Structural Characterization of the First Cyclotetramolybdenum Diynes with Bidentate Phosphines, $Mo_4Cl_4(\mu\text{-}Cl)_2(\mu\text{-}OMe)_2(\mu\text{-}dppm)_2$ and $Mo_4Cl_4(\mu_4\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OMe)_3(\mu\text{-}dmpm)_2$

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The first cyclotetramolybdenum diynes with bidentate phosphines, namely, $Mo_4Cl_4(\mu\text{-}Cl)_2(\mu\text{-}OMe)_2(\mu\text{-}dppm)_2$ (**1**) and $Mo_4Cl_4(\mu_4\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OMe)_3(\mu\text{-}dmpm)_2$ (**2**), have been synthesized by cycloaddition of $K_4Mo_2Cl_8$ in methanol followed by the reaction with dppm or dmpm ligand. The molecules of **1** reside on the crystallographic 2-fold axes in the centrosymmetric space group $C2/c$. The planar rectangular Mo_4 ring has bond lengths of 2.224(1) and 2.814(1) Å, which fall within the ranges established for Mo–Mo triple-, and single-bond distances, respectively. For compound **2**, there is an O atom capping the planar Mo_4 ring and the Mo–Mo bond distances are 2.449(3) and 2.452(3) Å for the short edges and 2.706(3) and 2.648(3) Å for the long edges of the rectangular unit. The arrangements of the Cl, OMe, and phosphine ligands are such as to give idealized C_{2v} symmetry in complex **1** and C_s symmetry in compound **2**. The crystal structures of **1** and **2** are fully described. Crystallographic data for these compounds are as follows: $\mathbf{1}\cdot 2C_6H_6$, monoclinic, space group $C2/c$, with $a = 27.180(6)$ Å, $b = 9.768(1)$ Å, $c = 26.553(4)$ Å, $\beta = 114.49(1)°$, $V = 6415(4)$ Å^3, $Z = 4$, $R = 0.0474$, and $R_w = 0.0761$; $\mathbf{2}\cdot C_6H_6\cdot C_4H_8O$ orthorhombic, space group $P2_12_12_1$, with $a = 13.895(4)$ Å, $b = 16.490(6)$ Å, $c = 18.181(4)$ Å, $V = 4166(4)$ Å^3, $Z = 4$, $R = 0.0526$, $R_w = 0.0616$.

Introduction

One of the interesting reactions discovered in quadruply bonded dinuclear compounds is the dimerization of compounds that contain Mo–Mo,[1–5] W–W,[6] Mo–W,[7] or Re–Re[8] quadruple bonds to form the rectangular cyclotetranuclear diynes. Pairs of dinuclear molecules undergo [2+2] cycloaddition by loss of the δ components to leave two triply bonded dimers which are joined together through two single bonds, and bridging ligands as well in most cases.[1–4,6–8] In $Mo_4(\mu\text{-}OMe)_2(\mu\text{-}OPr^i)_2(OPr^i)_8$,[5] where the starting dinuclear units have only triple bonds, the final M≡M units are joined only through the bridging ligands. Among the compounds of this type which have been reported in the literature, those with structure determinations are listed in Table I, and a total of five types of ligand arrangements have been observed as shown in Figure 1. The earliest example of such complexes was $Mo_4Cl_8(PEt_3)_4$, which was first reported and structurally characterized in 1978.[1] A recent structure re-examination has shown[4] the existence of subtle disorder in which 92% of the Mo_4 rectangles are in one orientation and 8% in an orientation perpendicular to the main one, but the originally reported molecular structure is qualitatively correct. Such a disorder was first reported to exist in the crystal structure of $Re_4Cl_8(\mu\text{-}O)_2(\mu\text{-}OMe)_2$,[8] where 3% of the Re_4 rectangles are in the second orientation which is perpendicular to the main one.

It will be noted that all complexes of this type reported in the literature contain only monodentate ligands. Using a synthetic technique modified from that used in the preparation of $Mo_4Cl_8(PR_3)_4$,[2,3] it has been possible to synthesize the first cyclotetramolybdenum diynes with bidentate phosphines, namely, $Mo_4Cl_4(\mu\text{-}Cl)_2(\mu\text{-}OMe)_2(\mu\text{-}dppm)_2$ (**1**) and $Mo_4Cl_4(\mu_4\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OMe)_3(\mu\text{-}dmpm)_2$ (**2**). The characterization of these compounds has been accomplished using X-ray crystallographic techniques and UV–vis spectroscopy.

Table I. Data for Cyclotetranuclear Diyne Complexes

complex	Mo–Mo(av), Å	ligand arrangement[a]	ref
$Mo_4Cl_8(PEt_3)_4$[b]	2.211(3), 2.901(2)	a	1, 4
$Mo_4Cl_8[P(OMe)_3]_4$	2.226(1), 2.878(1)	a	3
$W_4Cl_8(PBu^n{}_3)_4$	2.309(2), 2.840(1)	b	6
$Mo_2W_2Cl_8(PMe_3)_4$	2.275(1), 2.842(1)	b	7
$Mo_2W_2Cl_8(PBu_3)_4$	2.214(4), 2.904(3)	b	6
$Mo_4(\mu\text{-}OMe)_2(\mu\text{-}OPr^i)_2(OPr^i)_8$	2.238(1), 3.344(1)	c	5
$[Re_4Cl_8(\mu\text{-}OMe)_2(\mu\text{-}O)_2]^{2-}$[b]	2.261(1), 2.551(2)	d	8
$[Re_4Cl_8(\mu\text{-}OMe)(\mu\text{-}O)_2(\mu\text{-}Cl)]^{2-}$	2.246(2), 2.586(2)	e	8

[a] Refer to Figure 1. [b] Disordered structure.

