ments converged with unweighted and weighted agreement factors R = 0.030 and R_w = 0.036, respectively. The refinement with the enantiomorphous set of parameters converged with distinctly poorer agreement factors, i.e., R = 0.037 and R_w = 0.0047.

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Registry No. 1, 112988-65-5; (η^5-C_5Me_4Et)Re(CO)$_3$, 112988-64-4; $Re_2(CO)_{10}$, 14285-68-8; 1-ethyl-2,3,4,5-tetramethylcyclopentadiene, 83321-17-9.

Supplementary Material Available: A stereoscopic view of the unit cell, listings of anisotropic thermal parameters and calculated hydrogen atom positions, and complete listings of bond lengths and angles (8 pages); a table of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Reaction of *cis*-[$Mo_2(MeCO_2)_2(MeCN)_6$][BF_4]$_2$ with dmpe and *S,S*-dppb: Preparation, Crystal Structure, and Spectroscopic Properties of *trans*-[$Mo_2(MeCO_2)_2(dmpe)_2$][BF_4]$_2$ (dmpe = Bis(dimethylphosphino)ethane, *S,S*-dppb = (2*S*,3*S*)-Bis(diphenylphosphino)butane)

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cis-[$Mo_2(MeCO_2)_2(MeCN)_6$][BF_4]$_2$ reacts with dmpe in acetonitrile solution to give orange, air-stable [$Mo_2(MeCO_2)_2(dmpe)_2$][BF_4]$_2$·MeCN (**1**), which has been characterized by X-ray crystallography. The complex crystallizes in the space group $P2_1/n$ with unit cell dimensions a = 16.047 (8) Å, b = 11.582 (4) Å, c = 19.067 (4) Å, β = 101.03 (3)°, V = 3478 Å^3, and Z = 4. There are two independent molecules (**1a** and **1b**) of the cation in the unit cell. Both **1a** and **1b** have a trans ligand arrangement in which the MoPCCPMo rings adopt the novel half-chair conformation analogous to that of cyclohexene. Reaction of the chiral ligand *S,S*-dppb affords a product formulated as [$Mo_2(MeCO_2)_2$(*S,S*-dppb)$(MeCN)_2$]$^{2+}$. The CD spectrum of this complex shows that the diphosphine is coordinated to the Mo_2 unit in solution.

Introduction

Dimolybdenum tetraacetate reacts with the alkylating agents [Me_3O][BF_4] or [Et_3O][BF_4] to give exclusively, *cis*-[$Mo_2(MeCO_2)_2(MeCN)_6$][BF_4]$_2$ in which the quadruply bonded dimolybdenum unit is coordinated by two bridging acetate groups cis to each other.[1,2] The four coordination sites opposite the O–Mo bonds are occupied by acetonitrile molecules, and there are an additional two MeCN molecules in the axial positions. The equatorial ligators are eclipsed. This geometry, which is dictated by the bridging acetate ligands, also maximizes the δ bond overlap between the two molybdenum atoms.

The acetonitrile ligands in [$Mo_2(MeCO_2)_2(MeCN)_6$][BF_4]$_2$ are labile; the ^{1}H NMR spectrum in CD_3CN shows[1] a single resonance for the acetonitrile protons, indicating rapid exchange between axial and equatorial ligands and the solvent. The MeCN ligands may be replaced by a variety of monodentate species such as pyridine,[3] ammonia,[4] and DMF[4] to give complexes in which it is believed that the basic cis structure of [$Mo_2(MeCO_2)_2(MeCN)_6$]$^{2+}$ is preserved. Pimblett[3] showed that two of the equatorial acetonitriles could be replaced by the bidentate ligand dppm to give a complex of formula [$Mo_2(MeCO_2)_2$(dppm)$(MeCN)_2$][BF_4]$_2$. This was not structurally characterized, but once again it seems reasonable to suppose that the cis geometry is preserved. Attempts[3] to react [$Mo_2(MeCO_2)_2(MeCN)_6$][BF_4]$_2$ with dppe were, however, less successful. The solution changed color showing that some reaction had occurred, but the complex NMR spectrum implied a mixture of products. Analysis of the solid from the reaction suggested a formulation similar to that of the dppm complex, but the complex (or mixture) was unstable and could not be further characterized. Our attempts to react [$Mo_2(MeCO_2)_2(MeCN)_6$][BF_4]$_2$ with the chiral ligand *S,S*-dppb (vide infra) provide evidence that reaction takes place between [$Mo_2(MeCO_2)_2(MeCN)_6$][BF_4]$_2$ and the diphosphine ligand in solution. A pure product, however, has not yet been isolated.

