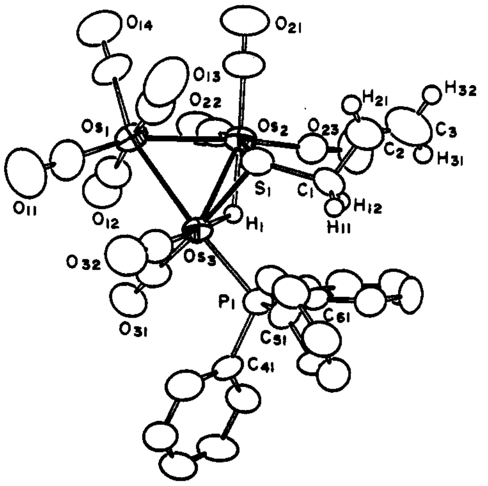

**Figure 5.** ORTEP diagram of $Os_3(CO)_9[\mu\text{-}SCH_2CH{=}CH_2](PPh_3)(\mu\text{-}H)$, 7, showing 50% probability thermal ellipsoids.

(3) Å is typical of a C–C double bond.

The ring-opening transformation of the thietane ligand in 1 to produce a thiametallacycle is in agreement with the results of our previous studies of triosmium complexes containing alkyl- and aryl-substituted thietane ligands.[5,7,8,10] Interestingly, these reactions seem to differ from the principal transformations of thietane on metal surfaces.[12a] Jensen and co-workers[24] recently observed that thietane undergoes a ring-opening S–C oxidative addition followed by C–Cl reductive elimination in its reaction with $Pd_2(\mu\text{-}Cl)_2Cl_2(PMe_3)_2$ to yield the complex $Pd_2Cl_2(\mu\text{-}Cl)(PMe_3)_2[\mu\text{-}SCH_2CH_2CH_2Cl]$.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Office of Basic Energy Sciences of the U.S. Department of Energy for support of this research.

**Supplementary Material Available:** Tables of hydrogen atom positional parameters and anisotropic thermal parameters for compounds 2, 4, and 8 (9 pages). Ordering information is given on any current masthead page. Supplemental data for compounds 1 and 6 were submitted previously.[4]

OM920029E

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# Synthesis and Chemistry of a Molybdenum Carbonyl Phosphinite Complex Containing a Ditopic Macrocyclic Ligand with Chelating Phosphorus-Donor and Crown Ether Characteristics

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The reaction of 1,3-bis(chlorophenylphosphino)propane with triethylene glycol in THF in the presence of $NEt_3$, using high-dilution conditions, gives a mixture of phosphinite products (as assessed by $^{31}P\{^1H\}$ NMR), one of which is the hybrid phosphinite macrocycle *meso*-11,15-diphenyl-1,4,7,10-tetraoxa-11,15-diphosphacyclopentadecane, $[15]P_2O_4$. This ligand was isolated as its "$Mo(CO)_4P_2$ complex" by reacting the mixture of phosphinite products with $Mo(CO)_4$(norbornadiene) under high-dilution conditions. Chromatographic workup of the products gave the complex *cis*-$Mo(CO)_4\{[15]P_2O_4\}$ in an overall yield of 15–20%. The structure of this complex has been determined by single-crystal X-ray diffraction analysis. Addition of RLi reagents (R = Me, Ph, $^n$Bu, $^t$Bu, $NEt_2$, $N^iPr_2$) to this complex gives products of the type *fac*-$Mo(CO)_3(RCOLi)\{[15]P_2O_4\}$ in which the $Li^+$ ion is encapsulated by the five oxygens of the RCO and $[15]P_2O_4$ ligands. The structure of *fac*-$Mo(CO)_3(MeCOLi)\{[15]P_2O_4\}$ has been determined by single-crystal X-ray analysis. A comparison of the relative rate of hydrolysis of $Mo(CO)_3(PhCOLi)P_2$ in wet THF solution to give LiOH + $C_6H_6$ + *cis*-$Mo(CO)_4P_2$ $\{P_2 = [15]P_2O_4$ and $Ph_2P(OCH_2CH_2)_3OPPh_2\}$ shows that the benzoylate complex in which $Li^+$ is encapsulated by the $[15]P_2O_4$ ligand is the more inert. The structure of *fac*-$[Mo(CO)_3Br\{[15]P_2O_4\}]Li$ is also reported.

## Introduction

A simple approach to the synthesis of heterodinuclear complexes containing low-oxidation-state transition metals and cations of groups 1A and 2A involves the synthesis of ditopic ligands which combine a subunit containing a "soft" binding site with one bearing a "hard" site.[1-8] Of particular relevance are hybrid P-donor crown ether ligands that combine a crown ether or cryptand functionality with one or more P-donor groups and the possible effect(s) that the presence of a proximal class 1A/2A cation may have on the reactivity of ligands coordinated to the transition metal. Recently we have described the synthesis of a range of ditopic $\alpha,\omega$-bis(diphenylphosphinite) polyether ligands and their amino analogues [e.g., $P_2\supset$ = $Ph_2POCH_2$-

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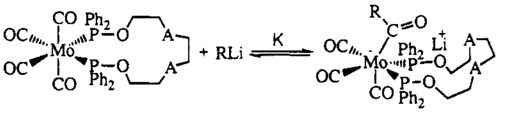
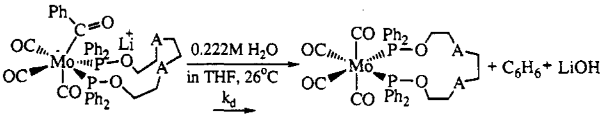
$(CH_2ACH_2)_nCH_2OPPh_2$ (A = O, NMe; $n$ = 1–4); $Ph_2PO(CH_2)_3A(CH_2)_3OPPh_2$ (A = O, NMe), etc.].[4-6] The cis chelation of these ligands to group 6 metal carbonyls gave metal–crown ether complexes of the type *cis*-$M(CO)_4(P_2\supset)$ (M = Cr, Mo, W) in which M is incorporated into the crown ether backbone. While $M(CO)_4(PR_3)_2$ complexes are unreactive toward RLi reagents,[9] the addition of RLi to a coordinated carbonyl group in these metal–crown ether complexes gave acylate/benzoylate complexes *fac*-$M(CO)_3(RCOLi)(P_2\supset)$ whose stabilities are determined by the ease of formation and degree of "preferential $Li^+$ cation binding" observed (e.g., **2**, eq 1). In particular, it



1 A = O, NMe 2

(1)

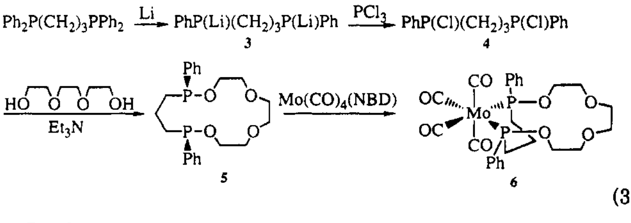
was found that metalla-12-crown-3, -13-crown-4 (e.g., **2**), and -14-crown-4 complexes were particularly stable as assessed by $K$ (eq 1) and $k_d$ values for the reaction of benzoylate complexes with $H_2O$ in THF (eq 2).[4] However,



2a A = O
2b A = NMe
1

(2)

while long-chain $\alpha,\omega$-bis(diphenylphosphinite) polyether ditopic ligands can be successfully complexed in a cis manner to substitutionally inert 18-electron metal complexes to generate chemically interesting metal–crown ether systems, the extension of this approach to substitutionally labile complexes requires further structural modification to the ditopic ligand. For example, the ligand $Ph_2POCH_2(CH_2OCH_2)_2CH_2OPPh_2$ {which is the precursor to the 13-crown-4 complex **1**} reacts with $Rh_2Cl_2(CO)_4$ to give the complex *trans*-$[Rh_2Cl_2(CO)_2\{Ph_2POCH_2(CH_2OCH_2)_2CH_2OPPh_2\}_2]$ and reacts with $Pt_2Cl_4(C_2H_4)_2$ to give *cis*-$Pt_2Cl_4\{Ph_2POCH_2(CH_2OCH_2)_2CH_2OPPh_2\}_2$, complexes which contain 26-atom rings rather than the desired 13-crown-4 structure.[10] A suitably modified ligand that should be capable of providing strong $Li^+$ binding in acyl/benzoyl complexes of substitutionally labile systems is the cis-chelating macrocyclic ligand *meso*-11,15-diphenyl-1,4,7,10-tetraoxa-11,15-diphosphapentadecane, $[15]P_2O_4$ (see compound **5**, eq 3). This ligand will maintain a *cis*-diphosphorus donor geometry and its complexes will have a 13-atom metal–crown ether ring regardless of the substitutional lability of the metal atom.