Results and Discussion

Synthesis. Previously, several synthetic methods for the cyclotetramolybdenum complexes $Mo_4Cl_8(PR_3)_4$ (PR_3 = PEt_3, $PPr^n{}_3$, $PBu^n{}_3$, PMe_2Ph, $P(OMe)_3$) were available (eqs 1–4),[2,9,10]

$$2K_4Mo_2Cl_8 + 4PR_3 \xrightarrow[\text{reflux}]{\text{MeOH}} Mo_4Cl_8(PR_3)_4 + 8KCl \quad (1)$$

$$2Mo_2(O_2CCH_3)_4 + 8Me_3SiCl + 4PR_3 \xrightarrow[\text{reflux}]{\text{THF}} Mo_4Cl_8(PR_3)_4 + 8Me_3Si(O_2CCH_3) \quad (2)$$

$$2Mo_2(O_2CCH_3)_4 + 4AlCl_3 + 4PR_3 \xrightarrow[\text{reflux}]{\text{THF}} Mo_4Cl_8(PR_3)_4 + 4AlCl(O_2CCH_3)_2 \quad (3)$$

$$2Mo_2Cl_4(PR_3)_4 + 2Mo(CO)_6 \xrightarrow[\text{reflux}]{C_6H_5Cl} Mo_4Cl_8(PR_3)_4 + 2Mo(CO)_4(PR_3)_2 + 4CO \quad (4)$$

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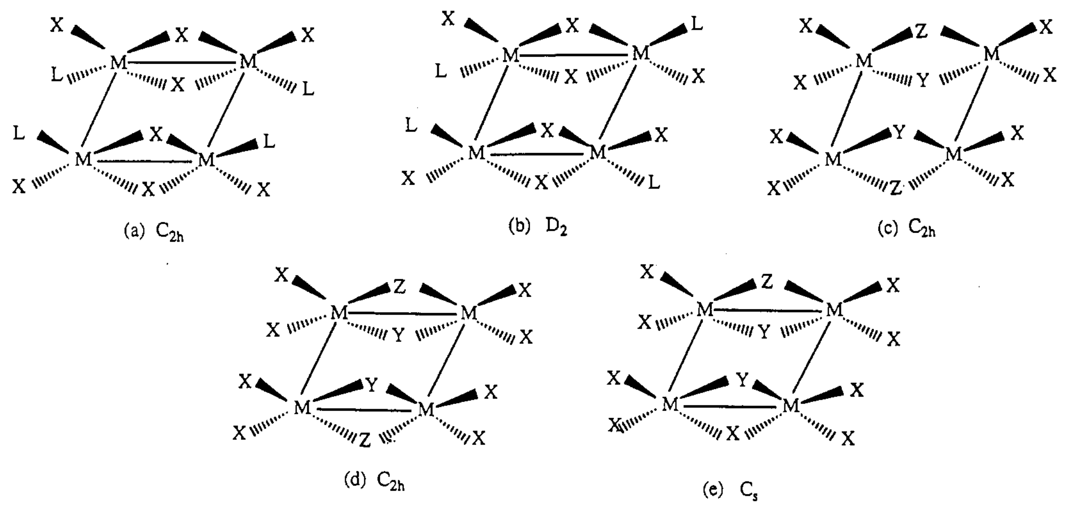

(a) C_{2h} (b) D_2 (c) C_{2h}

(d) C_{2h} (e) C_s

Figure 1. Ligand arrangements and geometries in rectangular cyclotetranuclear diynes.

all of which utilize quadruply bonded dimolybdenum(II) starting materials. A modified synthetic route was used for the preparation of the complex $Mo_4Cl_4(\mu\text{-}Cl)_2(\mu\text{-}OMe)_2(\mu\text{-}dppm)_2$ (**1**) where the starting quadruply bonded complex $K_4Mo_2Cl_8$ was first refluxed in MeOH for 24–36 h to give a brown-green solution, which further reacted with 1 equiv of dppm ligand to give the brown compound **1**. The absorption spectrum of the brown-green solution displays one strong absorption band at 415 nm but no distinct peak in the $\delta \rightarrow \delta^*$ transition region at *ca.* 500 –800 nm. Thus the reaction may be assumed to proceed according to eq 5.

$$\begin{array}{l} 2K_4Mo_2Cl_8 + 6MeOH \xrightarrow{\text{reflux 24–36 h}} \\ \quad Mo_4Cl_4(\mu\text{-}Cl)_2(\mu\text{-}OMe)_2(MeOH)_4 + 8KCl + 2HCl \qquad (5) \\ \quad \Big\downarrow \text{+ 2dppm (1:1)/reflux 3 h} \\ \quad Mo_4Cl_4(\mu\text{-}Cl)_2(\mu\text{-}OMe)_2(\mu\text{-}dppm)_2 + 4MeOH \\ \qquad \qquad \qquad \mathbf{1} \end{array}$$

Compound **1** was obtained as a brown solid in 35–40% yield. It is sparingly soluble in THF and CH_2Cl_2, and the absorption spectrum (THF solution) has shoulders around 460 and 630 nm on the absorption rising into the ultraviolet. Crystals of **1** were obtained after 2–3 weeks by slow diffusion of a benzene/hexanes mixture (v:v = 3:2) into the THF solution of the brown solid.

Although a compound with similar structure was expected for the cyclotetramolybdenum diyne with the dmpm ligand, prepared using the same synthetic route, brown $Mo_4Cl_4(\mu_4\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OMe)_3(\mu\text{-}dmpm)_2$ (**2**) was obtained but with lower yield (~10%), and a brown-green MeOH mother liquor was also obtained. Compound **2** is sparingly soluble in THF and CH_2Cl_2, and its absorption spectrum in THF has only a shoulder at 420 nm in the visible region. Crystals of **2** were obtained after 3 weeks by slow diffusion of hexanes into the THF/benzene (v:v = 5:2) solution of the brown solid. The absorption spectrum of the MeOH mother liquor has shoulders around 460, 600, and 800 nm, which indicates that there is probably no quadruply bonded complex in this MeOH solution. However, we have not been able to isolate or characterize a compound from this solution.

The reason for the formation of compound **2** instead of a compound analogous to **1** is not at this time understood. Probably the most likely cause of oxidation of Mo^{II} to Mo^{III} is the adventitious presence of dioxygen in the reaction mixture. A further study is required to clarify this aspect of the work, and will be carried out along with studies of some other examples we have encountered of unintended oxidations leading to the presence of μ_2- or μ_4-O atoms.

