complexes.

The ^1H NMR spectra of β-$Mo_2X_4(dppee)_2$ (X = Cl, Br) were recorded on CD_2Cl_2 solutions and show the phenyl protons along with the olefinic protons of the dppee ligands in the region between δ +7.2 and δ +8.4. It was not possible to identify the AA′XX′ pattern that is assigned to the olefinic protons of these complexes because they are obscured by the resonances due to the phenyl protons. The distinction between α- and β-$Mo_2Cl_4(dppee)_2$ isomers is revealed by differences in their $^{31}P\{^1H\}$ NMR spectra. The $^{31}P\{^1H\}$ NMR spectrum of α-$Mo_2Cl_4(dppee)_2$ (recorded in CD_2Cl_2) exhibits a singlet at δ + 35.9, while the β-isomer has a broad singlet at δ +16.8. The upfield shift seen in the spectrum of the latter compound is typical of the greater shielding associated with six-membered rings compared to that of their five-membered analogues.[2,20]

(2) X-ray Structural Results. Suitable crystals of β-$Mo_2Cl_4(dppee)_2$ were obtained for a single-crystal X-ray structure analysis. Two dimolybdenum units sharing essentially the same ligand atoms reside at the same crystallographic site. The major difference between the two is that the metal atoms occupy different sites, with the two metal–metal vectors being essentially orthogonal. In other words, the ligands of the two disordered models occupy nearly the same crystallographic positions. The populations of the metal atom sites were refined as described in the Experimental Section. The populations of major and minor components are 0.83 and 0.17, respectively.

Table IV lists coordinates of all atoms sites, along with equivalent isotropic displacement parameters. Selected bond distances and angles are given in Table V. Figure 1 is an ORTEP

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Table IV. Positional Parameters and Their Estimated Standard Deviations for β-$Mo_2Cl_4(dppee)_2$

