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Synthesis and Structural Characterization of Trioxo(η^5-ethyltetramethylcyclopentadienyl)rhenium, a Half-Sandwich Complex of Heptavalent Rhenium[†]

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A single-crystal X-ray structure determination of trioxo(η^5-ethyltetramethylcyclopentadienyl)rhenium(VII), (η^5-C_5Me_4Et)ReO_3 (**1**), has been performed. A three-legged piano-stool structure with the five-membered-ring ligand being centrally η^5-bonded to the trioxorhenium fragment is found. While the Re–O bond lengths (166.4 (4)–171.6 (4) pm) are consistent with double bonds, the Re–C(ring) distances (238.5 (4)–243.0 (4) pm) are unusually long in comparison to those in any low-valent half-sandwich complexes of rhenium described in the literature. This effect stems from the pronounced trans influence of the three strongly π-donating terminal oxo ligands. Compound **1** crystallizes from dichloromethane/*n*-hexane in the orthorhombic space group $P2_12_12_1$ with cell dimensions a = 849.6 (1) pm, b = 1310.2 (2) pm, c = 1075.3 (2) pm, $V = 1197 \times 10^6$ pm^3, and ρ(calcd) = 2.128 g·cm^{-3} (Z = 4).

Introduction

The discovery of trioxo(η^5-pentamethylcyclopentadienyl)rhenium, (η^5-C_5Me_5)ReO_3,[1] has led to extensive development of the chemistry of half-sandwich rhenium complexes in higher oxidation states.[2] Although this prototypal compound was unambiguously characterized as a genuine complex of heptavalent rhenium exhibiting one pentamethylcyclopentadienyl and three terminal oxo ligands,[1] single-crystal X-ray diffraction studies were hampered by what appears to be some complicated twinning problems.[3] We have now used the *ethyltetramethyl*cyclopentadienyl instead of the *pentamethyl*cyclopentadienyl ligand and report on the synthesis and the X-ray structure of the compound (η^5-C_5Me_4Et)ReO_3 (**1**), the first example of a structurally characterized half-sandwich complex of rhenium in its highest possible oxidation state.

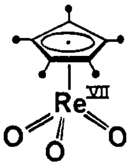

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Table I. Crystallographic Data for Trioxo(η^5-ethyltetramethylcyclopentadienyl)rhenium(VII) (**1**)

(a) Crystal Parameters	
empirical formula	$C_{11}H_{17}O_3Re$
fw	383.45
cryst color	yellow prism
cryst dimens, mm	0.50 × 0.45 × 0.70
radiation	Mo Kα (λ = 71.073 pm)
temp, °C	22 ± 1
space group	$P2_12_12_1$ (No. 19)
a, pm	849.6 (1)
b, pm	1310.2 (2)
c, pm	1075.3 (2)
V, pm^3	1197×10^6
Z	4
ρ(calcd), g·cm^{-3}	2.128
μ(Mo Kα), cm^{-1}	102.76
(b) Data Collection	
diffractometer	Enraf-Nonius CAD4
monochromator	graphite, incident beam
scan type	ω scan
scan time, s	60 (max)
scan width, deg	(1.00 + 0.35 tan θ) ± 25% for bkgd cors
max 2θ, deg	50
no. of rflns measd	8301 (h, ±10; k, ±15; l, ±12)
no. of indep reflns	2096
cors	Lorentz–polarization, numerical abs (0.0206–0.0854), extinctn [ϵ refined to $\epsilon = 0.9468 \times 10^{-8}$ in (F_c(cor) = $F_c/(1 + \epsilon F_c^2 Lp)$)]
std reflns	3 every 3600 s, intensity check; 3 every 197 rflns, orientation check
(c) Refinement	
soln	Patterson method
H atoms	not found, calcd, included but not refined
refinement	full-matrix least squares
minimization function	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
weighting scheme	$1/\sigma(F_o)^2$
anomalous dispersion	all non-H atoms
no. of rflns included	2036 [$I \geq 1.0\sigma(I)$]
no. of params refined	137
R	0.030[a]
R_w	0.036[b]
goodness of fit	5.206[c]
shift/error	0.00

[a] $R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$. [b] $R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum wF_o^2]^{0.5}$. [c] GOF = $[\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(\mathrm{NO} - \mathrm{NV})]^{0.5}$.