Table II. Crystallographic Data and Data Collection Parameters for **1** and **2**

formula	$Mo_4Cl_6P_4O_2C_{64}H_{62}$	$Mo_4Cl_7P_4O_5C_{23}H_{51}$
fw	1583.58	1163.49
space group (No.)	*C*2/*c* (15)	$P2_12_12_1$ (19)
a, Å	27.180(6)	13.895(4)
b, Å	9.768(1)	16.490(6)
c, Å	26.553(4)	18.181(4)
α, deg	(90)	(90)
β, deg	114.49(1)	(90)
γ, deg	(90)	(90)
V, Å^3	6415(4)	4166(4)
Z	4	4
ρ_{calc}, g cm^{-3}	1.64	1.855
μ(Mo Kα), cm^{-1}	11.39	17.853
λ, Å	0.710 73	0.710 73
T, °C	20 ± 1	–60 ± 1
transm coeff	0.998, 0.938	0.999, 0.913
$R(F_o)$,[a] $R_w(F_o)$[b]	0.0474, 0.0761	0.0526, 0.0616
quality-of-fit indicator[c]	1.694	1.459
largest peak, e/Å^3	0.468	0.869

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= \sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Structure and Bonding. Pertinent crystallographic information on the two new compounds that have been obtained is given in Table II. Tables III and IV list the positional and thermal parameters for complexes **1** and **2**, respectively.

Compound **1** crystallized in the space group *C*2/*c* with four molecules per unit cell, and the molecules reside on the crystallographic 2-fold axes. Figure 2 displays the ORTEP diagrams of one molecule viewed from different directions. The four Mo atoms form two long and two short Mo–Mo bonds and define a rectangle. The Mo–Mo bond distances are 2.224(1) Å for the short edges and 2.814(1) Å for the long ones. Each long Mo–Mo bond is bridged by one methoxy group and one Cl atom, while each short Mo–Mo bond is bridged by one dppm ligand. All the Mo–P bonds are trans to the bridging Mo–OMe bonds, which may be a result of the trans effect of the methoxy group versus the Cl atom. The Mo–O–Mo and Mo–Cl–Mo bridging angles are all acute. These acute angles and the Mo–Mo bond distance of 2.814(1) Å indicate the existence of a Mo–Mo single bond, and the bond distance is also consistent with those observed in the edge-sharing bioctahedral dimolybdenum complexes.[11,12] The short Mo–Mo bond distance, 2.224(1) Å, is in agreement

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Table III. Positional and Isotropic Equivalent Thermal Parameters and Their Estimated Standard Deviations for $Mo_4Cl_4(\mu\text{-}Cl)_2(\mu\text{-}OMe)_2(\mu\text{-}dppm)_2{\cdot}2C_6H_6$ (**1**)

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Mo(1)	0.42860(2)	0.73687(7)	0.21051(3)	2.88(2)
Mo(2)	0.47360(2)	0.73784(7)	0.30212(3)	2.84(2)
Cl(1)	0.46701(7)	0.5446(2)	0.18401(9)	3.34(5)
Cl(2)	0.35530(9)	0.8966(3)	0.1833(1)	5.77(9)
Cl(3)	0.42920(9)	0.9101(2)	0.3323(1)	5.01(8)
P(1)	0.36068(7)	0.5525(2)	0.20573(8)	2.61(5)
P(2)	0.42226(7)	0.5432(2)	0.32801(8)	2.69(5)
O(1)	0.4691(2)	0.8950(7)	0.1875(3)	4.1(2)
C(1)	0.3929(3)	0.4355(8)	0.2649(3)	2.9(2)
C(2)	0.4648(5)	1.024(1)	0.1806(6)	7.2(5)
C(3)	0.2944(3)	0.5888(8)	0.2060(3)	3.2(2)
C(4)	0.2515(3)	0.5009(9)	0.1769(4)	3.7(2)
C(5)	0.2031(3)	0.5163(9)	0.1827(4)	4.3(3)
C(6)	0.1991(3)	0.6137(9)	0.2194(4)	4.2(3)
C(7)	0.2419(3)	0.7005(9)	0.2468(4)	4.1(3)
C(8)	0.2896(3)	0.6886(9)	0.2393(3)	3.5(2)
C(9)	0.3444(3)	0.4432(9)	0.1451(3)	3.2(2)
C(10)	0.3255(4)	0.513(1)	0.0950(4)	5.2(3)
C(11)	0.3143(5)	0.433(1)	0.0458(5)	7.0(4)
C(12)	0.3201(5)	0.291(1)	0.0490(4)	6.0(4)
C(13)	0.3390(4)	0.226(1)	0.0988(4)	5.5(3)
C(14)	0.3507(3)	0.304(1)	0.1478(4)	4.2(3)
C(15)	0.4675(3)	0.4267(9)	0.3812(3)	3.2(2)
C(16)	0.4636(4)	0.287(1)	0.3773(4)	4.7(3)
C(17)	0.5002(5)	0.205(1)	0.4200(4)	5.9(3)
C(18)	0.5389(5)	0.269(1)	0.4661(4)	6.3(4)
C(19)	0.5426(4)	0.407(1)	0.4713(4)	5.1(3)
C(20)	0.5069(4)	0.489(1)	0.4283(4)	4.6(3)
C(21)	0.3693(3)	0.5665(9)	0.3534(3)	3.3(2)
C(22)	0.3304(3)	0.460(1)	0.3435(4)	4.9(3)
C(23)	0.2907(4)	0.480(1)	0.3643(4)	5.6(3)
C(24)	0.2900(4)	0.595(1)	0.3930(4)	5.4(3)
C(25)	0.3298(4)	0.696(1)	0.4039(4)	5.3(3)
C(26)	0.3693(3)	0.681(1)	0.3832(3)	3.8(2)
C(27)	0.147(2)	0.481(2)	0.5302(9)	26.2(7)*
C(28)	0.181(2)	0.414(2)	0.5114(9)	26.2(7)*
C(29)	0.165(2)	0.290(2)	0.4826(9)	26.2(7)*
C(30)	0.114(2)	0.235(2)	0.4726(9)	26.2(7)*
C(31)	0.080(2)	0.303(2)	0.4914(9)	26.2(7)*
C(32)	0.096(2)	0.426(2)	0.5202(9)	26.2(7)*

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. Starred values indicate that atoms were refined isotropically.

with those known for compounds with Mo–Mo triple bonds.[9] Therefore we can describe this Mo_4 ring as a metallacyclobutadiyne. Each Mo atom is also coordinated by a terminal Cl atom, and thus it is tetracoordinated (ignoring the direct Mo–Mo bonding).