(3)

In this paper we report the synthesis and a single-crystal X-ray diffraction analysis of the complex *cis*-$Mo(CO)_4\{[15]P_2O_4\}$ and a brief study of its reactions with RLi reagents. The X-ray diffraction analyses of the complexes *fac*-$Mo(CO)_3(CH_3COLi)\{[15]P_2O_4\}\cdot 2CH_2Cl_2$ and *fac*-$[Mo(CO)_3Br\{[15]P_2O_4\}]Li\cdot CH_2Cl_2$ are also included.

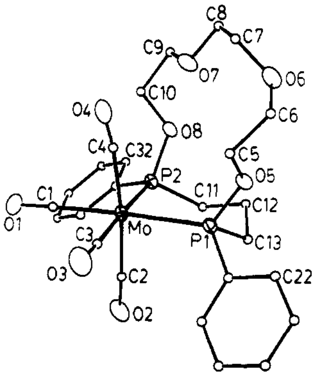


**Figure 1.** View of *cis*-$Mo(CO)_4\{[15]P_2O_4\}$ (**6**). Thermal ellipsoids for P, Li, Mo, and O atoms are drawn at the 25% probability level. C atoms have been assigned radii of arbitrary size.

## Results and Discussion

**Synthesis of the Ligand and Its Molybdenum Complex.** The synthesis of *cis*-$Mo(CO)_4\{[15]P_2O_4\}$, **6**, was carried out as shown in eq 3 without isolation or purification of the macrocyclic ligand $[15]P_2O_4$ (compound **5**). Issleib and Bottcher[11] have reported the preparation of 1,3-bis(chlorophenylphosphino)propane (**4**) by starting with $PhP(H)(CH_2)_3P(H)Ph$, treated with Li to cleave the P–H bond. The resultant dilithium diphosphide was then converted to **4** in 60% yield. We, however, have used $Ph_2P(CH_2)_3PPh_2$ as the starting material, as it is cheaper and easier to handle than $PhP(H)(CH_2)_3P(H)Ph$. Reaction of $Ph_2P(CH_2)_3PPh_2$ with lithium ribbon under ultrasound irradiation results in an efficient cleavage of Ph–P bonds[12,13] to yield the dilithium salt $PhP(Li)CH_2CH_2P(Li)Ph$, **3**. While $^tBuCl$ has been previously used to destroy the PhLi produced in this type of reaction,[12] we have found separation of the dilithium salt via crystallization to give more satisfactory results. The dilithium diphosphide salt **3** was treated with $PCl_3$ to give the dichloride **4**.[11] The overall yield for these two steps was 80%, and **4** was characterized by $^1H$ and $^{31}P\{^1H\}$ NMR. The dichloride **4** was reacted with a stoichiometric amount of triethylene glycol in dry THF in the presence of $Et_3N$ using high-dilution conditions to favor the formation of the crown ether $[15]P_2O_4$, **5**. Removal of $[Et_3NH]Cl$, by filtration, and the solvent gave an oily residue which, by $^{31}P\{^1H\}$ NMR, was a mixture of at least three major products. Besides the anticipated meso macrocycle $[15]P_2O_4$ (**5**), other products could be its racemic isomer and oligomeric phosphinito derivatives. Attempts to date to obtain a satisfactory separation of $[15]P_2O_4$ from this mixture have not proved successful. However, by reacting the mixture of phosphinito products with $Mo(CO)_4$(norbornadiene) in $CH_2Cl_2$, followed by a column chromatographic workup, it was possible to isolate **6** as colorless crystals with an overall yield of 20% based on the starting dichloride **4**. Complex **6** was characterized by IR, $^1H$ and $^{31}P\{^1H\}$ NMR, MS, and a single-crystal X-ray diffraction study (Figure 1).

Molecular models suggest that the racemic isomer of $[15]P_2O_4$ cannot form a monomeric *cis*-$Mo(CO)_4P_2$ complex owing to ring stain effects, and it is presumed that this ligand gives dimeric or polymeric products.

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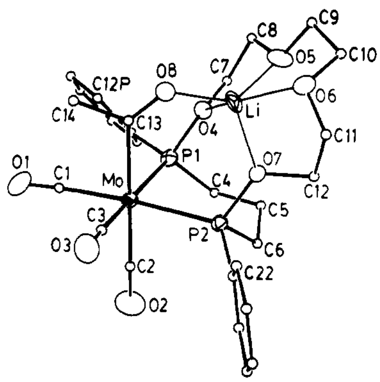


**Figure 2.** View of *fac*-$Mo(CO)_3(MeCOLi)\{[15]P_2O_4\}$ (**7b**).

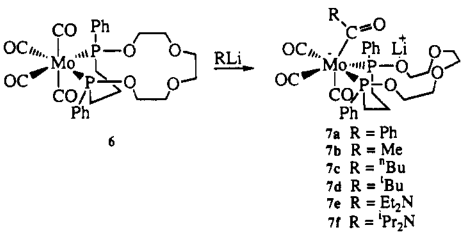
**Table I. IR Data for the Complexes *fac*-$Mo(CO)_3(RCOLi)\{[15]P_2O_4\}$ (7)**

| complex | R | ν(CO), $cm^{-1}$ in $CH_2Cl_2$ soln | | |
|---|---|---|---|---|
| **7a** | Ph | 1935 | 1850 | 1813 |
| **7b** | Me | 1934 | 1857 | 1811 |
| **7c** | $^nBu$ | 1932 | 1857 | 1811 |
| **7d** | $^tBu$ | 1927 | 1856 | 1802 |
| **7e** | $NEt_2$ | 1929 | 1851 | 1794 |
| **7f** | $N^iPr_2$ | 1928 | 1849 | 1792 |

**Table II. Pseudo-First-Order Rate Constant Data for the Reaction of Lithium Benzoylates with $H_2O$ (0.222 M) in THF (26 °C) (Eq 2)**

| complex | $k_{obs}$, $s^{-1}$ | rel *k'* | ref |
|---|---|---|---|
| **7a** | $2.8 \times 10^{-5}$ | 8 | this work |
| **2a** | $4.0 \times 10^{-3}$ | 1200 | 4 |
| **2b** | $3.4 \times 10^{-6}$ | 1 | 4 |

**Reactions of *cis*-$Mo(CO)_4\{[15]P_2O_4\}$.** As expected on the basis of previous studies[4] (e.g., eq 1), the complex *cis*-$Mo(CO)_4\{[15]P_2O_4\}$ reacted with various RLi reagents (R = Ph, Me, $^nBu$, $^tBu$, $NEt_2$, $N^iPr_2$) in THF or benzene to give *fac*-$Mo(CO)_3(RCOLi)\{[15]P_2O_4\}$, **7** (eq 4). These



(4)

6

7a R = Ph
7b R = Me
7c R = $^nBu$
7d R = $^tBu$
7e R = $Et_2N$
7f R = $^iPr_2N$

complexes were characterized primarily by the similarity of their IR spectrum (ν(CO) region) to those of complexes such as **2** (see Table I)[4] and by a single-crystal X-ray diffraction study of the acyl complex **7b** (see Figure 2).