In the belief that the steric bulk of the phenyl groups was responsible for the lack of reactivity of [$Mo_2(MeCO_2)_2(MeCN)_6$][BF_4]$_2$ with the diphosphine ligands (or the instability of the products) we have investigated the reaction between [$Mo_2(MeCO_2)_2(MeCN)_6$][BF_4]$_2$ and the less sterically demanding diphosphine dmpe. The reaction proceeded quantitatively to give an air-stable product, which analyzed as [$Mo_2(MeCO_2)_2(dmpe)_2$][BF_4]$_2$. The IR spectrum showed the absence of ligated acetonitrile while the ^{1}H NMR spectrum confirmed the stoichiometry of the complex and suggested the presence of trans phosphine ligands. Dimolybdenum complexes with two trans acetate groups are known, for example [$Mo_2(MeCO_2)_2Cl_2(PBu_3)_2$][5] and [$Mo_2(MeCO_2)_2Cl_4$]$^{2-}$,[6] but such a structure would require a cis to trans isomerization of the acetate groups during the course of the reaction. Both cis and trans structures of a complex containing two acetate and two diphosphine ligands bridging an Mo_2 unit have interesting steric implications, and consequently we have determined the crystal structure of [$Mo_2(MeCO_2)_2(dmpe)_2$][BF_4]$_2$.

Experimental Section

All manipulations were carried out under dry oxygen-free conditions by using vacuum line or Schlenk techniques. [$Mo_2(MeCO_2)_2(MeCN)_6$][BF_4]$_2$ was prepared as described in the literature.[1] The ligands dmpe and *S,S*-dppb were purchased from Strem Chemicals, Ltd. ^{1}H and ^{31}P NMR spectra were obtained on a Bruker WP 200 SY spectrometer.

Preparations: [$Mo_2(MeCO_2)_2(dmpe)_2$][BF_4]$_2$. A mixture of 2.189 g (3 mmol) of [$Mo_2(MeCO_2)_2(MeCN)_6$][BF_4]$_2$ and 0.90 g (6 mmol) of dmpe were placed in a reaction vessel with a Young's tap attached to a vacuum line. The vessel was evacuated and cooled in liquid nitrogen. Ca. 10 mL of purified degassed acetonitrile was condensed into the vessel, which was isolated from the vacuum and warmed slowly to room tem-

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0020-1669/88/1327-1257$01.50/0

Table I. Experimental Data for the Crystallographic Study

formula	$C_{16}H_{38}B_2F_8Mo_2O_4P_4 \cdot CH_3CN$
M_r	825.4
space group	$P2_1/n$ (No. 14, C_{2h}^5)
cryst syst	monoclinic
a/Å	16.047 (8)
b/Å	11.582 (4)
c/Å	19.067 (4)
β/deg	101.03 (3)
V/Å^3	3478 (2)
Z	4
D_{calcd}/g cm^{-3}	1.58
$F(000)$	1658
μ(Mo Kα)/cm^{-1}	9.5
T/K	298
scan mode	$\theta/2\theta$
θ range/deg	$2 \leqslant \theta \leqslant 22$
cryst size/mm	0.3 × 0.3 × 0.3
range of transmissn coeff cor	0.91–1.11
no. of data collcd	4701
no. of unique data	4244
std reflcns	$\bar{2}5\bar{1}$ $\bar{2}5\bar{1}$
observability criterion n: $I > n\sigma(I)$	3
no. of data in refinement	2874
no. of refined params	217/262
final R	0.043
final R_w	0.045
largest remaining feature in electron density map, e Å^{-3}	+0.74 (max); −0.64 (min)
shift/esd in last cycle	0.35 (max); 0.02 (av)

perature. The resulting orange solution was stripped of its acetonitrile to give an orange solid, which was washed with dichloromethane and ether. Crystals suitable for crystallography were grown by cooling a warm saturated solution of the complex in acetonitrile to −30 °C. Although the preparation was performed under strictly anaerobic conditions, $[Mo_2(MeCO_2)_2(dmpe)_2][BF_4]_2$ is air stable both in the solid state and in MeCN solution.