The Mo–P bond distances in complex **1**, 2.544(2) and 2.613(2) Å, are typical for this type of compound. Selected bond distances and angles are listed in Table V.

Crystals of compound **2** conform to the space group $P2_12_12_1$ with four molecules per unit cell. Figure 3 displays the ORTEP diagrams of one molecule viewed from two different directions. There is an O atom capping the Mo_4 rectangular ring. Each of the two short edges, with Mo(1)–Mo(2) = 2.449(3) Å and Mo(3)–Mo(4) = 2.452(3) Å, is now bridged by one dmpm ligand and one methoxy group. One of the long edges, Mo(2)–Mo(3) = 2.648(3) Å, is bridged by a Cl atom and a methoxy group, while the other is bridged by two Cl atoms. Here each Mo atom is also coordinated by one terminal Cl atom, and thus it is hexacoordinate for each Mo center, if we ignore the direct Mo–Mo bonding in this complex, instead of tetracoordinate, as observed in most of the other cyclotetranuclear diynes. The formal oxidation state of each Mo atom is +3 instead of +2 as in complex **1**.

Table IV. Positional and Isotropic Equivalent Thermal Parameters and Their Estimated Standard Deviations for $Mo_4Cl_4(\mu_4\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OMe)_3(\mu\text{-}dmpm)_2{\cdot}C_4H_8O{\cdot}C_6H_6$ (**2**)

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Mo(1)	0.0349(1)	0.4427(1)	0.5124(1)	2.56(4)
Mo(2)	0.1436(1)	0.4886(1)	0.6099(1)	2.54(4)
Mo(3)	0.1323(1)	0.3449(1)	0.6743(1)	2.38(4)
Mo(4)	0.0278(1)	0.2943(1)	0.5757(1)	2.37(4)
Cl(1)	−0.0892(4)	0.5008(4)	0.4338(4)	4.4(1)
Cl(2)	0.1783(5)	0.6131(4)	0.6754(4)	4.3(1)
Cl(3)	0.1504(5)	0.3241(4)	0.8067(3)	4.1(1)
Cl(4)	−0.1011(4)	0.1945(4)	0.5621(4)	4.2(2)
Cl(14)	0.0223(5)	0.3141(3)	0.4413(3)	3.3(1)
Cl(23)	0.2818(4)	0.4252(4)	0.6760(4)	3.9(1)
Cl(41)	−0.0982(4)	0.3969(3)	0.5901(3)	3.3(1)
P(1)	0.1412(5)	0.4882(4)	0.4077(4)	3.6(1)
P(2)	0.2721(4)	0.5428(4)	0.5236(4)	3.3(1)
P(3)	0.2448(4)	0.2259(4)	0.6722(3)	2.9(1)
P(4)	0.1360(5)	0.1752(4)	0.5434(4)	3.3(1)
O	0.145(1)	0.3723(7)	0.5600(6)	2.0(3)
O(12)	0.035(1)	0.5535(7)	0.5636(7)	2.7(3)
O(23)	0.0573(9)	0.4506(8)	0.6984(8)	2.6(3)
O(34)	0.016(1)	0.2700(9)	0.6868(8)	3.6(4)
C(1)	0.141(2)	0.424(2)	0.324(1)	6.3(7)
C(2)	0.110(2)	0.590(2)	0.371(2)	5.4(7)
C(3)	0.268(2)	0.493(2)	0.433(1)	4.5(6)
C(4)	0.268(2)	0.654(1)	0.509(1)	4.5(6)
C(5)	0.399(2)	0.528(1)	0.553(1)	4.2(6)
C(6)	0.370(2)	0.245(2)	0.704(1)	5.0(7)
C(7)	0.207(2)	0.143(1)	0.732(1)	4.8(6)
C(8)	0.257(2)	0.187(1)	0.578(1)	3.2(5)
C(9)	0.089(2)	0.076(1)	0.575(2)	5.5(7)
C(10)	0.153(2)	0.157(2)	0.445(2)	6.0(8)
C(11)	−0.047(2)	0.595(1)	0.600(1)	3.5(5)
C(12)	0.025(2)	0.490(2)	0.762(1)	4.5(6)
C(13)	−0.066(2)	0.278(1)	0.733(1)	3.9(6)*
O(1)	−0.439(2)	0.372(1)	0.729(1)	8.9(7)*
C(14)	−0.117(3)	0.344(2)	0.946(2)	8(1)*
C(15)	−0.181(2)	0.378(2)	0.998(2)	8(1)*
C(16)	−0.160(3)	0.368(2)	1.069(2)	12(1)*
C(17)	−0.091(2)	0.317(2)	1.085(2)	7.4(9)*
C(18)	−0.379(3)	0.445(2)	0.731(2)	8.0(9)*
C(19)	−0.287(2)	0.409(2)	0.762(2)	6.9(8)*
C(20)	−0.310(2)	0.327(2)	0.794(2)	6.9(8)*
C(21)	−0.398(3)	0.305(2)	0.757(2)	8.2(9)*
C(22)	−0.037(3)	0.286(2)	1.038(2)	8.2(9)*
C(23)	−0.046(3)	0.298(2)	0.965(2)	8.0(9)*

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. Starred values indicate that atoms were refined isotropically.

Selected bond distances and angles for compound **2** are listed in Table VI. The average Mo–P distance is 2.528(7) Å. The average Mo–Cl_t bond distance (2.437(6) Å) formed with the terminal Cl atoms is only slightly shorter than the average Mo–Cl_b distance (2.468(6) Å) formed with the bridging Cl ligand. The variation in the Mo–O bond distances is such that the Mo–O bonds formed with the bridging methoxy groups (average 2.06(1) Å) are about 0.06 Å shorter than those formed with the capping O atom (average 2.12(1) Å). All the Mo–O–Mo and Mo–Cl–Mo bridging angles are acute. It may be noted that the bridging Mo–O_b–Mo angle on the long edge Mo(2)–Mo(3) (78.6(5)°) is about 5° larger than the bridging angles on the short edges (average Mo–O_b–Mo = 73.5(5)°). The bridging Mo–Cl_b–Mo angles are the smallest, with an average of 66.0(2)°.