We have previously shown that the relative stability of benzoylate complexes such as **2** can be ascertained from a comparison of their pseudo-first-order rate constants $k_d$ for hydrolysis by 0.222 M $H_2O$ in THF at 26 °C to give "$Mo(CO)_4P_2$", LiOH, and benzene (e.g., eq 2).[4] Table II compares these rate constants for complex **7a** containing the macrocyclic $[15]P_2O_4$ ligand with the complexes **2a,b** containing structurally similar metal–crown ethers derived from α,ω-diphosphinite ligands. As expected, the $[15]P_2O_4$ system **7a** is more stable than the α,ω-$P_2O_4$ system **2a** but not quite as stable as the "α,ω-$P_2O_2N_2$" system **2b**.

We have previously reported that **1** (A = O, eq 1), reacts with LiBr in refluxing toluene to give *fac*-$[Mo(CO)_3Br\{Ph_2POCH_2(CH_2OCH_2)_2CH_2OPPh_2\}]Li$ as a highly insoluble product.[4] The high insolubility suggested a polymeric solid-state structure. In contrast, reaction of **6** with LiBr in refluxing toluene gave *fac*-$[Mo(CO)_3Br\{[15]P_2O_4\}]Li$ (**8**, eq 5) as a pale yellow solid which was readily recrystallized from dichloromethane and structurally characterized by single-crystal X-ray diffraction (Figure 3).

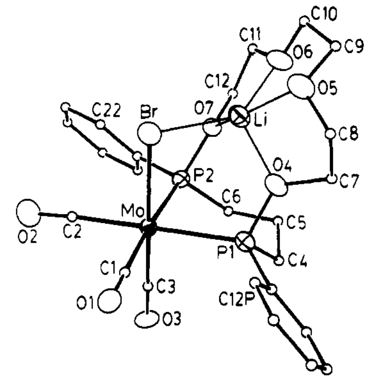
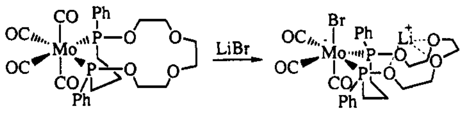


**Figure 3.** View of *fac*-$[Mo(CO)_3Br\{[15]P_2O_4\}]Li$ (**8**).

**Table III. Summary of Crystal Data for $Mo(CO)_4\{[15]P_2O_4\}$ (6), $Mo(CO)_3(MeCOLi)\{[15]P_2O_4\}$ (7b), and $[Mo(CO)_3Br\{[15]P_2O_4\}]Li$ (8)**

| | | | |
|---|---|---|---|
| compd | 6 | 7b·2[$CH_2Cl_2$] | 8·$CH_2Cl_2$ |
| empirical formula | $C_{25}H_{28}O_8MoP_2$ | $C_{26}H_{31}O_8LiMoP_2$ | $C_{24}H_{28}BrO_7LiMoP_2$ |
| $M_r$ | 614.4 | 806.2 | 758.2 |
| crystal class | triclinic | monoclinic | orthorhombic |
| space group | $P\bar{1}$ | $P2_1/n$ | *Pbca* |
| *a*, Å | 8.5638 (8) | 8.854 (2) | 14.508 (2) |
| *b*, Å | 10.7393 (12) | 18.943 (5) | 18.663 (3) |
| *c*, Å | 15.8444 (19) | 20.690 (14) | 23.129 (6) |
| α, deg | 109.206 (10) | | |
| β, deg | 98.148 (10) | 90.54 (3) | |
| γ, deg | 96.783 (9) | | |
| *V*, $Å^3$ | 1340.9 (3) | 3470 (3) | 6262.5 (2) |
| *Z* | 2 | 4 | 8 |
| $D_{calc}$, g $cm^{-3}$ | 1.52 | 1.54 | 1.61 |
| μ(Mo Kα), $cm^{-1}$ | 6.4 | 8.1 | 19.8 |
| *F*(000) | 628 | 1640 | 3040 |
| ω scan width, deg | 0.6 + 0.35 tan θ | 0.85 + 0.35 tan θ | 0.6 + 0.35 tan θ |
| range θ collected, deg | 1–27 (±*h*,±*k*,*l*) | 1–20 (±*h*,*k*,*l*) | 1–25 (*h*,*k*,*l*) |
| total no. reflns | 5837 | 3480 | 5498 |
| no. unique reflns | | 3236 | |
| $R_{int}$ | | 0.055 | |
| no. obsd data [$I>3\sigma(I)$] | 5391 | 2563 | 2826 |
| weighting *g* | 0.000 80 | 0.0239 | 0.000 23 |
| *R* | 0.023 | 0.089 | 0.036 |
| $R_w$ | 0.028 | 0.110 | 0.036 |
| goodness of fit | 1.24 | 0.994 | 1.65 |
| largest Δ/σ | 0.003 | 0.18 | 0.023 |
| paramrs refined | 326 | 265 | 352 |
| max density in Δ*F* map, e/$Å^3$ | 0.47 | 0.97 | 0.60 |



(5)

6

8

**Molecular Structures of $Mo(CO)_4\{[15]P_2O_4\}$ (6), $Mo(CO)_3(MeCOLi)\{[15]P_2O_4\}$ (7b), and $[Mo(CO)_3Br\{[15]P_2O_4\}]Li$ (8).** The molecular structures of **6**, **7b**, and **8** are shown in Figures 1–3. The structure of **6** confirms the synthesis of the $[15]P_2O_4$ ligand. The "$MoP_2C_3$ ring" adopts a chair conformation, and the four oxygen atoms of the metal–crown ether ring are all in relatively close proximity to one of the axial carbonyl ligands. Relatively minor reorganization is required on going to the acyl derivative **7b**. The $Li^+$ coordination environment in **7b** ap-

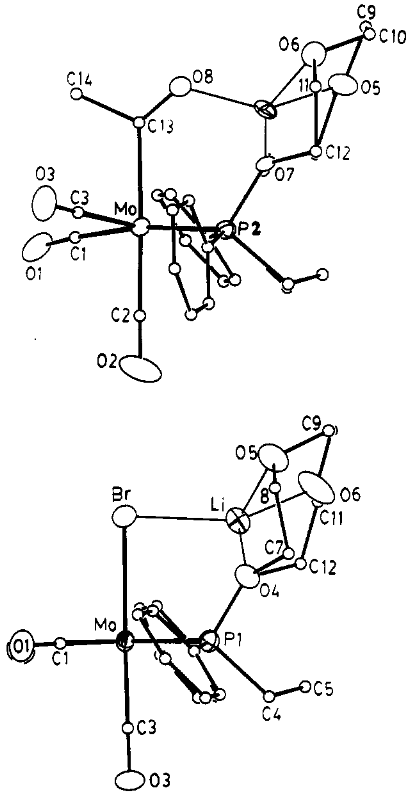


**Figure 4.** Comparison of the $Li^+$ coordination geometries of **7b** and **8** as viewed along the P···P axis.

proximates a square pyramid in which the shortest $Li^+$···O interaction is to the apical acyl oxygen. As previously observed for the structurally similar compound $Mo(CO)_3(PhCOLi)\{Ph_2POCH_2(CH_2OCH_2)_2CH_2OPPh_2\}$, **2a**,[1,14] there is some asymmetry in the bonding of the ligand ether oxygens (Li···O distances 1.95 and 2.23 Å in **7b** and 2.05 and 2.20 Å in **2a**). The significant rotation of the phenyl groups on going from **6** to **7b** or **8** probably reflects the conformational changes in the metal–crown ether ring and attempts to minimize intraligand repulsions.