atom	*x*	*y*	*z*	B,[a] Å^2
Mo′[b]	0.4702 (3)	0.2014 (4)	0.2425 (3)	2.9 (1)
Mo″[b]	0.5620 (4)	0.2604 (5)	0.3198 (3)	3.5 (2)
Mo(1)[c]	0.48352 (7)	0.19447 (9)	0.30874 (5)	3.12 (3)
Mo(2)[c]	0.53243 (7)	0.28855 (9)	0.24993 (5)	3.29 (3)
Cl(1)	0.4397 (2)	0.0299 (2)	0.2642 (1)	4.30 (9)
Cl(2)	0.4886 (2)	0.2760 (3)	0.4012 (1)	4.64 (9)
Cl(3)	0.4272 (2)	0.3392 (3)	0.1629 (2)	5.09 (9)
Cl(4)	0.6800 (2)	0.3108 (3)	0.2879 (2)	4.80 (9)
P(1)	0.6202 (2)	0.1016 (3)	0.3573 (1)	3.93 (9)
P(2)	0.3384 (2)	0.2703 (3)	0.2743 (2)	4.47 (9)
P(3)	0.5789 (2)	0.1394 (3)	0.1951 (1)	3.88 (9)
P(4)	0.5058 (2)	0.4562 (3)	0.2953 (2)	4.39 (9)
C(1)	0.7107 (9)	0.154 (1)	0.4119 (6)	5.7 (4)
C(2)	0.709 (1)	0.259 (1)	0.4308 (7)	6.3 (5)
C(3)	0.778 (1)	0.293 (2)	0.4743 (8)	8.1 (6)
C(4)	0.842 (1)	0.230 (2)	0.4996 (8)	7.9 (7)
C(5)	0.846 (1)	0.131 (2)	0.4853 (9)	9.7 (8)
C(6)	0.777 (1)	0.093 (1)	0.4381 (8)	8.5 (6)
C(7)	0.5982 (8)	−0.0021 (9)	0.4002 (5)	4.0 (3)
C(8)	0.603 (1)	0.016 (1)	0.4622 (6)	5.8 (4)
C(9)	0.585 (1)	−0.063 (1)	0.4984 (7)	6.9 (5)
C(10)	0.561 (1)	−0.158 (1)	0.4715 (8)	6.6 (5)
C(11)	0.556 (1)	−0.174 (1)	0.4113 (7)	6.1 (5)
C(12)	0.5742 (8)	−0.098 (1)	0.3773 (6)	4.6 (4)
C(13)	0.6627 (7)	0.0325 (9)	0.3049 (5)	3.8 (3)
C(14)	0.2644 (8)	0.247 (1)	0.2006 (6)	4.3 (4)
C(15)	0.2579 (8)	0.158 (1)	0.1740 (7)	5.5 (4)
C(16)	0.201 (1)	0.139 (2)	0.1137 (9)	7.9 (6)
C(17)	0.152 (1)	0.217 (2)	0.0847 (8)	8.1 (6)
C(18)	0.155 (1)	0.311 (2)	0.117 (1)	11.8 (8)
C(19)	0.209 (1)	0.327 (2)	0.1694 (9)	9.4 (6)
C(20)	0.2811 (7)	0.224 (1)	0.3223 (6)	4.7 (4)
C(21)	0.290 (2)	0.128 (2)	0.344 (1)	13 (1)
C(22)	0.229 (2)	0.081 (2)	0.370 (1)	12 (1)
C(23)	0.182 (1)	0.143 (2)	0.393 (1)	11.0 (9)
C(24)	0.192 (3)	0.239 (2)	0.386 (2)	19 (2)
C(25)	0.237 (2)	0.283 (2)	0.354 (2)	17 (2)
C(26)	0.3385 (9)	0.411 (1)	0.2830 (7)	5.9 (4)
C(27)	0.6410 (8)	0.198 (1)	0.1501 (6)	4.5 (4)
C(28)	0.727 (1)	0.194 (1)	0.1719 (7)	5.9 (5)
C(29)	0.768 (1)	0.245 (1)	0.1350 (9)	7.4 (6)
C(30)	0.728 (1)	0.299 (1)	0.0791 (8)	7.0 (6)
C(31)	0.644 (1)	0.297 (1)	0.0657 (6)	6.4 (5)
C(32)	0.5985 (9)	0.249 (1)	0.1000 (6)	5.5 (4)
C(33)	0.5160 (8)	0.052 (1)	0.1358 (6)	4.2 (4)
C(34)	0.4322 (9)	0.065 (1)	0.1187 (6)	6.3 (5)
C(35)	0.385 (1)	−0.001 (1)	0.0717 (8)	7.9 (6)
C(36)	0.421 (1)	−0.073 (1)	0.0451 (7)	6.6 (6)
C(37)	0.506 (1)	−0.080 (1)	0.0641 (7)	6.5 (6)
C(38)	0.556 (1)	−0.017 (4)	0.1091 (7)	5.8 (5)
C(39)	0.6505 (7)	0.051 (1)	0.2438 (6)	4.8 (4)
C(40)	0.5614 (9)	0.5028 (9)	0.3701 (6)	5.1 (4)
C(41)	0.645 (1)	0.511 (1)	0.3834 (6)	5.8 (5)
C(42)	0.689 (1)	0.549 (1)	0.4383 (7)	6.0 (5)
C(43)	0.651 (1)	0.578 (1)	0.4821 (8)	6.9 (5)
C(44)	0.567 (1)	0.568 (1)	0.4689 (7)	6.7 (6)
C(45)	0.5196 (9)	0.531 (1)	0.4151 (6)	5.6 (4)
C(46)	0.527 (1)	0.566 (2)	0.2505 (9)	9.0 (7)
C(47)	0.499 (2)	0.661 (2)	0.259 (1)	15 (1)
C(48)	0.521 (2)	0.744 (2)	0.228 (1)	14 (1)
C(49)	0.565 (4)	0.725 (4)	0.189 (2)	26 (2)
C(50)	0.592 (2)	0.626 (4)	0.176 (2)	23 (2)
C(51)	0.569 (1)	0.540 (2)	0.208 (1)	13 (1)
C(52)	0.3944 (8)	0.473 (1)	0.2923 (6)	5.2 (4)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Site modeled as 0.17 Mo. [c] Site modeled as 0.83 Mo.

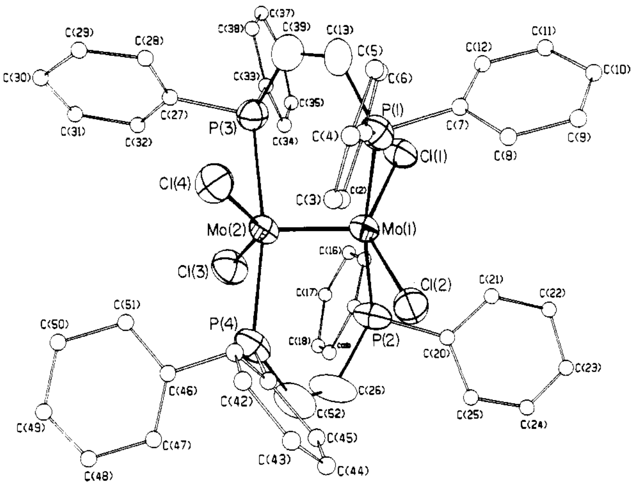

Figure 1. ORTEP drawing of β-$Mo_2Cl_4(dppee)_2$. Coordinates are those of the major component in the crystal structure. Phenyl carbon atoms are shown as circles of arbitrary radius. All other atoms are given as their 50% probability ellipsoids.