Previously five types of isomeric forms of cyclotetranuclear diynes have been structurally characterized as shown in Figure 1 and Table I. In the two new molybdenum compounds reported here, the ligand arrangement in compound **1** displays an idealized C_{2v} symmetry, with two mirrors perpendicularly bisecting the two long edges or the two short edges of the rectangle. The ligand arrangement in complex **2** has an idealized C_s symmetry, with the mirror defined by the capping O atom, the three bridging Cl atoms, and the O atom of one of the bridging methoxy groups.

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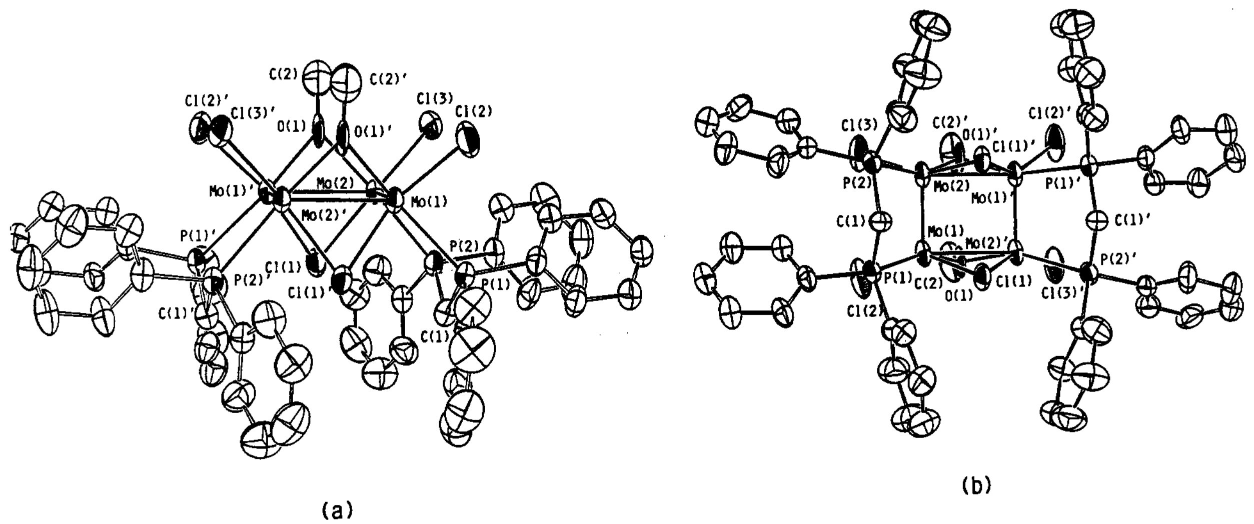

Figure 2. ORTEP diagrams of complex 1: (a) side view; (b) top view. Thermal ellipsoids are drawn at the 50% probability level.

Table V. Selected Bond Distances (Å) and Angles (deg) for $Mo_4Cl_4(\mu\text{-}Cl)_2(\mu\text{-}OMe)_2(\mu\text{-}dppm)_2{\cdot}2C_6H_6$ (1)[a]

Distances			
Mo(1)-Mo(2)	2.224(1)	Mo(1)-O(1)	2.128(7)
Mo(1)-Mo(2)′	2.814(1)	Mo(2)-Cl(1)	2.410(2)
Mo(1)-Cl(1)	2.392(2)	Mo(2)-Cl(3)	2.394(3)
Mo(1)-Cl(2)	2.394(2)	Mo(2)-P(2)	2.613(2)
Mo(1)-P(1)	2.544(2)	Mo(2)-O(1)	2.121(6)

Angles			
Mo(2)-Mo(1)-Mo(2)′	90.69(3)	Mo(1)-Mo(2)-Cl(1)	101.16(6)
Mo(2)-Mo(1)-Cl(1)	102.47(5)	Mo(1)-Mo(2)-Cl(3)	104.13(7)
Mo(2)-Mo(1)-Cl(2)	109.81(9)	Mo(1)-Mo(2)-P(2)	99.97(5)
Mo(2)-Mo(1)-P(1)	96.67(5)	Mo(1)-Mo(2)-O(1)	100.7(2)
Mo(2)-Mo(1)-O(1)	101.3(2)	Mo(1)′-Mo(2)-Cl(1)	53.82(6)
Mo(2)-Mo(1)-Cl(1)	54.44(5)	Mo(1)′-Mo(2)-Cl(3)	132.41(7)
Mo(2)-Mo(1)-Cl(2)	132.13(8)	Mo(1)′-Mo(2)-P(2)	131.51(5)
Mo(2)-Mo(1)-P(1)	134.29(6)	Mo(1)′-Mo(2)-O(1)	48.6(2)
Mo(2)′-Mo(1)-O(1)	48.4(2)	Cl(1)-Mo(2)-Cl(3)	153.86(9)
Cl(1)-Mo(1)-Cl(2)	146.41(9)	Cl(1)-Mo(2)-P(2)	77.71(7)
Cl(1)-Mo(1)-P(1)	79.97(7)	Cl(1)-Mo(2)-O(1)	97.9(2)
Cl(1)-Mo(1)-O(1)	98.3(2)	Cl(3)-Mo(2)-P(2)	91.44(9)
Cl(2)-Mo(1)-P(1)	87.16(8)	Cl(3)-Mo(2)-O(1)	83.8(2)
Cl(2)-Mo(1)-O(1)	84.6(2)	P(2)-Mo(2)-O(1)	159.3(2)
P(1)-Mo(1)-O(1)	161.9(2)	Mo(1)-Cl(1)-Mo(2)	71.75(6)
Mo(1)-Mo(2)-Mo(1)′	89.31(4)	Mo(1)-O(1)-Mo(2)	82.9(2)

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

Experimental Section

All syntheses, manipulations, and spectroscopic studies were carried out under an atmosphere of nitrogen unless otherwise specified. Standard Schlenk and vacuum line techniques were used. Commercial grade solvents were dried and deoxygenated by refluxing at least 24 h over appropriate reagents and freshly distilled prior to use. THF, benzene, and hexanes were purified by distillation from potassium/sodium benzophenone ketyl, and methanol was purified by distillation from magnesium methoxide.