Reaction of $[Mo_2(MeCO_2)_2(MeCN)_6][BF_4]_2$ with *S,S*-dppb. By use of the method described above $[Mo_2(MeCO_2)_2(MeCN)_6][BF_4]_2$ was reacted with various molar equivalents of *S,S*-dppb. In all cases a purple solution was produced from which a purple solid was isolated. Elemental analysis suggested that this was almost pure $[Mo_2(MeCO_2)_2(S,S\text{-dppb})(MeCN)_2][BF_4]_2$. Anal. Calcd for $Mo_2C_{36}H_{40}B_2F_8O_4P_2$: C, 44.85; H, 4.18; P, 6.43; F, 15.76. Found: C, 45.15; H, 4.20; P, 5.98; F, 16.04.

Crystal Structure Determination. Details of data collection procedures and structural refinement are given in Table I. Crystals of $[Mo_2(MeCO_2)_2(dmpe)_2][BF_4]_2 \cdot MeCN$ grew as translucent well-formed orange prisms from acetonitrile, but rapidly clouded on removal from the mother liquor. A segment ca. 0.3 × 0.3 × 0.3 mm was cut from a larger crystal and immediately coated in glue to prevent solvent loss. Data were collected at ambient temperature on an Enraf-Nonius CAD4F automated diffractometer, with graphite-monochromated X-radiation (λ = 0.71069 Å). Unit cell parameters were determined by refinement of the setting angles ($\theta \geqslant 12°$) of 25 reflections. Standards were measured every 2 h during data collection, and no significant decay was observed. Lorentz/polarization and absorption (DIFABS[7]) corrections were applied. Systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) uniquely indicated the monoclinic space group $P2_1/n$ (No. 14, C_{2h}^5). The structure was solved by direct methods (MITHRIL[8]) and subsequent electron density syntheses. All non-hydrogen atoms were allowed anisotropic thermal motion. Hydrogen atoms were included at calculated positions (C–H = 1.0 Å) and were held fixed during refinement with fixed isotropic (0.05 Å) thermal parameters. Refinement was by full-matrix least squares. Due to matrix size limitations the parameter list was divided into two sections and each refined separately. The function minimized was $w(|F_o| - |F_c|)^2$ with the weighting function $w = [\sigma^2(F_o)]^{-1}$ used and judged satisfactory. $\sigma(F_o)$ was estimated from counting statistics. Neutral-atom scattering factors were taken from ref 9 with corrections applied for anomalous scattering. All calculations were carried out on a Gould-SEL 32/27 minicomputer using the GX suite of programs.[10] The final positional parameters and isotropic thermal parameters are given in Table II and the principal bond lengths and angles in Table III.

Table II. Final Positional Parameters (Fractional Coordinates) with Esd's in Parentheses and Equivalent Isotropic Thermal Parameters, U_{eq} (Å^2), for the Complex $[Mo_2(Me_2PCH_2CH_2PMe_2)_2(O_2CCH_3)_2]^{2+}(BF_4^-)_2 \cdot MeCN$