Table V. Selected Bond Distances (Å) and Angles (deg) for β-$Mo_2Cl_4(dppee)_2$[a]

	Distances		
Mo′–Mo″	2.142 (7)	P(1)–C(13)	1.815 (13)
Mo(1)–Mo(2)	2.163 (2)	P(2)–C(14)	1.821 (12)
Mo(1)–Cl(1)	2.412 (3)	P(2)–C(20)	1.773 (15)
Mo(1)–Cl(2)	2.360 (4)	P(2)–C(26)	1.859 (14)
Mo(1)–P(1)	2.567 (3)	P(3)–C(27)	1.84 (2)
Mo(1)–P(2)	2.554 (4)	P(3)–C(33)	1.865 (12)
Mo(2)–Cl(3)	2.362 (3)	P(3)–C(39)	1.812 (13)
Mo(2)–Cl(4)	2.413 (3)	P(4)–C(40)	1.814 (13)
Mo(2)–P(3)	2.570 (4)	P(4)–C(46)	1.86 (2)
Mo(2)–P(4)	2.529 (4)	P(4)–C(52)	1.878 (14)
P(1)–C(1)	1.814 14)	C(13)–C(39)	1.38 (2)
P(1)–C(7)	1.780 (13)	C(26)–C(52)	1.22 (2)
	Angles		
Mo(2)–Mo(1)–Cl(1)	111.7 (1)	C(1)–P(1)–C(13)	103.5 (7)
Mo(2)–Mo(1)–Cl(2)	112.6 (1)	C(7)–P(1)–C(13)	99.9 (6)
Mo(2)–Mo(1)–P(1)	94.9 (1)	Mo(1)–P(2)–C(14)	124.5 (5)
Mo(2)–Mo(1)–P(2)	95.1 (1)	Mo(1)–P(2)–C(20)	108.8 (4)
Cl(1)–Mo(1)–Cl(2)	135.7 (1)	Mo(1)–P(2)–C(26)	112.5 (5)
Cl(1)–Mo(1)–P(1)	83.7 (1)	C(14)–P(2)–C(20)	99.8 (6)
Cl(1)–Mo(1)–P(2)	93.7 (1)	C(14)–P(2)–C(26)	104.3 (6)
Cl(2)–Mo(1)–P(1)	91.5 (1)	C(20)–P(2)–C(26)	104.7 (7)
Cl(2)–Mo(1)–P(2)	83.5 (1)	Mo(2)–P(3)–C(27)	105.1 (4)
P(1)–Mo(1)–P(2)	169.9 (1)	Mo(2)–P(3)–C(33)	129.5 (4)
Mo(1)–Mo(2)–Cl(3)	111.1 (1)	Mo(2)–P(3)–C(39)	115.3 (5)
Mo(1)–Mo(2)–Cl(4)	112.5 (1)	C(27)–P(3)–C(33)	98.3 (6)
Mo(1)–Mo(2)–P(3)	95.7 (1)	C(27)–P(3)–C(39)	103.2 (6)
Mo(1)–Mo(2)–P(4)	95.3 (1)	C(33)–P(3)–C(39)	101.5 (6)
Cl(3)–Mo(2)–Cl(4)	136.3 (1)	Mo(2)–P(4)–C(40)	125.4 (4)
Cl(3)–Mo(2)–P(3)	93.4 (1)	Mo(2)–P(4)–C(46)	110.8 (7)
Cl(3)–Mo(2)–P(4)	85.8 (1)	Mo(2)–P(4)–C(52)	112.4 (4)
Cl(4)–Mo(2)–P(3)	80.8 (1)	C(40)–P(4)–C(46)	97.8 (7)
Cl(4)–Mo(2)–P(4)	91.9 (1)	C(40)–P(4)–C(52)	103.7 (7)
P(3)–Mo(2)–P(4)	168.6 (1)	C(46)–P(4)–C(52)	103.9 (8)
Mo(1)–P(1)–C(1)	126.7 (5)	P(1)–C(13)–C(39)	128 (1)
Mo(1)–P(1)–C(7)	107.4 (4)	P(2)–C(26)–C(52)	131 (1)
Mo(1)–P(1)–C(13)	115.2 (3)	P(3)–C(39)–C(13)	128 (1)
C(1)–P(1)–C(7)	100.0 (6)	P(4)–C(52)–C(26)	131 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

plot of the major molecule, with the atom-labeling scheme indicated.