A question of interest with respect to the structure of **8** was whether or not the $Li^+$ ion would coordinate to the axial bromide ligand or with the π-electrons of the axial carbonyl ligand. The observed structure clearly indicates a distinct Br···$Li^+$ interaction (2.48 Å). A comparison of the structures of **7b** and **8** (Figure 4) shows very little change in the coordination geometry of the lithium ion, though the asymmetry in the $Li^+$···ether oxygen bonding is less in **8** (2.06 and 2.13 Å). The more symmetrical nature of the bonding in **8** *vis-à-vis* **7b** is also apparent in the BrMoP angles of **8** (89 and 91°) compared to the C(acyl)MoP angles of **7b** (87 and 97°). Encapsulation of $Li^+$ on going from **6** to **7b** or **8** results in a slight decrease of PMoP from 87 to 83° together with a reduction in MoPO from 120 to ca. 111°. It should be noted that the presence of the "$P(CH_2)_3P$" linkage in **8** prevents the formation of a polymeric structure of the type envisaged for $[Mo(CO)_3Br\{Ph_2POCH_2(CH_2OCH_2)_2CH_2OPPh_2\}]Li$.[4]

Current research is aimed at isolating the $[15]P_2O_4$ ligand in reasonable yield and extending our studies of cooperativity effects to kinetically labile transition-metal $[15]P_2O_4/Li^+$ systems.

**Table IV. Positional and Thermal Parameters and Their Esd's for $Mo(CO)_4\{[15]P_2O_4\}$ (6)**

| atom | *x* | *y* | *z* | $U_{eq}$,[a] Å$^2$ |
|---|---|---|---|---|
| Mo | 0.11411 (1) | 0.21417 (1) | 0.31007 (1) | 0.03029 (9) |
| P1 | 0.29688 (5) | 0.13025 (4) | 0.20085 (1) | 0.03334 (21) |
| P2 | 0.30267 (5) | 0.16226 (4) | 0.42574 (1) | 0.03129 (20) |
| O1 | −0.10974 (18) | 0.33457 (16) | 0.44449 (11) | 0.0593 (9) |
| O2 | 0.32496 (21) | 0.50519 (14) | 0.38388 (12) | 0.0651 (10) |
| O3 | −0.11338 (22) | 0.28608 (20) | 0.16631 (12) | 0.0838 (12) |
| O4 | −0.14502 (18) | −0.05201 (15) | 0.24658 (12) | 0.0623 (9) |
| O5 | 0.28150 (15) | −0.02928 (11) | 0.14526 (8) | 0.0413 (6) |
| O6 | 0.19084 (19) | −0.31394 (14) | 0.10822 (11) | 0.0613 (9) |
| O7 | 0.10610 (18) | −0.22572 (12) | 0.28713 (9) | 0.0510 (7) |
| O8 | 0.29366 (14) | 0.00887 (11) | 0.42444 (8) | 0.0396 (6) |
| C1 | −0.02702 (19) | 0.28988 (17) | 0.39767 (12) | 0.0379 (8) |
| C2 | 0.25258 (23) | 0.39954 (18) | 0.35587 (12) | 0.0427 (9) |
| C3 | −0.02742 (24) | 0.26033 (20) | 0.21732 (12) | 0.0483 (10) |
| C4 | −0.04451 (21) | 0.03754 (18) | 0.26902 (13) | 0.0429 (9) |
| C5 | 0.13154 (25) | −0.10703 (18) | 0.09151 (15) | 0.0512 (11) |
| C6 | 0.1552 (3) | −0.24778 (18) | 0.04602 (14) | 0.0513 (11) |
| C7 | 0.0541 (3) | −0.36891 (20) | 0.13381 (14) | 0.0574 (12) |
| C8 | 0.0959 (3) | −0.36038 (19) | 0.23038 (15) | 0.0576 (12) |
| C9 | 0.13606 (26) | −0.20887 (18) | 0.38010 (14) | 0.0490 (10) |
| C10 | 0.15081 (23) | −0.06301 (18) | 0.43451 (12) | 0.0447 (9) |
| C11 | 0.51305 (19) | 0.18653 (18) | 0.41775 (12) | 0.0405 (9) |
| C12 | 0.54859 (20) | 0.10312 (19) | 0.32584 (12) | 0.0436 (9) |
| C13 | 0.50913 (20) | 0.15999 (18) | 0.25046 (12) | 0.0420 (9) |
| C21 | 0.31169 (21) | 0.19973 (17) | 0.11041 (12) | 0.0410 (9) |
| C22 | 0.35526 (29) | 0.12428 (21) | 0.02993 (14) | 0.0612 (12) |
| C23 | 0.3815 (3) | 0.18085 (27) | −0.03487 (16) | 0.0736 (15) |
| C24 | 0.36656 (29) | 0.31204 (26) | −0.01998 (16) | 0.0727 (14) |
| C25 | 0.3238 (3) | 0.38752 (22) | 0.05829 (17) | 0.0649 (13) |
| C26 | 0.29511 (25) | 0.33010 (18) | 0.12281 (14) | 0.0521 (11) |
| C31 | 0.31764 (19) | 0.25789 (16) | 0.54692 (11) | 0.0360 (8) |
| C32 | 0.39065 (27) | 0.21008 (20) | 0.61142 (13) | 0.0526 (11) |
| C33 | 0.4074 (3) | 0.28358 (24) | 0.70400 (14) | 0.0660 (14) |
| C34 | 0.3542 (3) | 0.40342 (23) | 0.73139 (14) | 0.0591 (12) |
| C35 | 0.28405 (24) | 0.45217 (19) | 0.66792 (13) | 0.0487 (10) |
| C36 | 0.26606 (21) | 0.38010 (17) | 0.57544 (12) | 0.0395 (8) |

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

## Experimental Section

$^1H$ and $^{31}P\{^1H\}$ NMR spectra were recorded on Varian Gemini 200 and XL-200 spectrometers. Chemical shifts for P are referenced to 85% $H_3PO_4$. Infrared spectra were recorded on a Nicolet 10DX, Fourier transform infrared spectrometer. MS spectra were taken on a VG 70-250S mass spectrometer. Fast atom bombardment ionization method was used when Xe atoms accelerated to 8 keV. A laboratory ultrasound cleaner was used for ultrasonic irradiation (Bransonic 220, Branson Cleaning Equipment Co., Shelton, CT). All reactions were carried out under a nitrogen atmosphere. Dichloromethane was distilled from $P_2O_5$; triethylamine was distilled over $LiAlH_4$; diethyl ether, tetrahydrofuran, and benzene were distilled from sodium benzophenone ketyl. The bis(diphenylphosphino)propane was purchased from Strem Chemicals. Trichlorophosphine was purchased from BDH Chemicals Ltd. and distilled before use. Phenyllithium and methyllithium solutions were purchased from Aldrich Chemical Co. and standardized with diphenylacetic acid prior to use. $Mo(CO)_4$(2,5-norbornadiene) was prepared by a published method.[15]

**1,3-Bis(chlorophenylphosphino)propane (4).** To a solution of 40.0 g (0.097 mol) of bis(diphenylphosphino)propane in 400 mL of THF was added 6.72 g (0.97 mol) of freshly cut lithium metal ribbon. The mixture was ultrasonically irradiated at 0 °C for 4 h. During the irradiation, the yellow dilithium salt $PhP(Li)CH_2CH_2CH_2(Li)PPh$ began to precipitate out. The unreacted lithium metal was removed and the reaction mixture heated until all the solid dissolved. The solution was concentrated under vacuum to about 250 mL and left in the freezer overnight. The precipitated dilithium salt was collected by filtration and dried

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(15) Werner, J.; Prinz, R. *Chem. Ber.* **1967**, *100*, 265.