	x/a	y/b	z/c	U_{aq}[a]
Mo(1)	0.47422 (4)	0.03741 (6)	0.95046 (4)	0.030
Mo(2)	0.46908 (5)	0.07051 (6)	0.47190 (4)	0.032
P(1)	0.63825 (15)	0.10217 (22)	1.11181 (12)	0.044
P(2)	0.55078 (17)	0.22872 (22)	0.94254 (12)	0.047
P(3)	0.61865 (16)	0.00660 (20)	0.64433 (12)	0.044
P(4)	0.51389 (16)	0.24877 (20)	0.54777 (12)	0.043
O(1)	0.5652 (4)	−0.0435 (5)	0.9008 (3)	0.044
O(2)	0.6200 (3)	−0.1229 (5)	1.0065 (3)	0.042
O(3)	0.5739 (4)	0.1000 (5)	0.4210 (3)	0.041
O(4)	0.6389 (3)	−0.0480 (5)	0.4809 (3)	0.042
C(1)	0.6204 (6)	−0.1075 (8)	0.9400 (5)	0.045
C(S1)	−0.0114 (11)	0.0874 (12)	0.6916 (8)	0.102
C(2)	0.6880 (6)	−0.1640 (9)	0.9088 (5)	0.071
C(S2)	0.0451 (12)	0.0562 (15)	0.7559 (8)	0.162
C(3)	0.6388 (5)	0.0356 (8)	0.4383 (4)	0.042
C(4)	0.7153 (6)	0.0598 (9)	0.4069 (5)	0.066
C(5)	0.6497 (7)	0.2489 (9)	1.0790 (6)	0.082
C(6)	0.6521 (7)	0.2600 (10)	1.0033 (5)	0.081
C(7)	0.6245 (12)	0.1557 (11)	0.6603 (8)	0.164
C(8)	0.5846 (10)	0.2372 (10)	0.6326 (6)	0.118
C(11)	0.7429 (6)	0.0404 (10)	1.1211 (5)	0.073
C(12)	0.6217 (7)	0.1315 (9)	1.2018 (5)	0.068
C(21)	0.5841 (6)	0.2471 (9)	0.8580 (5)	0.069
C(22)	0.4823 (8)	0.3501 (9)	0.9485 (5)	0.089
C(31)	0.7284 (6)	−0.0391 (10)	0.6572 (5)	0.078
C(32)	0.5847 (8)	−0.0485 (13)	0.7220 (5)	0.105
C(41)	0.4246 (8)	0.3282 (9)	0.5673 (5)	0.081
C(42)	0.5680 (6)	0.3497 (8)	0.4998 (5)	0.065
B(1)	0.3512 (10)	0.1983 (15)	0.7640 (8)	0.075
B(2)	0.8409 (13)	0.1341 (15)	0.8573 (10)	0.092
F(1)	0.3922 (4)	0.1462 (6)	0.8245 (3)	0.091
F(2)	0.2742 (5)	0.1623 (8)	0.7434 (4)	0.138
F(3)	0.3645 (8)	0.3061 (7)	0.7613 (5)	0.197
F(4)	0.3901 (7)	0.1535 (11)	0.7115 (5)	0.198
F(5)	0.8914 (6)	0.0442 (7)	0.8593 (5)	0.132
F(6)	0.8875 (5)	0.2258 (6)	0.8915 (4)	0.109
F(7)	0.7983 (8)	0.1628 (8)	0.7976 (5)	0.198
F(8)	0.7872 (6)	0.1028 (10)	0.9041 (7)	0.193
N(S1)	−0.0516 (11)	0.1073 (13)	0.6387 (7)	0.143

[a] $U_{eq} = {}^1/_3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

Results and Discussion

Structure of $[Mo_2(MeCO_2)_2(dmpe)_2][BF_4]_2$. The compound $[Mo_2(MeCO_2)_2(dmpe)_2][BF_4]_2$ (**1**) crystallizes in the space group $P2_1/n$ with two independent half molecules of the cation in the asymmetric unit. The structures of the two cations are respectively shown in parts a and b of Figure 1. The two centrosymmetric $[Mo_2(MeCO_2)_2(dmpe)_2]^{2+}$ molecules have the same basic structure consisting of an Mo_2 unit bridged by two trans acetate groups and two trans dmpe molecules, the oxygen and phosphorus ligators being strictly eclipsed. The only significant difference between **1a** and **1b** is in the length of the C–C bond in the carbon backbone. In **1a** the bond has a normal length, C(5)–C(6) = 1.46 (1) Å, whereas in **1b** C(7)–C(8) = 1.20 (2) Å and the anisotropic thermal elipsoids of C(7) and C(8) are very large. This phenomenon is common in dmpe complexes[11,12] and is due either to the λ and δ conformations of the MoPCCPMo chelate rings being in dynamic equilibrium in the solid or to a static conformational disorder. There was no evidence from difference Fourier maps for a discrete disorder in the conformation of the C(7)–C(8) bond. Figure 2 shows a view of molecule **1a** looking down the Mo–Mo bond and illustrates the eclipsed Mo–P bonds. The Mo–Mo bond lengths in the two molecules are identical within error [Mo(1)–Mo(1′) = 2.099 (1) Å and Mo(2)–Mo(2′) = 2.096 (1) Å].