The major and minor molecules at a given crystallographic site are conformational enantiomers. The torsional angles about the metal–metal bond in the minor component are similar in magnitude and opposite in sign to those in the major molecule. Figure 2 shows views along the metal–metal bonds for the two components. Although the populations of the two conformers at a given site are not equal, the crystal is racemic because the space group requires equal numbers of asymmetric units with opposite handedness.

The general arrangement of the structure of β-$Mo_2Cl_4(dppee)_2$ is thus identical with that reported[3] for the analogous β-$Re_2Cl_4(dppee)_2$. (The crystallographic unit cells are also nearly identical for the two cases.)

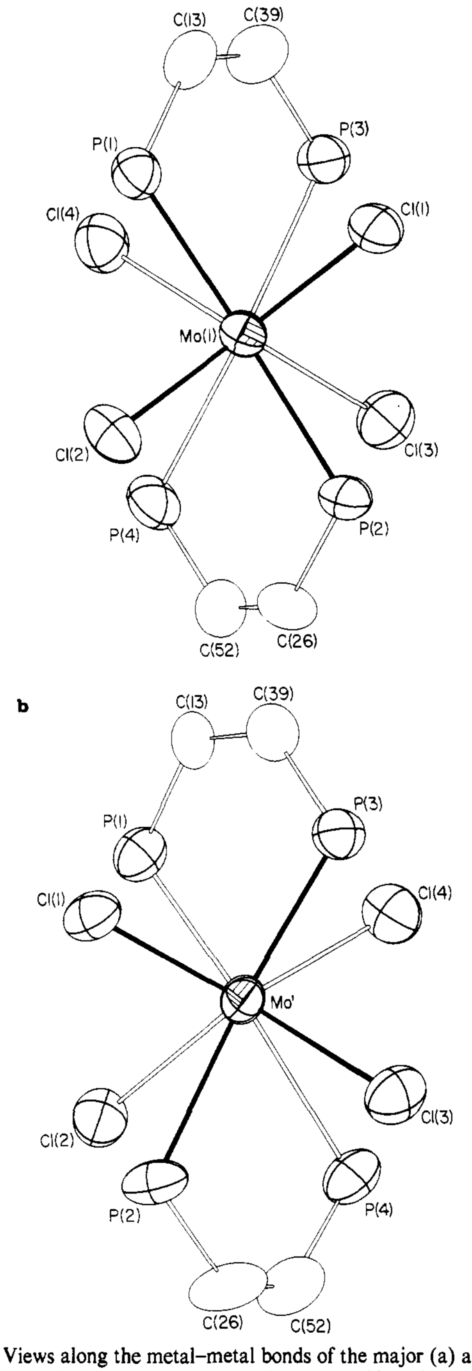

Figure 2. Views along the metal–metal bonds of the major (a) and minor (b) components in the crystal structure of β-$Mo_2Cl_4(dppee)_2$, showing the torsional angles about the metal–metal bonds. In (a) atom Mo(2) is obscured by Mo(1). In (b) atom Mo″ is obscured by Mo′.

The $Mo\overset{4}{-}Mo$ bond lengths are 2.163 (2) and 2.142 (7) Å in the major and minor components, respectively. The δ-bond between the metal atoms is somewhat weakened by the twist of the ligand set about the metal–metal bond. Considering the major component (see Figure 2a), the average P–Mo–Mo–Cl torsional angle is −25.5 [8]°,[21] and the individual values range from −23.9 (1) to −26.9 (1)°. The situation is quite similar for the minor component (Figure 2b), in which the P–Mo–Mo–Cl torsion angles range from 24.6 (3) to 30.0 (3)° and have a mean value of 26.7 [12]°. The P–Mo–Mo–P torsional angles do not vary greatly between the major and minor molecules (P(1)–Mo(1)–Mo(2)–P(3) = 58.4 (1)°; P(2)–Mo(1)–Mo(2)–P(4) 60.6 (1)°; P(3)–Mo′–Mo″–P(4) = −65.8 (3°); P(2)–Mo′–Mo″–P(4) = −57.8 (2)°).