Results and Discussion

The title compound (η^5-C_5Me_4Et)ReO_3 (**1**) is best prepared by the now well-established oxidation of the tricarbonyl (η^5-C_5Me_4Et)$Re(CO)_3$ with hydrogen peroxide in a two-phase benzene-water system.[2,4] It shows spectroscopic properties analogous to those of the prototypal pentamethylcyclopentadienyl derivative (η^5-C_5Me_5)ReO_3. The title compound crystallizes from dichloromethane/*n*-hexane at −30 °C as yellow crystals. The lattice contains discrete monomeric molecules without any significant intermolecular contacts. The molecular geometry along with the crystallographic numbering scheme is shown in Figure 1. The final atomic coordinates are listed in Table II. The interatomic distances and angles are given in Table III.

The coordination geometry around rhenium is best described as essentially pyramidal, if the five-membered hydrocarbon ring is considered as monodentate. Thus, the overall structure of **1** is that of a trioxorhenium fragment (three facially arranged oxygen atoms at rhenium) coordinating to an ethyltetramethylcyclopentadienyl ligand in a central η^5 fashion, resulting in a three-legged "piano stool" geometry.

The structural details of the trioxorhenium fragment very much resemble those encountered in a number of heptavalent rhenium coordination compounds containing three terminal oxo ligands in a facial arrangement (cf. Table IV). No direct oxygen–oxygen contacts are present, excluding the presence of a peroxide ligand,

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[†] Multiple Bonds between Main-Group Elements and Transition Metals. 48. Part 47: Herrmann, W. A.; Hecht, Ch.; Herdtweck, E. *J. Organomet. Chem.*, in press.

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Table II. Final Positional Parameters of the Title Compound **1** (Including Estimated Standard Deviations)

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Re	0.47653 (4)	0.20250 (3)	0.24075 (3)	2.817 (6)
O1	0.5668 (8)	0.3110 (6)	0.2036 (7)	5.8 (2)
O2	0.6045 (9)	0.1349 (7)	0.3328 (8)	7.6 (2)
O3	0.4658 (9)	0.1342 (6)	0.1059 (7)	6.2 (2)
C11	0.1951 (8)	0.1986 (6)	0.2357 (8)	2.7 (2)
C12	0.2401 (9)	0.3002 (6)	0.2616 (8)	2.8 (2)
C13	0.3158 (10)	0.3023 (7)	0.3827 (8)	2.8 (2)
C14	0.3166 (10)	0.2020 (8)	0.4267 (7)	2.6 (2)
C15	0.2443 (11)	0.1357 (7)	0.3351 (8)	2.6 (2)
C21	0.1110 (13)	0.1625 (8)	0.1185 (9)	4.5 (3)
C22	0.2102 (14)	0.3926 (9)	0.1847 (9)	4.8 (3)
C23	0.3822 (13)	0.3959 (9)	0.4433 (10)	5.0 (3)
C24	0.3831 (13)	0.1661 (9)	0.5459 (9)	4.7 (3)
C25	0.2265 (15)	0.0233 (9)	0.3449 (11)	4.9 (3)
C31	−0.0680 (13)	0.1676 (11)	0.1393 (10)	6.3 (3)
Cp[b]	0.2623	0.2277	0.3283	

[a] The equivalent isotropic parameters are defined as $B_{eq} = {}^4/_3[a^2B(11) + b^2B(22) + c^2B(33)]$. [b] Cp denotes the center of the ethyltetramethylcyclopentadienyl ligand.

Table III. Interatomic Distances (pm) and Angles (deg) and Their Standard Deviations