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Table III. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[Mo_2(Me_2PCH_2CH_2PMe_2)_2(O_2CCH_3)_2]^{2+}(BF_4^-)_2 \cdot MeCN$

molecule 1		molecule 2	
	Bonds		
Mo(1)–Mo(1′)	2.099 (1)	Mo(2)–Mo(2′)	2.096 (1)
Mo(1)–P(1′)	2.542 (3)	Mo(2)–P(3′)	2.549 (3)
Mo(1)–P(2)	2.552 (3)	Mo(2)–P(4)	2.544 (3)
Mo(1)–O(1)	2.106 (6)	Mo(2)–O(3)	2.124 (6)
Mo(1)–O(2′)	2.100 (6)	Mo(2)–O(4′)	2.116 (6)
C(1)–O(1)	1.28 (1)	C(3)–O(3)	1.27 (1)
C(1)–O(2)	1.28 (1)	C(3)–O(4)	1.26 (1)
C(1)–C(2)	1.48 (1)	C(3)–C(4)	1.49 (1)
P(1)–C(5)	1.83 (1)	P(3)–C(7)	1.75 (1)
P(1)–C(11)	1.80 (1)	P(3)–C(31)	1.81 (1)
P(1)–C(12)	1.82 (1)	P(3)–C(32)	1.79 (1)
P(2)–C(6)	1.84 (1)	P(4)–C(8)	1.79 (1)
P(2)–C(21)	1.81 (1)	P(4)–C(41)	1.80 (1)
P(2)–C(22)	1.80 (1)	P(4)–C(42)	1.80 (1)
C(5)–C(6)	1.46 (1)	C(7)–C(8)	1.20 (2)
	Angles		
Mo(1)–Mo(1′)–P(1)	106.3 (1)	Mo(2)–Mo(2′)–P(3)	107.5 (1)
Mo(1′)–Mo(1)–P(2)	107.5 (1)	Mo(2′)–Mo(2)–P(4)	106.7 (1)
Mo(1)–Mo(1′)–O(2)	91.9 (2)	Mo(2)–Mo(2′)–O(4)	91.9 (2)
Mo(1′)–Mo(1)–O(1)	91.9 (2)	Mo(2′)–Mo(2)–O(3)	91.1 (2)
Mo(1)–O(1)–C(1)	117.3 (6)	Mo(2)–O(3)–C(3)	117.9 (6)
Mo(1′)–O(2)–C(1)	117.5 (6)	Mo(2′)–O(4)–C(3)	117.8 (6)
O(1)–C(1)–O(2)	121.5 (8)	O(3)–C(3)–O(4)	121.8 (8)
O(1)–C(1)–C(2)	119.9 (9)	O(3)–C(3)–C(4)	118.8 (9)
O(2)–C(1)–C(2)	118.6 (9)	O(4)–C(3)–C(4)	120.1 (8)