**Table V. Selected Bond Distances (Å) and Bond Angles (deg) for $Mo(CO)_4\{[15]P_2O_4\}$ (6)**

| | | | | | |
|---|---|---|---|---|---|
| | | Bond Distances | | | |
| Mo–P1 | 2.5163 (5) | P2–O8 | 1.633 (1) | O6–C7 | 1.418 (3) |
| Mo–P2 | 2.5146 (5) | P2–C11 | 1.818 (2) | O7–C8 | 1.414 (3) |
| Mo–C1 | 2.003 (2) | P2–C31 | 1.833 (2) | O7–C9 | 1.405 (2) |
| Mo–C2 | 2.036 (2) | O1–C1 | 1.130 (2) | O8–C10 | 1.425 (2) |
| Mo–C3 | 1.998 (2) | O2–C2 | 1.137 (3) | C5–C6 | 1.497 (3) |
| Mo–C4 | 2.048 (2) | O3–C3 | 1.139 (3) | C7–C8 | 1.491 (3) |
| P1–O5 | 1.628 (1) | O4–C4 | 1.134 (3) | C9–C10 | 1.499 (3) |
| P1–C13 | 1.821 (2) | O5–C5 | 1.429 (3) | C11–C12 | 1.532 (4) |
| P1–C21 | 1.833 (2) | O6–C6 | 1.413 (3) | C12–C13 | 1.529 (3) |
| | | Bond Angles | | | |
| P2–Mo–P1 | 86.84 (2) | C2–Mo–C1 | 87.88 (8) | C11–P2–O8 | 95.33 (8) |
| C1–Mo–P1 | 177.28 (6) | C3–Mo–C1 | 87.58 (8) | C31–P2–O8 | 102.31 (7) |
| C2–Mo–P1 | 89.52 (6) | C4–Mo–C1 | 86.48 (8) | C10–O8–P2 | 120.95 (12) |
| C3–Mo–P1 | 91.67 (6) | O1–C1–Mo | 177.11 (17) | C31–P2–C11 | 99.97 (8) |
| C4–Mo–P1 | 96.09 (5) | C3–Mo–C2 | 91.21 (8) | C12–C11–P2 | 114.28 (12) |
| O5–P1–Mo | 120.71 (5) | C4–Mo–C2 | 173.92 (8) | C6–C5–O5 | 108.50 (18) |
| C13–P1–Mo | 116.12 (6) | O2–C2–Mo | 176.85 (18) | C7–O6–C6 | 114.05 (18) |
| C21–P1–Mo | 118.92 (6) | C4–Mo–C3 | 86.30 (8) | C5–C6–O6 | 112.85 (17) |
| C1–Mo–P2 | 93.82 (5) | O3–C3–Mo | 177.07 (19) | C8–C7–O6 | 109.43 (20) |
| C2–Mo–P2 | 86.73 (6) | O4–C4–Mo | 172.53 (17) | C9–O7–C8 | 112.41 (15) |
| C3–Mo–P2 | 177.46 (6) | C13–P1–O5 | 96.37 (8) | C7–C8–O7 | 108.19 (18) |
| C4–Mo–P2 | 95.90 (6) | C21–P1–O5 | 101.56 (8) | C10–C9–O7 | 108.47 (16) |
| O8–P2–Mo | 120.42 (5) | C5–O5–P1 | 120.46 (12) | C9–C10–O8 | 109.27 (16) |
| C11–P2–Mo | 115.69 (6) | C21–P1–C13 | 98.79 (9) | C13–C12–C11 | 114.09 (16) |
| C31–P2–Mo | 118.88 (6) | C12–C13–P1 | 114.75 (13) | | |

under vacuum. The salt was added to 300 mL of diethyl ether and the suspension cooled to −78 °C. A solution of 51 mL (80 g, 0.58 mol) of $PCl_3$ dissolved in 50 mL of diethyl ether was added to the stirred suspension during a 10-min period. A yellow precipitate formed during the addition. The reaction mixture was kept cooled (−78 °C) and stirred for 15 min and then warmed to room temperature and stirred for a further 30 min. The mixture was filtered under nitrogen via a Schlenk tube and the filtrate evaporated to yield 1,3-bis(chlorophenylphosphino)propane (4) as a colorless, viscous oil, 81% yield. $^1H$ NMR (200 MHz) $\delta$ 1.65–1.90 (m, 2 H), 2.08–2.25 (m, 4 H), 7.30–7.75 (m, 10 H); $^{31}P\{^1H\}$ NMR (80.98 MHz) $\delta$ 92.15 (lit.[11] 92.5). The product is pure enough to be used in the next reaction step.

***meso*-11,15-Diphenyl-1,4,7,10-tetraoxa-11,15-diphosphacyclopentadecane, $[15]P_2O_4$ (5).** A solution of 10.0 g (0.03 mol) of 1,3-bis(chlorophenylphosphino)propane dissolved in 300 mL of THF was loaded into a Marriotte-type pressure-equalizing constant-addition funnel. Exactly 1 equiv of triethylene glycol (4.56 g, 0.03 mol) was dissolved in 300 mL of THF and likewise loaded in a second Marriotte-type addition funnel. The two solutions were added simultaneously and dropwise with stirring to a solution of $Et_3N$ (9.21 g, 0.091 mol) dissolved in 2000 mL of THF over a period of 10–12 h. A white precipitate of $[Et_3NH]Cl$ slowly formed. After being stirred for 10 h, the mixture was filtered under nitrogen via a Schlenk tube to remove the precipitated $[Et_3NH]Cl$. Evaporation of the filtrate yielded a colorless, viscous oil in quantitative yield. After standing in the freezer for several days, the oil solidified to a white, soft solid. This product is a mixture of the desired monomeric $[15]P_2O_4$ ligand together with the presumed racemic isomer and higher molecular weight polymeric compounds. No further purification was carried out for this product. $^1H$ NMR (200 MHz) $\delta$ 1.4–1.7 (m, 2 H), 1.8–2.1 (m, 4 H), 3.5–4.0 (m, 12 H), 7.25–7.6 (m, 10 H). The $^{31}P\{^1H\}$ NMR (80.98 MHz) contained three overlapping resonances in the range 122.2–122.9 ppm.

**Metal–Crown Ether Complex 6.** The previously reported procedure was followed.[4] Separately dissolved in 250 mL of $CH_2Cl_2$ were 14.07 g of the above mixture of phosphinites (ca. 0.07 mol in P-donor centers) and 10.39 g (0.035 mol) of $Mo(CO)_4(NBD)$. These solutions were slowly added at the same rate to 500 mL of $CH_2Cl_2$. Removal of the solvent and column chromatography on fluorosil/$CH_2Cl_2$ eluent resulted in the isolation of 6 as colorless crystals in 17.2% yield. IR ($CH_2Cl_2$ solution) $\nu$(CO) 2023, 1933, 1903 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ 1.8–2.0 (m, 2 H), 2.4–2.75 (m, 4 H), 3.6–4.0 (m, 12 H), 7.3–7.7 (m, 10 H); $^{31}P\{^1H\}$ NMR (80.89 MHz) $\delta$ 137.88; MS, *m/z* (rel intensity) 618 (11), 617 (14), 616 [M($^{98}$Mo), 31%], 615 (18), 614 (20), 612 (9), 611 (6), 610