The backbone of the dppee ligand maintains its structural rigidity in β-$Mo_2Cl_4(dppee)_2$. The two planes are nearly orthogonal, forming a dihedral angle of 87.5 (3)°.

The most remarkable aspect of this structure, which we did not expect, is that the torsional angles about the M–M bonds are essentially identical for both the Mo_2^{4+} and Re_2^{4+} molecules. This is surprising because the net triple bond in the Re_2^{4+} unit is free of any rotational barrier, whereas the δ component of the bond in Mo_2^{4+} would favor an eclipsed conformation (i.e., a torsional angle of 0°). We therefore expected the torsional angle in the molybdenum compound to be smaller than that in the rhenium molecule. We cannot say with certainty why this is not observed. The most likely explanation is that the conformational demands of the ligand portions of the two rings that are fused along the M–M bonds are so strong that the resistance offered by the Mo–Mo δ-bond is negligible in comparison. This may not be too surprising when it is remembered that loss of δ-bond energy will be proportional to the cosine of the smaller torsional angle (ca. 25°), which is 0.90. Thus, only about 10% of what is not a large bond energy anyhow (perhaps 10–15 kcal mol^{-1}) is actually sacrificed in the Mo_2^{4+} case.

(3) Preparation and Properties of $Mo_2I_4(dppee)_2$. The reaction between $Mo_2(O_2CCH_3)_4$ and *cis*-dppee in the presence of Me_3SiI in THF at room temperature for 5 min affords the yellow-green complex $Mo_2I_4(dppee)_2$. This procedure is similar to one of those we used to prepare α- and β-$Mo_2X_4(dppee)_2$ (X = Cl, Br) (vide supra) and also resembles that used to obtain β-$Mo_2I_4(dppe)_2$,[22] although toluene is substituted for THF as the reaction solvent in the case of the latter complex.

A CV of $Mo_2I_4(dppee)_2$ in 0.1 M TBAH–CH_2Cl_2 revealed the presence of a reversible oxidation at $E_{1/2}$ = +0.61 V and an irreversible reduction at $E_{p,c}$ = −1.1 V vs Ag/AgCl. This behavior is almost exactly that reported for β-$Mo_2I_4(dppe)_2$ in 0.2 M TBAH–CH_2Cl_2.[22] The electronic absorption spectrum of a freshly prepared solution of $Mo_2I_4(dppee)_2$ in CH_2Cl_2 shows an intense band at 690 nm ($\epsilon \simeq 3300$), a shoulder at ~530 nm, and a sharp intense band at 444 nm ($\epsilon \simeq 6700$). These properties are similar to those observed for the structurally characterized complex β-$Mo_2I_4(dppe)_2$.[22] Of considerable interest is the finding that β-$Mo_2I_4(dppe)_2$ exists in both twisted (mean torsional angle $\chi \simeq$ 26°) and eclipsed (χ = 0°) conformations in the crystalline state.[22] If the sample of $Mo_2I_4(dppee)_2$ we have prepared is indeed the β-isomeric form, its spectral properties ($\delta \rightarrow \delta^*$ transition at 690 nm) are much closer to those expected for an "eclipsed" geometry, on the basis of the spectral properties that have been reported for the different forms of β-$Mo_2I_4(dppe)_2$. Alternatively, its formulation as α-$Mo_2I_4(dppee)_2$ is a strong possibility since the compounds α-$Mo_2X_4(dppee)_2$ (X = Cl, Br) have their $\delta \rightarrow \delta^*$ transition located in the region 680–700 nm (Table II). We cannot yet differentiate between these two structural possibilities for $Mo_2I_4(dppee)_2$.

(4) Preparation and Properties of *trans*-$MoX_2(dppee)_2$. When $K_4Mo_2Cl_8$ and $(NH_4)_4Mo_2Br_8$ are reacted with *cis*-dppee in refluxing 1-propanol for periods of several days, small quantities of the mononuclear complexes *trans*-$MoX_2(dppee)_2$ are formed. We have not pursued a detailed characterization of these species since other complexes of this type, viz., *trans*-$MoX_2(dppbe)_2$ (dppbe = 1,2-bis(diphenylphosphino)benzene), have recently been the subject of a much more extensive study.[23] Suffice it to say that the disruption of the $(Mo\overset{4}{-}Mo)^{4+}$ core to give mononuclear Mo(II) species is now a well-recognized reaction pathway under forcing reaction conditions (such as refluxing 1-propanol), especially in the presence of bidentate phosphine ligands.[13,23]

The identification of the chloro complex *trans*-$MoCl_2(dppee)_2$ was based upon a comparison of its electrochemical and spectroscopic properties with those reported for the complexes *trans*-$MoX_2(L\text{-}L)_2$ (X = Cl, Br; L-L = dppe, dppbe, dmpe).[13,23-25]

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[21] The deviation in square brackets is calculated as $[\,] = [\sum_i \Delta_i^2/n(n-1)]^{1/2}$, in which Δ_i is the deviation of the *i*th value from the mean of the set of *n* values.