Re–O1	166.4 (4)	Re–C13	243.0 (4)
Re–O2	171.6 (4)	Re–C14	241.8 (3)
Re–O3	170.7 (3)	Re–C15	238.5 (4)
Re–C11	239.2 (3)	Re–Cp	207.5
Re–C12	239.2 (3)		
C11–C12	141.3 (5)	C12–C22	148.8 (6)
C12–C13	145.2 (5)	C13–C23	149.9 (6)
C13–C14	139.7 (6)	C14–C24	147.8 (6)
C14–C15	144.9 (6)	C15–C25	148.4 (6)
C15–C11	141.3 (5)	C21–C31	153.8 (7)
C11–C21	152.4 (6)		
O1–Re–O2	106.7 (2)	O1–Re–Cp	112.1
O1–Re–O3	105.6 (2)	O2–Re–Cp	112.1
O2–Re–O3	104.7 (2)	O3–Re–Cp	115.0
C15–C11–C12	108.7 (3)	C13–C14–C15	109.3 (3)
C11–C12–C13	108.3 (3)	C14–C15–C11	106.9 (4)
C12–C13–C14	106.8 (4)		
C15–C11–C21	125.7 (4)	C14–C13–C23	128.3 (4)
C12–C11–C21	125.6 (4)	C13–C14–C24	126.5 (4)
C11–C12–C22	127.7 (4)	C15–C14–C24	124.1 (4)
C13–C12–C22	123.9 (4)	C14–C15–C25	126.1 (4)
C12–C13–C23	124.9 (4)	C11–C15–C25	127.0 (4)
C11–C21–C31	109.3 (4)		

which would imply the formulation of **1** as (η^5-C_5Me_4Et)Re(O)(η^2-O_2), a complex of formally pentavalent rhenium. The O–Re–O angles are around 105°, with the sum of the three angles amounting to 317.0°. The rhenium–oxygen bond distances vary from 166.4 (4) to 171.6 (4) pm; they are fully consistent with typical double bonds.[5] Comparable complexes containing the ReO_3 fragment together with their pertinent structural features are listed in Table IV. No sensible discrimination can be made between the perrhenate anion with a Re–O bond order of $1^3/_4$[6] and the perrhenyl cation $[LReO_3]^+$ (L = c-$C_6H_{15}N_3$, 1,4,7-triazacyclononane) with a bond order of 2[12] solely on the basis of Re–O bond distances. Furthermore, the effect of additional ligands at the rhenium center is not clearly manifested in the Re–O bond distances. IR data on the $\nu(ReO_3)$ values are probably more informative. However, terminal Re–O bond lengths in a large

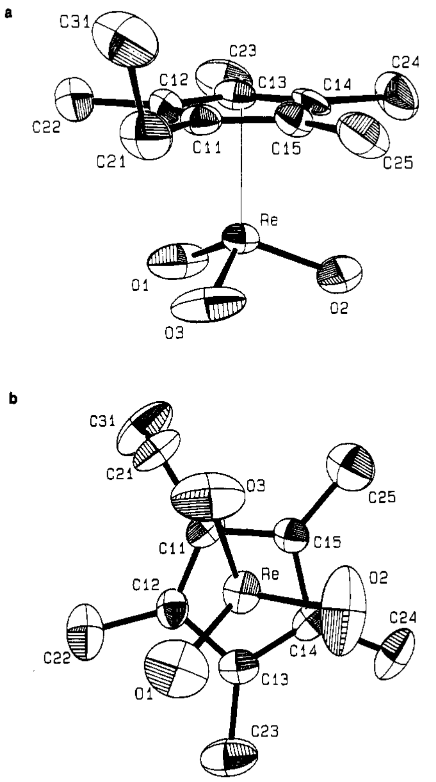

Figure 1. Two ORTEP representations of (η^5-C_5Me_4Et)ReO_3: (a) side view; (b) top view. Atoms are drawn with 50% probability thermal ellipsoids.

Table IV. Structural Features of Complexes Containing the *fac*-ReO_3 Unit

compd	coordn sphere around Re[a]	mean Re–O bond dist, pm	mean O–Re–O angle, deg	ref
(η^5-C_5Me_4Et)ReO_3	t	170	105	this work
$KReO_4$	t	172	110	6
$(Me_3SiO)ReO_3$	t	165	110	7
$Rb[SReO_3]$	t	173	108	8
$Re_2O_7(H_2O)_2$	t	174	109	9
	o	175	105	
$Re_2O_7(C_5H_5N)_2$	o	172	104	10
$Cs_2[Cl_3ReO_3]$	o	170	103	11
$[(c\text{-}C_6H_{15}N_3)ReO_3]Cl$	o	176	103	12

[a] Abbreviations: t = tetrahedral (pyramidal); o = octahedral.