**Table VI. Positional and Thermal Parameters and Their Esd's for $Mo(CO)_3(MeCOLi)\{[15]P_2O_4\}$ (7b)[a,b]**

| atom | *x* | *y* | *z* | $U_{eq}$, Å$^2$ |
|---|---|---|---|---|
| Mo | 0.035 08 (10) | 0.159 19 (6) | 0.176 97 (5) | 0.034 9 (10) |
| P1 | 0.240 9 (4) | 0.159 48 (18) | 0.257 10 (19) | 0.040 0 (23) |
| P2 | 0.234 3 (3) | 0.126 27 (18) | 0.103 91 (18) | 0.038 2 (21) |
| O1 | −0.195 7 (11) | 0.227 9 (7) | 0.273 1 (6) | 0.088 (9) |
| O2 | 0.105 3 (18) | 0.310 1 (6) | 0.125 3 (8) | 0.114 (11) |
| O3 | −0.209 5 (11) | 0.131 5 (7) | 0.069 1 (6) | 0.085 (9) |
| O4 | 0.302 0 (7) | 0.078 0 (5) | 0.269 6 (4) | 0.041 (5) |
| O5 | 0.353 8 (9) | −0.088 6 (5) | 0.140 1 (5) | 0.063 (7) |
| O6 | 0.443 0 (11) | −0.037 1 (5) | 0.250 5 (6) | 0.072 (7) |
| O7 | 0.295 9 (8) | 0.042 9 (4) | 0.113 9 (5) | 0.047 (5) |
| O8 | 0.057 2 (8) | −0.003 7 (4) | 0.213 7 (5) | 0.050 (6) |
| C1 | −0.111 8 (15) | 0.200 0 (8) | 0.238 6 (7) | 0.051 (4) |
| C2 | 0.077 2 (14) | 0.253 3 (9) | 0.142 4 (8) | 0.052 (4) |
| C3 | −0.123 5 (16) | 0.142 7 (7) | 0.109 4 (8) | 0.046 (4) |
| C4 | 0.416 3 (13) | 0.205 9 (7) | 0.234 8 (7) | 0.047 (4) |
| C5 | 0.490 2 (15) | 0.170 0 (7) | 0.176 0 (7) | 0.044 (3) |
| C6 | 0.411 7 (13) | 0.174 7 (7) | 0.110 3 (7) | 0.045 (3) |
| C8 | 0.434 2 (20) | −0.015 7 (10) | 0.316 0 (9) | 0.078 (5) |
| C9 | 0.466 8 (18) | −0.111 1 (9) | 0.238 8 (8) | 0.073 (5) |
| C10 | 0.476 2 (16) | −0.118 9 (9) | 0.169 3 (8) | 0.063 (4) |
| C11 | 0.372 2 (17) | −0.066 3 (8) | 0.074 8 (8) | 0.066 (4) |
| C12 | 0.407 4 (15) | 0.008 0 (8) | 0.074 9 (8) | 0.061 (4) |
| C13 | −0.021 2 (13) | 0.047 1 (7) | 0.212 3 (6) | 0.040 (3) |
| C14 | −0.183 9 (15) | 0.033 7 (9) | 0.232 3 (8) | 0.064 (4) |
| C11P | 0.207 8 (13) | 0.190 6 (7) | 0.339 8 (7) | 0.045 (3) |
| C12P | 0.096 0 (17) | 0.157 3 (8) | 0.374 0 (8) | 0.062 (4) |
| C13 | 0.068 8 (22) | 0.175 6 (10) | 0.440 0 (10) | 0.088 (6) |
| C14 | 0.158 7 (17) | 0.226 8 (9) | 0.465 9 (9) | 0.075 (5) |
| C15 | 0.269 3 (16) | 0.257 5 (9) | 0.434 6 (9) | 0.075 (5) |
| C16 | 0.293 0 (14) | 0.239 3 (8) | 0.370 8 (8) | 0.057 (4) |
| C21 | 0.197 1 (12) | 0.131 8 (7) | 0.018 8 (6) | 0.038 (3) |
| C22 | 0.126 7 (17) | 0.076 5 (9) | −0.011 4 (9) | 0.075 (5) |
| C23 | 0.090 6 (18) | 0.077 0 (10) | −0.076 9 (9) | 0.080 (5) |
| C24 | 0.125 0 (19) | 0.136 1 (10) | −0.112 3 (11) | 0.086 (6) |
| C25 | 0.188 2 (16) | 0.190 6 (9) | −0.083 9 (9) | 0.069 (4) |
| C26 | 0.227 0 (14) | 0.188 0 (8) | −0.019 1 (7) | 0.052 (4) |
| Li | 0.270 6 (25) | −0.000 4 (12) | 0.201 8 (16) | 0.069 (17) |
| C1S | −0.028 (4) | 0.101 2 (16) | 0.646 0 (18) | 0.20 (3) |
| Cl1 | 0.149 4 (11) | 0.145 0 (4) | 0.652 0 (6) | 0.179 (8) |
| Cl2 | −0.019 5 (20) | 0.042 4 (8) | 0.587 9 (7) | 0.313 (17) |
| C2S | 0.50 | 0.00 | 0.50 | 0.31 (8) |
| Cl3 | 0.667 2 (17) | 0.105 9 (10) | 0.444 1 (11) | 0.201 (17) |
| Cl4 | 0.404 (5) | 0.077 2 (25) | 0.500 2 (14) | 0.40 (5) |

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$. [b] Cl3 and Cl4 are sites for the disordered chlorine atom which each have occupancy 0.5.

**Table VII. Selected Bond Distance (Å) and Bond Angles (deg) for *fac*-Mo(CO)$_3$(MeCOLi){[15]P$_2$O$_4$} (7b)**

| | | | | | |
|---|---|---|---|---|---|
| | | Bond Distances | | | |
| Mo–P1 | 2.452 (4) | P2–C21 | 1.792 (14) | O6–Li | 2.231 (28) |
| Mo–P2 | 2.416 (4) | O1–C1 | 1.162 (19) | O7–C12 | 1.441 (17) |
| Mo–C13 | 2.301 (14) | O2–C2 | 1.161 (21) | O7–Li | 2.009 (14) |
| Mo–C1 | 1.986 (14) | O3–C3 | 1.144 (19) | O8–C13 | 1.188 (15) |
| Mo–C2 | 1.958 (16) | O4–C7 | 1.401 (18) | P8–Li | 1.908 (23) |
| Mo–C3 | 1.996 (15) | O4–Li | 2.061 (29) | C4–C5 | 1.546 (19) |
| P1–O4 | 1.655 (9) | O5–C8 | 1.418 (22) | C5–C6 | 1.523 (19) |
| P1–C4 | 1.846 (13) | O5–C9 | 1.438 (20) | C7–C8 | 1.499 (24) |
| P1–C11P | 1.835 (15) | O5–Li | 1.949 (28) | C9–C10 | 1.449 (24) |
| P2–O7 | 1.683 (9) | O6–C10 | 1.363 (18) | C11–C12 | 1.441 (22) |
| P2–C6 | 1.822 (13) | O6–C11 | 1.426 (20) | C13–C14 | 1.524 (18) |
| | | Bond Angles | | | |
| P2–Mo–P1 | 83.18 (12) | C14–C13–Mo | 116.6 (9) | O6–Li–O4 | 152.4 (12) |
| C1–Mo–P1 | 93.0 (4) | C2–Mo–C1 | 90.5 (6) | O7–Li–O4 | 107.8 (11) |
| C2–Mo–P1 | 95.9 (4) | C3–Mo–C1 | 92.8 (6) | O8–Li–O4 | 93.6 (12) |
| C3–Mo–P1 | 170.7 (4) | C3–Mo–C2 | 91.3 (4) | Li–O5–C8 | 110.0 (13) |
| C13–Mo–P1 | 87.1 (3) | C4–P1–O4 | 102.1 (5) | Li–O5–C9 | 112.1 (11) |
| O4–P1–Mo | 110.1 (3) | C11P–P1–O4 | 102.0 (5) | O6–Li–O5 | 76.6 (9) |
| C4–P1–Mo | 117.0 (4) | C7–O4–P1 | 121.8 (8) | O7–Li–O5 | 121.3 (13) |
| C11P–P1–Mo | 120.4 (4) | Li–O4–P1 | 121.6 (9) | O8–Li–O5 | 133.9 (17) |
| C1–Mo–P2 | 171.3 (4) | C11P–P1–C4 | 102.8 (6) | Li–O6–C10 | 109.1 (12) |
| C2–Mo–P2 | 82.2 (4) | C6–P2–O7 | 100.7 (5) | Li–O6–C11 | 111.2 (11) |
| C3–Mo–P2 | 92.0 (4) | C21–P2–O7 | 103.4 (6) | O7–Li–O6 | 75.4 (11) |
| C13–Mo–P2 | 97.0 (3) | C12–O7–P2 | 125.8 (9) | O8–Li–O6 | 112.5 (12) |
| O7–P2–Mo | 113.8 (3) | Li–O7–P2 | 117.1 (8) | Li–O7–C12 | 113.7 (10) |
| C6–P2–Mo | 117.3 (5) | C21–P2–C6 | 101.1 (6) | O8–Li–O7 | 104.4 (13) |
| C21–P2–Mo | 118.3 (4) | Li–O4–C7 | 113.4 (10) | Li–O8–C13 | 123.3 (11) |
| O8–C13–Mo | 128.9 (9) | O5–Li–O4 | 78.7 (11) | | |