Bis(dimethylphosphino)methane (dmpm) and bis(diphenylphosphino)methane ligands were purchased from Strem Chemicals. The former was diluted to 1.0 g of dmpm in 5 mL of hexanes (1.47 M solution), and the latter was used as received. $K_4Mo_2Cl_8$[13] was prepared according to a published procedure. The UV–vis data were collected on a Cary 17-D spectrometer. Analyses were carried out by Galbraith Laboratories, Inc.

Preparation of $Mo_4Cl_4(\mu\text{-}Cl)_2(\mu\text{-}OMe)_2(\mu\text{-}dppm)_2$ (1). A 0.20-g sample (0.31 mmol) of $K_4Mo_2Cl_8$ was suspended in 50 mL of methanol in a 100 mL three-neck flask equipped with a reflux condenser. This mixture was refluxed for 24–36 h to give a brown-green solution. A 0.12-g amount of the dppm ligand (0.31 mmol) was added, and the solution was refluxed for an additional 3 h to give a brown solid and a brown solution. The solid was filtered off, washed with 2 × 10 mL of acetone and 2 x 30 mL of diethyl ether, and vacuum-dried overnight. Yield: 35–40%. Anal. Calc for $Mo_4Cl_6P_4O_2C_{52}H_{50}$: C, 43.57; H, 3.53. Found: C, 42.30; H, 3.32. UV–vis spectrum in THF: 460 (sh), 630 nm (sh).

Crystals of 1 were obtained by slow diffusion of a benzene/hexanes (6:4) mixture into the THF solution of the brown solid.

Preparation of $Mo_4Cl_4(\mu_4\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OMe)_3(\mu\text{-}dmpm)_2$ (2). A 0.20-g sample (0.31 mmol) of $K_4Mo_2Cl_8$ was suspended in 50 mL of methanol in a 100-mL three-neck flask equipped with a reflux condenser. This mixture was refluxed for 24–36 h to give a brown-green solution. A 0.21-mL solution of dmpm in hexanes (1.47 M, 0.31 mmol of dmpm ligand) was added, and the solution was refluxed for an additional 4 h to give a brown solid and a brown-green solution. This solid was filtered off, washed with 2 × 30 mL of diethyl ether, and dried under reduced pressure overnight. Yield: 10%. Anal. Calc for $Mo_4Cl_7P_4O_4C_{13}H_{37}$: C, 15.40; H, 3.68. Found: C, 14.91; H, 3.70. UV–vis spectrum in THF: 420 nm (sh).

Crystals of 2 were obtained from slow diffusion of hexanes into the THF/benzene (5:2) solution of the brown solid.

X-ray Crystallography. General Procedure. Single-crystal diffraction experiments were conducted on a Syntex P3 or an Enraf-Nonius CAD-4 automated diffractometer using Mo Kα radiation. Routine unit cell identification and intensity data collection procedures were followed utilizing the options specified in Table I and the general procedures previously described.[14] Lattice dimensions and Laue symmetry were verified using axial photographs. Three standard reflections were measured periodically during data collections to monitor any gain or loss in intensity or change of the crystal orientation.

The structures of 1 and 2 were determined by a general procedure that has been fully described elsewhere.[14] Data reduction was carried out by standard methods with the use of well-established computational procedures.[15] The computations were done with Enraf-Nonius SDP and SHELX-76 software on the VAX computer. The structure factors were obtained after a Lorentz and polarization correction. Empirical absorption corrections based on azimuthal (ψ) scans of reflections with Eulerian angle χ near 90° were applied to all the data.[16] Pertinent crystallographic information on both structures is given in Table II. Tables III and IV list the positional and thermal parameters for complexes 1 and 2, respectively. Tables V and VI list the selected bond distances and angles for each of the structures. Tables of anisotropic thermal parameters and complete tables of bond distances and angles are available as supplementary material.

Compound 1. A brown block crystal of dimensions of 0.40 × 0.40 × 0.30 mm was protected with a 1:1 mixture of mother liquor and deoxygenated mineral oil in a Lindemann capillary. Indexing based on

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(15) Crystallographic computing on compounds 1 and 2 was done on a local area VAX cluster employing the VAX/VMS V5.4 computer.

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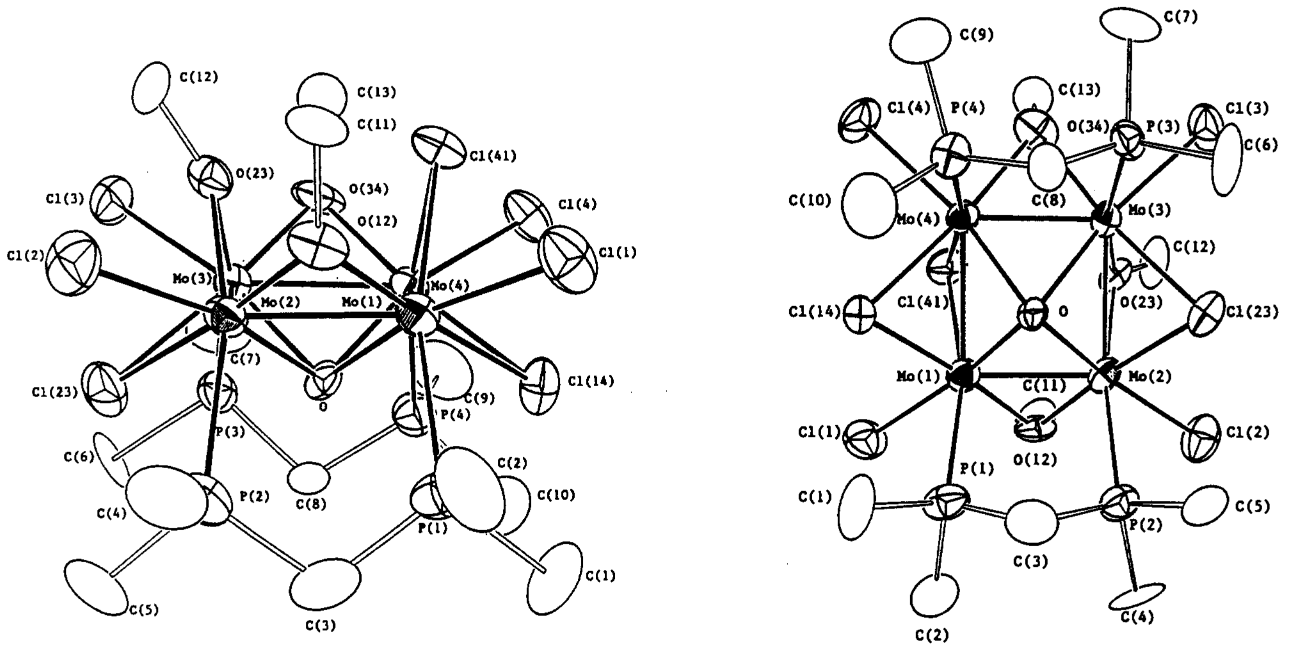