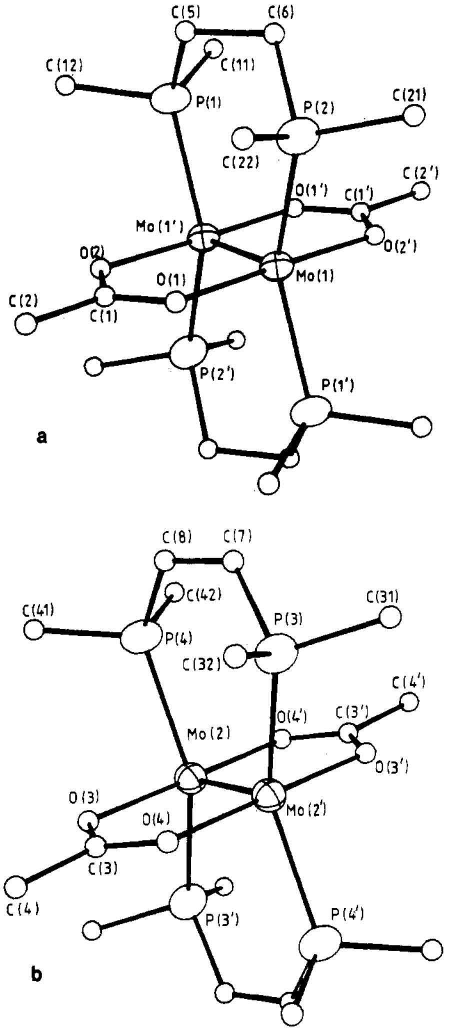

Figure 1. (a) View of molecule **1a**. (b) View of molecule **1b**. Thermal ellipsoids for Mo and P represent 50% probability; C and O are represented by spheres of arbitrary size.

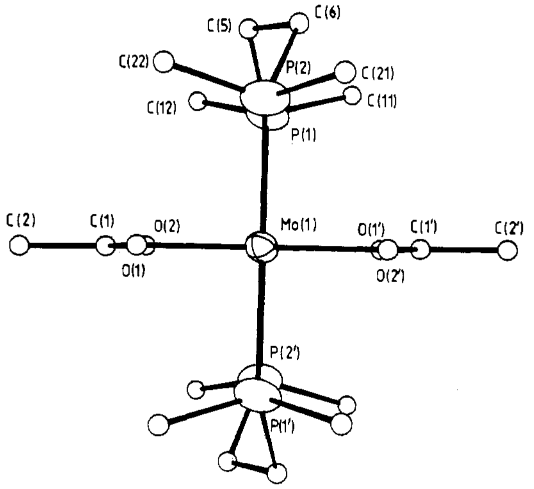

Figure 2. View of molecule **1a** down the Mo–Mo bond showing the eclipsed ligators.

The trans acetate groups have the expected planar geometry and have dimensions similar to those in other Mo–Mo compounds.[1,5,6] The trans dmpe ligands, however, adopt an eclipsed geometry, the MoPCCPMo ring having the novel half-chair conformation analogous to cyclohexene. Indeed the two trans dmpe rings can be considered to be the heterocyclic equivalent of 1,2,3,4,5,6,7,8-octahydronaphthalene. The MoMoP angle is wider (106.9°) in this conformation than in the more common twisted structures adopted by $[Mo_2Cl_4(dmpe)_2]$[13] (98.4°) and $[Mo_2Br_4(dmpe)_2]$[12] (101.7°). The two MoPCCPMo rings necessarily have opposite chirality to give the overall idealized D_{2h} symmetry of the complex.

The only other example of a dimolybdenum complex containing eclipsed Mo–P bonds in a six-membered MoPCCPMo ring is $[Mo_2(dppe)_2I_4]$ (**2**), whose structure has recently been determined.[14] There are two major differences between the complexes. First, the eclipsed isomer of **2** only exists in the crystal, the complex reverting to the more usual staggered geometry in solution. Since the eclipsed nature of $[Mo_2(MeCO_2)_2(dmpe)_2]^{2+}$ is determined by the acetate ligands, however, the structure remains the same in solution and in the solid state. More importantly the conformation of the MoPCCPMo rings is different in the two complexes. In **1**, as described above, the ring has a half-chair conformation; in **2**, in contrast, the six-membered ring is in the half-boat conformation. Conformational analysis suggests that the half-chair conformation should be the more stable, and the fact that $[Mo_2(dppe)_2I_4]$ adopts the less stable half-boat conformation is probably determined by arrangement of the phenyl groups in the crystal, which can adopt a face-to-face arrangement when the ring is in the half-boat conformation.