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The bromo analogue *trans*-$MoBr_2(dppee)_2$ was characterized only from its electrochemical properties in a mixture with β-$Mo_2Br_4(dppee)_2$ (see Experimental Section).

A CV of *trans*-$MoCl_2(dppee)_2$ in 0.1 M TBAH–CH_2Cl_2 shows processes that are assigned to the oxidation Mo(III) → Mo(IV) and the Mo(III)/Mo(II) and Mo(II)/Mo(I) couples, at $E_{p,a}$ = +1.38 V, $E_{1/2}$(ox) = +0.04 V, and $E_{1/2}$(red) = −1.8 V vs Ag/AgCl, respectively. The bromo analogue *trans*-$MoBr_2(dppee)_2$ shows processes at $E_{p,a} \simeq +1.2$ V and $E_{1/2}$(ox) = +0.07 V vs Ag/AgCl; the process at negative potentials due to the Mo(II)/Mo(I) couple was not well-defined because of the presence of impurities. These electrochemical redox properties are very similar to those reported for *trans*-$MoX_2(dppbe)_2$.[23]

The electronic absorption spectrum of *trans*-$MoCl_2(dppee)_2$ in CH_2Cl_2 exhibits an intense peak at 332 nm ($\epsilon \sim 7600$), indicative of a charge-transfer transition,[4,23] and a shoulder at ~370 nm. The solid-state electronic absorption spectrum recorded as a Nujol mull shows an intense band at ~330 nm. These properties are similar to those reported for *trans*-$MoBr_2(dppe)_2$[13] and *trans*-$MoX_2(dppbe)_2$.[23]

The low-frequency IR spectrum of *trans*-$MoCl_2(dppee)_2$, recorded as a Nujol mull, shows a single ν(Mo–Cl) mode at 310 cm^{-1}, which supports its assignment as the trans isomer. Similar results have been reported for *trans*-$MoCl_2(dppbe)_2$ (ν(Mo–Cl) at 314 cm^{-1})[23] and *trans*-$MoCl_2(diars)_2$ (ν(Mo–Cl) at 299 cm^{-1}).[26]

The oxidation of *trans*-$MoCl_2(dppee)_2$ with $NOPF_6$ in CH_3CN affords the blue salt $[MoCl_2(dppee)_2]PF_6$. This complex shows the expected electrochemical redox properties with the process at $E_{1/2}$ = +0.04 V now corresponding to a reduction. A conductivity measurement on a solution of this complex in CH_3CN ($\Lambda_M = 133\ \Omega^{-1}\ cm^2\ mol^{-1}$ for $C_M = 1.36 \times 10^{-4}$ M) showed its expected behavior as a 1:1 electrolyte. This complex is ESR active, with a sharp signal in the X-band spectrum centered at $g = 1.93$. This behavior is similar to that observed for *trans*-$[MoCl_2(dppbe)_2]PF_6$.[23]

(5) Conclusions. The synthesis and characterization of the new species α- and β-$Mo_2X_4(dppee)_2$, $Mo_2I_4(dppee)_2$, and *trans*-$MoX_2(dppee)_2$ have been successfully accomplished. The β-isomers of $Mo_2X_4(dppee)_2$ represent the first examples of dimolybdenum(II) species that contain two fused six-membered rings that incorporate one $Mo\overset{4}{-}Mo$ bond and two C=C bonds. The α-isomers are similar to their dppe analogues in that they undergo isomerization in solution to form the thermodynamically favored β-forms. These results are in contrast to those observed for the dirhenium(II) analogues $Re_2X_4(dppee)_2$, where no evidence for $\alpha \rightleftarrows \beta$ isomerization has yet been observed.[2]

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Supplementary Material Available: For the crystal structure of β-$Mo_2Cl_4(dppee)_2$, a table of crystallographic data and data collection parameters and full tables of bond distances, bond angles, torsional angles, and anisotropic displacement parameters (8 pages); a listing of observed and calculated structure factors (27 pages).

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