(a) (b)

Figure 3. ORTEP diagrams of complex 2: (a) side view; (b) top view. Thermal ellipsoids are drawn at the 50% probability level.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $Mo_4Cl_4(\mu_4\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OMe)_3(\mu\text{-}dmpm)_2 \cdot C_4H_8O \cdot C_6H_6$ (**2**)[a]

Distances							
Mo(1)–Mo(2)	2.449(3)	Mo(2)–O(23)	2.10(1)	Mo(1)–O(12)	2.05(1)	Mo(3)–O(34)	2.04(1)
Mo(1)–Mo(4)	2.706(3)	Mo(3)–Mo(4)	2.452(3)	Mo(2)–Mo(3)	2.648(3)	Mo(4)–Cl(4)	2.445(6)
Mo(1)–Cl(1)	2.436(7)	Mo(3)–Cl(3)	2.445(6)	Mo(2)–Cl(2)	2.421(6)	Mo(4)–Cl(14)	2.467(6)
Mo(1)–Cl(14)	2.490(6)	Mo(3)–Cl(23)	2.464(6)	Mo(2)–Cl(23)	2.494(6)	Mo(4)–Cl(41)	2.448(6)
Mo(1)–Cl(41)	2.447(6)	Mo(3)–P(3)	2.509(6)	Mo(2)–P(2)	2.539(7)	Mo(4)–P(4)	2.542(7)
Mo(1)–P(1)	2.523(7)	Mo(3)–O	2.13(1)	Mo(2)–O	2.12(1)	Mo(4)–O	2.10(1)
Mo(1)–O	2.11(1)	Mo(3)–O(23)	2.08(1)	Mo(2)–O(12)	2.03(1)	Mo(4)–O(34)	2.07(1)
Angles							
Mo(2)–Mo(1)–Mo(4)	89.65(8)	Cl(1)–Mo(1)–P(1)	81.7(2)	Mo(2)–Mo(3)–O(23)	51.1(4)	Cl(23)–Mo(3)–O(23)	88.2(4)
Mo(2)–Mo(1)–Cl(1)	137.7(2)	Cl(1)–Mo(1)–O	166.4(4)	Mo(2)–Mo(3)–O(34)	129.6(4)	Cl(23)–Mo(3)–O(34)	171.4(4)
Mo(2)–Mo(1)–Cl(14)	133.1(2)	Cl(1)–Mo(1)–O(12)	85.2(4)	Mo(4)–Mo(3)–Cl(3)	137.1(2)	P(3)–Mo(3)–O	95.7(4)
Mo(2)–Mo(1)–Cl(41)	98.2(2)	Cl(14)–Mo(1)–Cl(41)	89.1(2)	Mo(4)–Mo(3)–Cl(23)	133.7(2)	P(3)–Mo(3)–O(23)	166.3(4)
Mo(2)–Mo(1)–P(1)	95.4(2)	Cl(14)–Mo(1)–P(1)	84.4(2)	Mo(4)–Mo(3)–P(3)	95.3(2)	P(3)–Mo(3)–O(34)	91.2(4)
Mo(2)–Mo(1)–O	54.9(3)	Cl(14)–Mo(1)–O	78.2(4)	Mo(4)–Mo(3)–O	53.9(4)	O–Mo(3)–O(23)	94.0(5)
Mo(2)–Mo(1)–O(12)	52.8(4)	Cl(14)–Mo(1)–O(12)	174.1(4)	Mo(4)–Mo(3)–O(23)	98.2(4)	O–Mo(3)–O(34)	107.6(5)
Mo(4)–Mo(1)–Cl(1)	125.4(2)	Cl(41)–Mo(1)–P(1)	165.9(2)	Mo(4)–Mo(3)–O(34)	53.8(4)	O(23)–Mo(3)–O(34)	95.0(6)
Mo(4)–Mo(1)–Cl(14)	56.5(1)	Cl(41)–Mo(1)–O	98.2(4)	Cl(3)–Mo(3)–Cl(23)	88.6(2)	Mo(1)–Mo(4)–Mo(3)	88.97(8)
Mo(4)–Mo(1)–Cl(41)	56.5(1)	Cl(41)–Mo(1)–O(12)	90.8(4)	Cl(3)–Mo(3)–P(3)	80.8(2)	Mo(1)–Mo(4)–Cl(4)	126.3(2)
Mo(4)–Mo(1)–P(1)	127.7(2)	P(1)–Mo(1)–O	92.7(4)	Cl(3)–Mo(3)–O	168.5(4)	Mo(1)–Mo(4)–Cl(14)	57.3(1)
Mo(4)–Mo(1)–O	49.8(4)	P(1)–Mo(1)–O(12)	94.4(4)	Cl(3)–Mo(3)–O(23)	87.8(4)	Mo(1)–Mo(4)–Cl(41)	56.4(1)
Mo(4)–Mo(1)–O(12)	127.8(4)	O–Mo(1)–O(12)	107.7(5)	Cl(3)–Mo(3)–O(34)	83.5(4)	Mo(1)–Mo(4)–P(4)	125.4(2)
Cl(1)–Mo(1)–Cl(14)	88.9(2)	Mo(1)–Mo(2)–Mo(3)	90.39(8)	Cl(23)–Mo(3)–P(3)	84.0(2)	Mo(1)–Mo(4)–O	50.1(4)
Cl(1)–Mo(1)–Cl(41)	85.7(2)	Mo(1)–Mo(2)–Cl(2)	137.8(2)	Mo(1)–Mo(4)–O(34)	126.5(4)	Cl(14)–Mo(4)–O(34)	172.8(4)
Mo(1)–Mo(2)–Cl(23)	133.9(2)	Cl(2)–Mo(2)–O(23)	89.4(4)	Mo(3)–Mo(4)–Cl(4)	137.4(2)	Cl(41)–Mo(4)–P(4)	168.9(2)
Mo(1)–Mo(2)–P(2)	95.4(2)	Cl(23)–Mo(2)–P(2)	84.5(2)	Mo(3)–Mo(4)–Cl(14)	134.2(2)	Cl(41)–Mo(4)–O	98.5(4)
Mo(1)–Mo(2)–O	54.4(4)	Cl(23)–Mo(2)–O	79.6(4)	Mo(3)–Mo(4)–Cl(41)	96.3(2)	Cl(41)–Mo(4)–O(34)	88.5(4)
Mo(1)–Mo(2)–O(12)	53.5(4)	Cl(23)–Mo(2)–O(12)	172.6(4)	Mo(3)–Mo(4)–P(4)	94.7(2)	P(4)–Mo(4)–O	89.0(4)
Mo(1)–Mo(2)–O(23)	96.3(4)	Cl(23)–Mo(2)–O(23)	86.9(4)	Mo(3)–Mo(4)–O	55.3(3)	P(4)–Mo(4)–O(34)	97.0(4)
Mo(3)–Mo(2)–Cl(2)	123.6(2)	P(2)–Mo(2)–O	92.6(4)	Mo(3)–Mo(4)–O(34)	52.9(4)	O–Mo(4)–O(34)	108.2(5)
Mo(3)–Mo(2)–Cl(23)	57.2(1)	P(2)–Mo(2)–O(12)	94.6(4)	Cl(4)–Mo(4)–Cl(14)	88.1(2)	Mo(1)–Cl(14)–Mo(4)	66.2(1)
Mo(3)–Mo(2)–P(2)	129.0(2)	P(2)–Mo(2)–O(23)	168.2(4)	Cl(4)–Mo(4)–Cl(41)	87.2(2)	Mo(2)–Cl(23)–Mo(3)	64.6(2)
Mo(3)–Mo(2)–O	51.7(3)	O–Mo(2)–O(12)	107.8(5)	Cl(4)–Mo(4)–P(4)	83.7(2)	Mo(1)–Cl(41)–Mo(4)	67.1(2)
Mo(3)–Mo(2)–O(12)	127.6(4)	O–Mo(2)–O(23)	93.7(5)	Cl(4)–Mo(4)–O	165.7(4)	Mo(1)–O–Mo(2)	70.8(4)
Mo(3)–Mo(2)–O(23)	50.3(4)	O(12)–Mo(2)–O(23)	92.9(5)	Cl(4)–Mo(4)–O(34)	84.9(4)	Mo(1)–O–Mo(3)	117.1(6)
Cl(2)–Mo(2)–Cl(23)	88.0(2)	Mo(2)–Mo(3)–Mo(4)	90.94(9)	Cl(14)–Mo(4)–Cl(41)	89.6(2)	Mo(1)–O–Mo(4)	80.1(5)
Cl(2)–Mo(2)–P(2)	82.3(2)	Mo(2)–Mo(3)–Cl(3)	123.7(2)	Cl(14)–Mo(4)–P(4)	83.8(2)	Mo(2)–O–Mo(3)	77.0(4)
Cl(2)–Mo(2)–O	167.0(4)	Mo(2)–Mo(3)–Cl(23)	58.3(2)	Cl(14)–Mo(4)–O	78.9(4)	Mo(2)–O–Mo(4)	119.2(6)
Cl(2)–Mo(2)–O(12)	84.5(4)	Mo(2)–Mo(3)–P(3)	131.0(2)	Mo(3)–O–Mo(4)	70.8(4)	Mo(2)–O(23)–Mo(3)	78.6(5)
Mo(2)–Mo(3)–O	51.3(3)	Cl(23)–Mo(3)–O	80.0(4)	Mo(1)–O(12)–Mo(2)	73.7(4)	Mo(3)–O(34)–Mo(4)	73.3(5)