**Table VIII. Postional and Thermal Parameters and Their Esd's for [Mo(CO)$_3$Br{[15]P$_2$O$_4$}]Li (8)[a]**

| atom | $x$ | $y$ | $z$ | $U_{eq}$, Å$^2$ |
|---|---|---|---|---|
| Mo | 0.019 72 (3) | 0.146 62 (3) | 0.157 77 (2) | 0.037 51 (28) |
| Br | 0.013 42 (5) | 0.158 28 (4) | 0.038 92 (3) | 0.059 5 (4) |
| P1 | −0.094 75 (11) | 0.048 92 (9) | 0.156 01 (8) | 0.045 8 (10) |
| P2 | −0.118 66 (12) | 0.221 88 (9) | 0.164 44 (8) | 0.049 3 (11) |
| O1 | 0.188 8 (3) | 0.041 86 (26) | 0.153 55 (22) | 0.076 (4) |
| O2 | 0.160 7 (4) | 0.273 05 (26) | 0.167 82 (21) | 0.076 (4) |
| O3 | 0.019 5 (3) | 0.142 44 (23) | 0.290 81 (19) | 0.066 (3) |
| O4 | −0.155 63 (28) | 0.050 84 (22) | 0.095 52 (17) | 0.056 3 (30) |
| O5 | −0.202 1 (4) | 0.062 4 (3) | −0.016 11 (23) | 0.082 (4) |
| O6 | −0.280 6 (4) | 0.179 0 (4) | 0.019 44 (29) | 0.117 (6) |
| O7 | −0.179 35 (27) | 0.218 82 (22) | 0.104 17 (17) | 0.052 4 (28) |
| C1 | 0.126 4 (4) | 0.079 5 (3) | 0.154 35 (28) | 0.046 (4) |
| C2 | 0.108 4 (4) | 0.227 5 (3) | 0.162 37 (27) | 0.048 (4) |
| C3 | 0.020 4 (4) | 0.142 6 (3) | 0.240 76 (27) | 0.045 (4) |
| C4 | −0.183 4 (5) | 0.055 0 (4) | 0.211 54 (29) | 0.069 (5) |
| C5 | −0.247 1 (5) | 0.121 1 (4) | 0.206 6 (4) | 0.080 (6) |
| C6 | −0.203 6 (5) | 0.192 6 (4) | 0.218 12 (29) | 0.072 (6) |
| C7 | −0.212 2 (5) | −0.005 5 (4) | 0.072 4 (4) | 0.081 (6) |
| C8 | −0.194 6 (6) | −0.007 1 (4) | 0.009 1 (4) | 0.094 (8) |
| C9 | −0.288 8 (6) | 0.079 9 (5) | −0.039 1 (4) | 0.103 (8) |
| C10 | −0.303 0 (6) | 0.156 6 (5) | −0.035 4 (4) | 0.096 (7) |
| C11 | −0.291 4 (7) | 0.247 9 (5) | 0.036 0 (4) | 0.129 (9) |
| C12 | −0.263 5 (5) | 0.258 5 (4) | 0.095 2 (4) | 0.085 (6) |
| C11P | −0.059 6 (4) | −0.044 3 (3) | 0.160 37 (27) | 0.046 (4) |
| C12P | 0.003 9 (5) | −0.088 0 (4) | 0.119 4 (3) | 0.066 (5) |
| C13 | 0.035 3 (6) | −0.137 2 (4) | 0.119 0 (3) | 0.074 (6) |
| C14 | 0.002 5 (6) | −0.185 3 (4) | 0.159 9 (3) | 0.074 (6) |
| C15 | −0.059 3 (5) | −0.163 2 (4) | 0.199 9 (3) | 0.069 (6) |
| C16 | −0.090 3 (5) | −0.093 2 (4) | 0.200 52 (29) | 0.062 (5) |
| C21 | −0.106 7 (5) | 0.317 4 (4) | 0.176 0 (3) | 0.064 (5) |
| C22 | −0.055 7 (6) | 0.354 3 (4) | 0.135 6 (4) | 0.088 (6) |
| C23 | −0.039 5 (7) | 0.426 8 (5) | 0.140 8 (5) | 0.124 (9) |
| C24 | −0.072 9 (9) | 0.462 8 (6) | 0.187 5 (7) | 0.143 (13) |
| C25 | −0.123 6 (8) | 0.427 3 (6) | 0.228 1 (6) | 0.127 (11) |
| C26 | −0.142 2 (6) | 0.354 3 (5) | 0.223 6 (4) | 0.094 (7) |
| Li$^+$ | −0.155 5 (8) | 0.138 3 (6) | 0.046 1 (5) | 0.063 (8) |
| CS | 0.446 7 (9) | 0.159 3 (6) | 0.066 1 (5) | 0.197 (14) |
| Cl1 | 0.340 43 (24) | 0.164 25 (21) | 0.097 22 (15) | 0.178 (3) |
| Cl2 | 0.462 38 (26) | 0.088 55 (19) | 0.024 98 (18) | 0.196 (4) |

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

(13), 560 (M$^+$ − 2CO, 5), 532 (M − 3CO, 100), 504 (M − 4CO, 13), *m/z* calcd for $C_{25}H_{28}MoO_8P_2$ with Mo$^{98}$ 616.3, found 616.2. The isotopic pattern is consistent with the calculated isotopic pattern. Anal. Calcd for $C_{25}H_{28}MoO_8P_2$: C, 48.87; H, 4.59. Found: C, 48.54; H, 4.48.

***fac*-Mo(CO)$_3$(PhCOLi){[15]P$_2$O$_4$} (7a).** Mo(CO)$_4${[15]P$_2$O$_4$} (0.30 g) was dissolved in 8 mL of dry benzene and 1.1 equiv of phenyllithium added. The pale yellow solution went immediately orange, and an orange precipitate formed. The orange precipitate *fac*-Mo(CO)$_3$(PhCOLi){[15]P$_2$O$_4$} was redissolved in dry $CH_2Cl_2$, filtered through a fine glass frit, and pumped to reduce the volume. Addition of hexane gave the required product as an orange powder (53%). Anal. Calcd for $C_{31}H_{33}LiMoO_8P_2$: C, 53.32; H, 4.76. Found: C, 52.89; H, 4.57.

***fac*-Mo(CO)$_3$(MeCOLi){[15]P$_2$O$_4$} (7b)** was similarly isolated as a yellow precipitate (62%). Recrystallization from the minimum of $CH_2Cl_2$ at −20 °C gave pale yellow crystals of **7b** suitable for X-ray diffraction studies. Anal. Calcd for $C_{26}H_{31}LiMoO_8P_2 \cdot 2CH_2Cl_2$: C, 41.71; H, 4.38. Found: C, 42.58; H, 4.56.