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Table V. Distances between Ring-Carbon Atoms and Rhenium in Half-Sandwich Complexes

compd	oxidn state	mean C(ring)–Re bond dist, pm	ref
$(\eta^5\text{-}C_5Me_4Et)ReO_3$	7	240	this work
$(\eta^5\text{-}C_5Me_5)ReOCl_2$	5	232	14
trans-$(\eta^5\text{-}C_5H_5)Re(CO)_2H(CH_2Ph)$	3	229	15
trans-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Br_2$	3	231	16
cis-$(\eta^5\text{-}C_5Me_5)Re(CO)_2I_2$	3	230	16
$(\eta^5\text{-}C_5H_5)Re(NO)(CHO)(PPh_3)$	1	231	17
$(\eta^5\text{-}C_5H_4SiMe_3)Re(CO)_3$	1	230	18

number of pentavalent rhenium half-sandwich complexes of the general type $(\eta^5\text{-}C_5R_5)Re(O)(X)(Y)$ (X, Y = one-electron ligands) are significantly shorter. This is due to some partial triple-bond character of these bonds, their values being on the order of 165 pm.[2] Similarly, the rhenium-to-oxygen bond lengths in the Re(III) complexes $ReOI(MeC{\equiv}CMe)_2$ and $[ReO(MeC{\equiv}CMe)_2(NC_5H_5)][SbF_6]$ amount to 169.7 (3) and 169.2 (3) pm, respectively.[5] Therefore, a bond order of 2 can be safely assigned to the Re–O bond in **1**.

The coordination of the trioxorhenium fragment to the five-membered π-ligand is highly symmetric, if one neglects the presence of one ethyl group in place of a methyl group. The C–C bond distances within the ring are comparable to those in other transition-metal complexes containing the $\eta^5\text{-}C_5Me_4Et$ ligand, with an average value of 142.5 (5) pm, as are the other carbon–carbon bond lengths.[13] The ring is planar within 1 esd of an individual atomic distance (3.2 pm maximum deviation from planarity), while the methyl carbon atom C31 lies 147.5 pm out of the ring plane away from the rhenium atom. The Re–(C11–C15) bond distances are in the range 238.5 (4)–243.0 (4) pm, and the distance between the centroid and the rhenium center is 207.5 pm. The conformation is such that the Re–O1 bond is in a staggered position relative to the vector connecting C15 and the ring centroid. No tilt is observed between the $\eta^5\text{-}C_5Me_4Et$ ligand and the plane containing all three oxygen atoms. This feature is in sharp contrast to the slipped coordination of the C_5Me_5 ring ($\eta^3{:}\eta^2$ coordination instead of η^5) observed in all complexes of the type $(\eta^5\text{-}C_5R_5)Re(O)(X)(Y)$ due to the strong trans influence of the terminal oxo ligand.[19] However, the pronounced trans influence of the oxo ligands causes the overall bond distance of the C_5Me_4Et ligand to the rhenium center to be significantly greater than in any other structurally characterized half-sandwich complex of rhenium, regardless of the presence of ring substituents, of rhenium's oxidation state, and of the nature of additional ligands. A selection of representative examples are listed in Table V for the sake of comparison. While the average Re–C(ring) bond distance in **1** is 240.3 (3) pm, the corresponding values of other half-sandwich complexes of rhenium range between 229 and 232 pm. We believe that this bond lengthening results from a lack of back-bonding from the rhenium(VII) center, which is electronically saturated by the three strongly π-donating oxo ligands, to the five-membered ring ligand, leading to a somewhat more ionic bonding between the hydrocarbon ligand and the trioxorhenium fragment, ReO_3.[20] In addition, we note the absence of the bending back of the four methyl groups and the methylene group away from the rhenium center, a structural pecularity also resulting from the lack of any steric interactions of the ring ligand with the metal fragment. At present, we are searching for chemical evidence for this proposed bonding situation. One possibility might involve replacement of the five-membered ring by other anionic ligands such as CH_3^-, to give the known methyl derivative CH_3ReO_3.[21]