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

25 reflections with 2θ values ranging from 20 to 31° resulted in a monoclinic cell. Diffraction data were collected, via 2θ–ω scan motion, at 20°C on a Syntex P3 equivalent diffractometer using Mo Kα radiation. The space group was determined to be *C*2/*c* or *Cc* from the systematic absences in the data. The centrosymmetric space group *C*2/*c* was selected for the initial refinement, and this choice proved satisfactory.

The direct methods program in SHELXS-86[17] led to the location of the positions of two Mo atoms on a tetragonal skeleton. The use of alternating difference Fourier maps and least-squares refinements gave the positions of all the remaining non-hydrogen atoms. After all the non-hydrogen atoms had been refined anisotropically to convergence, the difference Fourier map revealed six significant peaks which appeared to be a benzene molecule. This molecule was then refined with a rigid-body model in program SHELX-76 to convergence. The high thermal parameters suggest that there may be only partial occupancy, but we chose to leave things as they were at this point rather than to introduce and juggle another arbitrary parameter. The final residuals are listed in Table II. The largest peak on a difference Fourier map following the final refinement had a density of about 0.5 e/Å^3.

Compound 2. A brown crystal of dimensions 0.15 × 0.15 × 0.10 mm was mounted with epoxy cement on the tip of a quartz fiber and kept at −60 °C during the data collection. An accurate cell was determined from 25 reflections ranging from 17 to 25°. Data collection was carried out using an ω-scan motion on an Enraf-Nonius CAD-4 automated diffractometer equipped with graphite-monochromated Mo Kα radiation. There was no observable decay during the data collection. The space group $P2_12_12_1$ was obtained from the systematic absences in the data. After averaging of the equivalent reflections, 3261 unique data remained.

The positions of the heavy atoms were determined by the direct methods program in SHELXS-86. A series of full-matrix least-squares refinements followed by difference Fourier maps revealed the positions of all the other non-hydrogen atoms. All non-hydrogen atoms were then refined anisotropically to convergence. The difference Fourier map subsequently revealed the positions of atoms of one THF molecule and one benzene molecule, which were refined isotropically to convergence in SDP. The other enantiomorph was then refined to convergence and it was found to give significantly higher R values. The final refinement figures are listed in Table II.

Acknowledgment. Financial support from the National Science Foundation is appreciated.

Supplementary Material Available: Full lists of crystallographic data, bond distances, bond angles, and anisotropic thermal parameters (15 pages). Ordering information is given on any current masthead.

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