Spectroscopic Studies on $[Mo_2(MeCO_2)_2(dmpe)_2][BF_4]_2$. The original indication that the dmpe ligands were in the trans position came from the ^1H NMR spectrum of $[Mo_2(MeCO_2)_2(dmpe)_2][BF_4]_2$. The six methyl protons arising from the two acetate ligands occur as a singlet at 2.84 ppm, which may be compared with the 2.82 ppm value for $[Mo_2(MeCO_2)_2(MeCN)_6]^{2+}$.[1] The resonances due to the dmpe ligands consist of eight CH_2 protons at 2.0 ppm (broad) and a multiplet (quintet) centred on 1.34 ppm that is ascribed to 24 equivalent P–Me protons exhibiting $A_3A'_3XX'$ coupling, which implies strongly coupled and, therefore, trans phosphorus atoms ($^2J_{PP}$ is approximately 10 times larger for trans than for cis phosphorus atoms[15]). The eclipsed dmpm complex $[Mo_2(dmpm)_2Cl_4]$, in contrast, shows a singlet for its P–Me resonance,[16] which may imply that the

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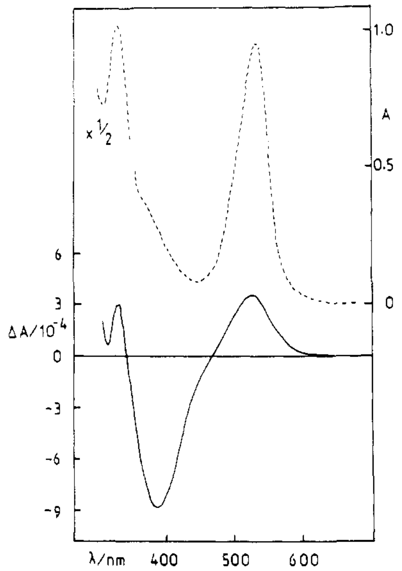

Figure 3. Absorption (dashed line) and CD (full line) spectra of a MeCN solution of $[Mo_2(MeCO_2)_2(S,S\text{-dppb})(MeCN)_2][BF_4]_2$.

methyl groups are exchanging axial and equatorial positions. The ^{31}P NMR spectrum shows a single sharp resonance at 4.81 ppm at room temperature that is not affected by cooling and reflects the structural rigidity of $[Mo_2(MeCO_2)_2(dmpe)_2]^{2+}$. This is in contrast to the ^{31}P spectrum of $[Mo_2(dppe)_2I_4]$, the only other bridged dimolybdenum diphosphine complex whose NMR has been reported, which could not be observed[14] at room temperature. The low-temperature ^{31}P NMR of this compound showed a temperature variation consistent with an interconversion of the Λ and Δ forms of the molecule via the eclipsed conformer.

The electronic absorption spectrum of $[Mo_2(MeCO_2)_2(dmpe)_2]^{2+}$ shows a band at 19 880 cm^{-1} (ϵ = 1330 mol L^{-1}) that is due to the $\delta_{xy} \rightarrow \delta_{xy}{}^*$ transition. The energy of this transition is somewhat lower than in other complexes containing trans acetate bridges; for example in $[Mo_2(MeCO_2)_4]$ (bond length 2.0934 Å), it occurs at 22 980 cm^{-1} and in $[Mo_2(MeCO_2)_2Cl_4]$ (bond length 2.086 Å) it comes at 20 200 cm^{-1}. This is consistent with the longer Mo–Mo bond length in the phosphine complex.

The IR spectrum shows a very weak carbonyl stretching vibration consistent with the centrosymmetric structure of the complex, and the resonance Raman (488.0 nm excited) spectrum exhibits a short progression in the Mo–Mo stretching vibration with a wavenumber of 391 cm^{-1}, which is slightly lower than the Mo–Mo stretching wavenumber of $Mo_2(MeCO_2)_4$ (406 cm^{-1}).