The complexes **7c–f** could likewise be obtained as yellow-orange solids. Characterization of these products was based solely on the similarity of their infrared spectra (Table I) to those of **7a,b** and their structural analogues *fac*-Mo(CO)$_3$(RCOLi){$Ph_2POCH_2(CH_2OCH_2)_2CH_2OPPh_2$}.[4]

***fac*-[Mo(CO)$_3$Br{[15]P$_2$O$_4$}]Li (8).** To a solution of 0.10 g (0.16 mmol) of **6** in 5 mL of toluene was added excess LiBr (0.30 g, 3.5 mmol). The mixture was heated under reflux for 18 h. The solvent was removed by vacuum and the residue extracted with 30 mL of $CH_2Cl_2$. The solution was filtered via Schlenk tube and the filtrate evaporated to yield **8** as a slight yellow microcrystalline solid in 62% yield. IR($CH_2Cl_2$ solution) $\nu$(CO) 1951, 1875, 1794 cm$^{-1}$. Anal. Calcd for $C_{24}H_{28}BrLiMoO_7P_2 \cdot CH_2Cl_2$: C, 39.61; H, 3.99. Found: C, 39.82; H, 4.07.

**X-ray Structural Determination.** All crystals had dimensions in the range 0.25–0.45 mm. Intensity data for all compounds were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature, using graphite monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 73 Å). The $\omega$–2$\theta$ scan technique was applied with variable scan speeds. The intensities of three standard reflections were measured every 2 h. For compound **6**, these showed no variation, but for compounds **7b**·2[$CH_2Cl_2$] and **8**·[$CH_2Cl_2$], linear

**Table IX. Selected Bond Distances (Å) and Bond Angles (deg) for *fac*-[Mo(CO)$_3$Br{[15]P$_2$O$_4$}]Li (8)**

| | | | | | |
|---|---|---|---|---|---|
| | | Bond Distances | | | |
| Mo–Br | 2.7590 (13) | P2–C6 | 1.833 (7) | O6–C10 | 1.376 (11) |
| Mo–P1 | 2.4667 (18) | P2–C21 | 1.811 (7) | O6–C11 | 1.350 (12) |
| Mo–P2 | 2.4550 (18) | O1–C1 | 1.147 (8) | O6–Li | 2.062 (13) |
| Mo–C1 | 1.992 (6) | O2–C2 | 1.146 (8) | O7–C12 | 1.442 (8) |
| Mo–C2 | 1.986 (6) | O3–C3 | 1.158 (8) | O7–Li | 2.045 (12) |
| Mo–C3 | 1.921 (6) | O4–C7 | 1.437 (9) | C4–C5 | 1.545 (11) |
| Br–Li | 2.484 (12) | O4–Li | 1.992 (12) | C5–C6 | 1.500 (11) |
| P1–O4 | 1.655 (4) | O5–C8 | 1.425 (10) | C7–C8 | 1.487 (12) |
| P1–C4 | 1.821 (7) | O5–C9 | 1.405 (10) | C9–C10 | 1.449 (13) |
| P1–C11P | 1.815 (6) | O5–Li | 2.130 (13) | C11–C12 | 1.443 (13) |
| P2–O7 | 1.650 (4) | | | | |
| | | Bond Angles | | | |
| P1–Mo–Br | 91.12 (5) | O7–P2–Mo | 111.32 (17) | C21–P2–O7 | 102.10 (30) |
| P2–Mo–Br | 89.45 (5) | C6–P2–Mo | 114.98 (24) | C12–O7–P2 | 123.7 (4) |
| C1–Mo–Br | 92.05 (19) | C21–P2–Mo | 119.64 (25) | Li–O7–P2 | 119.3 (4) |
| C2–Mo–Br | 90.85 (18) | C2–Mo–C1 | 88.68 (25) | C21–P2–C6 | 104.9 (3) |
| C3–Mo–Br | 177.20 (18) | C3–Mo–C1 | 90.65 (26) | Li–O4–C7 | 112.8 (5) |
| Li–Br–Mo | 87.36 (27) | C3–Mo–C2 | 88.44 (25) | O5–Li–O4 | 80.9 (5) |
| P2–Mo–P1 | 82.73 (6) | O4–Li–Br | 99.4 (5) | O6–Li–O4 | 118.2 (6) |
| C1–Mo–P1 | 93.31 (18) | O5–Li–Br | 111.6 (5) | O7–Li–O4 | 103.0 (5) |
| C2–Mo–P1 | 177.15 (19) | O6–Li–Br | 142.5 (6) | Li–O5–C8 | 107.7 (6) |
| C3–Mo–P1 | 89.49 (18) | O7–Li–Br | 95.8 (5) | Li–O5–C9 | 112.7 (6) |
| O4–P1–Mo | 110.93 (17) | C4–P1–O4 | 102.58 (27) | O6–Li–O5 | 76.3 (5) |
| C4–P1–Mo | 114.68 (24) | C11P–P1–O4 | 102.57 (26) | O7–Li–O5 | 151.5 (6) |
| C11P–P1–Mo | 121.20 (21) | C7–O4–P1 | 127.1 (4) | Li–O6–C10 | 111.9 (6) |
| C1–Mo–P2 | 175.79 (18) | Li–O4–P1 | 120.1 (14) | Li–O6–C11 | 111.6 (6) |
| C2–Mo–P2 | 95.23 (19) | C11P–P1–C4 | 102.7 (3) | O7–Li–O6 | 77.1 (5) |
| C3–Mo–P2 | 87.91 (18) | C6–P2–O7 | 101.71 (27) | Li–O7–C12 | 115.3 (5) |

intensity decay of 30% and 7%, respectively, was observed and subsequently corrected for. An empirical absorption[16] was applied to the data for **6** (maximum and minimum corrections 1.152 and 0.962) and **7b**·**2**[CH$_2$Cl$_2$] (maximum and minimum corrections 1.220 and 0.666) but not for **8**·[CH$_2$Cl$_2$]. The space groups of **7b**·**2**[CH$_2$Cl$_2$] and **8**·[CH$_2$Cl$_2$] were determined uniquely by systematic absences. The space group of **6** was either $P1$ or $P\bar{1}$. $P\bar{1}$ was chosen and confirmed by successful refinement.

In each compound, the Mo atom position was determined from a Patterson map, and other non-hydrogen atoms were located from successive Fourier and difference Fourier maps.

For each structure, all non-hydrogen atoms were refined anisotropically (except for compound **7b**·**2**[CH$_2$Cl$_2$] in which C atoms were refined with isotropic thermal parameters) by full-matrix least-squares to minimize $\Sigma w(F_o - F_c)^2$, where $w^{-1} = \sigma^2(F) + gF^2$, and the $g$ value was a refined parameter. Hydrogen atoms were positioned on geometric grounds (C–H 0.95 Å), and the general hydrogen atom thermal parameters for **6**, **7b**·**2**[CH$_2$Cl$_2$], and **8**·[CH$_2$Cl$_2$] were 0.062 (1), 0.069 (4), and 0.12 Å$^2$. Crystal data, details of data collection, and least-squares parameters are listed in Table III. Atomic coordinates are given in Tables IV, VI, and VIII. Details of molecular geometry are given in Tables V, VII, and IX. Figures 1–3 are views of the molecules prepared using ORTEP.[18]

Atomic scattering factors were taken from *International Tables for X-ray Crystallography*.[19] All calculations were carried out on an Apollo computer using NRCVAX,[20] SHELX76,[21] and SHELX86.[17]

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**Registry No.** 4, 60600-31-9; 5, 141319-75-7; 6, 141319-76-8; 7a, 141319-77-9; 7b, 141319-78-0; 7b·2CH$_2$Cl$_2$, 141319-84-8; 7c, 141319-79-1; 7d, 141319-80-4; 7e, 141319-81-5; 7f, 141319-82-6; 8, 141319-83-7; 8·CH$_2$Cl$_2$, 141319-85-9; Mo(CO)$_4$(NBD), 12146-37-1; bis(diphenylphosphino)propane, 6737-42-4; triethylene glycol, 112-27-6.

**Supplementary Material Available:** Tables of calculated hydrogen coordinates (Tables S1, S5, and S9), anisotropic thermal parameters (Tables S2, S6, and S10), and bond lengths, bond angles, and torsion angles (Tables S4, S8, and S12) for complexes 6, 7b, and 8 (23 pages). Ordering information is given on any current masthead page.

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