Experimental Part

(1) Tricarbonyl(η^5-ethyltetramethylcyclopentadienyl)rhenium(I). This compound was synthesized analogously to the method for $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ from $Re_2(CO)_{10}$ (Strem Chemicals) and 1-ethyl-2,3,4,5-tetramethylcyclopentadiene according to the procedure given by Gladysz et al.[22] The crude product was recrystallized from *n*-hexane as colorless crystals: yield 85%; mp 79 °C. ^{1}H NMR (270 MHz, C_6D_6, 28 °C, δ): 2.08 (q, 2 H; $^3J_{HH}$ = 7.7 Hz; CH_2CH$_3$), 1.75 (s, 6 H; 2 × CH$_3$), 1.71 (s, 6 H; 2 × CH$_3$), 0.75 (t, 3 H; $^3J_{HH}$ = 7.7 Hz; CH$_2$CH_3). ^{13}C NMR (60.8 MHz, C_6D_6, 28 °C, δ): 198.3 (*C*O); 103.6 (*C*CH$_2$CH$_3$); 98.7, 98.2 (*C*CH$_3$); 18.8 (*C*H$_2$CH$_3$); 16.7 (CH$_2$*C*H$_3$); 10.3, 10.1 (C*C*H$_3$). IR (*n*-hexane, cm^{-1}): 2014 s, 1923 vs [ν(CO)]. EI-MS (50 °C, 70 eV, *m/e*): 420 (M$^+$). Anal. Calcd for $C_{14}H_{17}O_3Re$: C, 40.09; H, 4.08. Found: C, 40.22; H, 4.06.

(2) Trioxo(η^5-ethyltetramethylcyclopentadienyl)rhenium(VII) (1). A mixture of $(\eta^5\text{-}C_5Me_4Et)Re(CO)_3$ (1.00 g, 2.38 mmol) in benzene (35 mL), concentrated sulfuric acid (0.5 mL), and aqueous hydrogen peroxide (30%, 25 mL) was refluxed for 7 h with vigorous stirring. After approximately 2 h the organic layer turned dark red and more hydrogen peroxide (5 mL) was added. The bluish aqueous layer was separated from the intensely yellow organic layer and extracted with toluene (3 × 5 mL). The combined extracts were washed with water and dried over anhydrous $MgSO_4$. The solvent was then removed in vacuo, and the crude product recrystallized at −25 °C from toluene/*n*-hexane (1/2) as bright yellow needles: yield 400 mg (44%); mp 145 °C. From the aqueous phase ca. 35% of the Re was recovered as $KReO_4$ by concentration and subsequent addition of excess potassium hydroxide. ^{1}H NMR (270 MHz, C_6D_6, 28 °C, δ): 2.17 (q, 2 H; $^3J_{HH}$ = 7.7 Hz; CH_2CH$_3$), 1.76 (s, 6 H, 2 × CH$_3$), 1.62 (s, 6 H, 2 × CH$_3$), 0.74 (t, 3 H; $^3J_{HH}$ = 7.7 Hz; CH$_2$CH_3). ^{13}C NMR (60.8 MHz, C_6D_6, 28 °C, δ): 122.0 (*C*CH$_2$CH$_3$); 120.0, 119.9 (*C*CH$_3$); 18.8 (*C*H$_2$CH$_3$); 13.2 (CH$_2$*C*H$_3$); 9.94, 9.68 (C*C*H$_3$). IR (KBr, cm^{-1}): 920 s [$\nu(ReO_3)_{sym}$], 887 vs [$\nu(ReO_3)_{asym}$], 405 m [$\delta(ReO_3)$]. EI-MS (70 °C, 70 eV, *m/e*): 384 (M$^+$). Anal. Calcd for $C_{11}H_{17}O_3Re$: C, 34.46; H, 4.47; O, 12.52; Re, 48.56. Found: C, 34.31; H, 4.47; O, 12.38; Re, 47.03.

(3) Crystal Structure Determinations. Crystal data and details of the X-ray diffraction experiments are reported in Table I. The compound, yellow crystals of which were grown by cooling techniques from *n*-hexane/dichloromethane solutions, crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19; systematic absences $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), $00l$ ($l = 2n + 1$)). Cell constants were obtained from least-squares refinement by using a set of 53 reflections in the range $40° \le 2\theta \le 50°$; the orientation matrix was determined by using a set of 25 reflections in the range $19° \le 2\theta \le 30°$. During data collection neither deorientation nor decay was detected. All crystallographic calculations were performed by using the program package STRUX II.[23] The Re atom was determined from the Patterson function. All remaining non-hydrogen atoms were located by successive structure factor calculations and difference Fourier maps. Hydrogen atoms were not found; their ideal positions were added to the calculations but were not refined. Refine-

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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.

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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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