Reaction of $[Mo_2(MeCO_2)_2(MeCN)_6][BF_4]_2$ with *S*,*S*-dppb. Addition of 1 molar equiv or more of *S*,*S*-dppb to $[Mo_2(MeCO_2)_2(MeCN)_6][BF_4]_2$ in acetonitrile solution produces a purple solution from which a purple solid is obtained. Analysis suggests the product has the formula $[Mo_2(MeCO_2)_2(S,S\text{-dppb})(MeCN)_2][BF_4]_2$. The IR spectrum confirms the presence of MeCN and *S*,*S*-dppb. The ^1H NMR in CD_3CN solution, however, indicates the presence of a mixture, probably of complex, free phosphine, and $[Mo_2(MeCO_2)_2(MeCN)_6][BF_4]_2$. Because the ligand is chiral, we can use the CD spectrum of a solution of the dimolybdenum complex to give information as to whether or not the *S*,*S*-dppb is coordinated to the metal dimer. The absorption and CD spectra of a MeCN solution of the complex is shown in Figure 3. The absorption due to the $\delta_{xy} \rightarrow \delta_{xy}{}^*$ transition clearly shows an associated Cotton effect, thus proving that *S*,*S*-dppb has coordinated to the Mo_2 unit. The size of the dissymmetry factors (3.5×10^{-4} for the $\delta_{xy} \rightarrow \delta_{xy}{}^*$ transition and -3.2×10^{-3} for the $\delta_{xy} \rightarrow \delta_{x^2-y^2}$ transition are those expected for a complex whose ligators are very nearly eclipsed.[17,18] (The relevant values for $[Mo_2(S,S\text{-dppb})_2Cl_4]$, which is twisted by 23° about the Mo–Mo bond, are -5.8×10^{-3} and 7.3×10^{-2}, respectively.[18]) It is therefore most likely that *S*,*S*-dppb coordinates to the Mo_2 unit to give a six-membered ring with the same half-chair conformation as is found in $[Mo_2(MeCO_2)_2(dmpe)_2]^{2+}$. The magnitude of the dissymmetry factor for the $\delta_{xy} \rightarrow \delta_{xy}{}^*$ transition can be used to give a very crude estimate of the twist about the Mo–Mo bond of about 1–2°. The sign of the CD tells us unambiguously that the twist is in the clockwise direction, which is opposite to the twist in the *trans*-bis(diphosphine) complex $[Mo_2Cl_4(S,S\text{-dppb})_2]$.

Reaction of *cis*-$[Mo_2(MeCO_2)_2(MeCN)_6][BF_4]_2$ with Diphosphines. *cis*-$[Mo_2(MeCO_2)_2(MeCN)_6]^{2+}$ reacts with 2 mol of dmpe to give exclusively the trans isomer of $[Mo_2(MeCO_2)_2(dmpe)_2][BF_4]_2$. Two possibilities for the mechanism of the reaction are, therefore, prior formation of the cis isomer of $[Mo_2(MeCO_2)_2(dmpe)_2][BF_4]_2$ followed by a cis to trans isomerization or direct formation of the trans isomer by attack of a dmpe ligand between the cis acetate groups of $[Mo_2(MeCO_2)_2(MeCN)_6]$. The reaction occurs at the melting point of MeCN, and there is no evidence of a change in color as the reaction mixture warms up. There is therefore no evidence for an isomerization, and the most likely course of events is the formation of a 1:1 complex with cis acetate ligands, one bridging dmpe, and two MeCN ligands followed by attack between the cis acetate groups by a second molecule of dmpe to give the product. This suggestion has the virtue of explaining why the phenyl-substituted diphosphines (including dppm) do not react with $[Mo_2(MeCO_2)_2(MeCN)_6]^{2+}$ to form 2:1 complexes. The crystal structure of $[Mo_2(MeCO_2)_2(dmpe)_2][BF_4]_2$ suggests that there is no steric reason why bis(diphenylphosphines) should not form analogous trans bis complexes. Furthermore the eclipsed trans complexes $[Mo_2(dppe)_2I_4]$ and $[Mo_2(dppm)_2Cl_4]$ have been prepared. However if the mechanism of formation involves attack between the acetate ligands it is easy to see why dmpe can form a trans bis complex while dppm, dppe, and *S*,*S*-dppb cannot. The lack of stability shown by the 1:1 complexes of the diphenyldiphosphine ligands is most probably a reflection of the lability of the MeCN ligands in these compounds.

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Registry No. 1·MeCN, 113009-09-9; $[Mo_2(MeCO_2)_2(MeCN)_6][BF_4]_2$, 98542-25-7; $[Mo_2(MeCO_2)_2(S,S\text{-dppb})(MeCN)_2][BF_4]_2$, 113009-11-3.

Supplementary Material Available: Tables of anisotropic thermal parameters and calculated hydrogen positional parameters and a complete listing of bond lengths and bond angles (5 pages); a list of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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