Synthesis and X-ray Crystal Structure of *trans*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}$, a Molecular Gyroscope Formed by Trans Coordination of a Bis(phosphine) Ligand in an Octahedral Metal Complex

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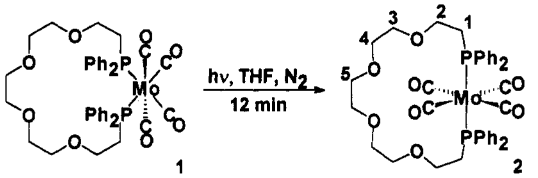
Summary: Photolysis of cis-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}$ *(1) in THF under nitrogen gives trans-*$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}$ *(2). Complex 2 is the first example of a metalla crown ether in which the α,ω-bis(phosphorus donor)polyether ligand is trans coordinated. It is also a rare example of an octahedral complex with a trans-spanning bis(phosphine) ligand.*

Metalla crown ethers are a unique class of transition-metal complexes that are formed when α,ω-bis(phosphorus donor)polyether ligands, which contain at least three ether oxygens, chelate transition metals.[1–3] Metalla crown ethers, like the crown ethers, are able to bind hard metal cations[1,3] and small molecules.[3b] They are also able to activate carbonyl ligands on the transition metal to nucleophilic attack.[1] These properties suggest that metalla crown ethers could exhibit catalytic activities and selectivities that are quite different from those of those of complexes with simple bis(phosphine) ligands.

In all reported metalla crown ethers, the phosphorus-donor groups are cis coordinated. Metalla crown ethers with trans-coordinated phosphorus-donor groups are of interest because the very different orientations of the phosphorus-donor groups in these complexes should result in different conformations of the metalla crown ether rings. This, in turn, should change the abilities of these metalla crown ethers to bind hard metal cations and small molecules and to activate ligands coordinated to the metal center.

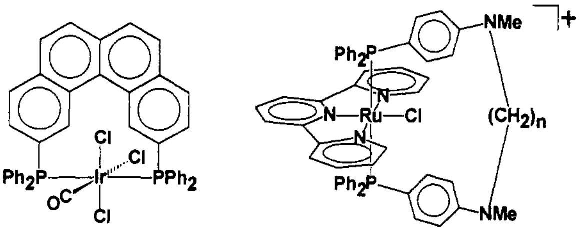
We now wish to report that the known metalla crown ether *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}$ (1) isomerizes in solution to yield *trans*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}$ (2), the first example of a metalla crown ether with trans-coordinated phosphorus-donor groups. The isomerization of 1 to 2 occurs slowly in chloroform-*d* solution even at 5 °C in the dark (approximately 15% isomerization after 24 days). In contrast, this isomerization is essentially complete (by TLC on silica gel) after photolysis of a THF solution of 1 under a nitrogen atmosphere for 12 min (eq 1)and gives a 45% yield of 2.[4] The rate of the isomerization is similar to that observed for the isomerization of *cis*-$Mo(CO)_4(Ph_2PMe)_2$ to *trans*-$Mo(CO)_4(Ph_2PMe)_2$, indicating that the metalla crown ether does not affect the rate of the isomerization. It is of interest to note that when the photolysis of 1 is run under a carbon monoxide atmosphere, 2 is isolated in only 6% yield. The infrared spectrum of the reaction mixture indicates that most of the product(s) of the photolysis is monosubstituted, suggesting that a phosphine ligand is displaced from 1 during photolysis under carbon monoxide.



1 2 (1)

Complex 2 is of interest because only three octahedral complexes with trans-spanning bis(phosphine) ligands, shown Chart 1, have been reported.[5,6] In contrast, a variety

Chart 1



3 4a (n = 5), 4b (n= 6)

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[3] (a) Varshney, A.; Gray, G. M. *Inorg. Chem.* 1991, *30*, 1748. (b) Varshney, A.; Webster, M. L.; Gray, G. M. *Inorg. Chem.* 1992, *31*, 2580.

[4] A solution of 0.200 g (0.267 mmol) of *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}$ (1) in 250 mL of dry, degassed THF was placed in an Ace concentric photochemical reactor with a 350-W mercury vapor lamp. The solution was cooled with water circulating between the lamp and the solution, and nitrogen was slowly bubbled through the solution as it was irradiated. After 12 min of irradiation, the solution had changed from pale yellow to dark amber, and TLC on silica plates using a 2:5 ethyl acetate–hexanes solvent system indicated that no starting material remained. The THF was removed under vacuum, and the brown oily residue was chromatographed on silica gel using a 1:1 ethyl acetate–hexanes mixture to yield 0.090 g of *trans*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}$ (2). Recrystallization from a dichloromethane–methanol mixture gave analytically pure 2. Anal. Calcd for $C_{38}H_{40}MoO_8P_2$: C, 58.32; H, 5.15. Found: C, 57.82; H, 5.33.

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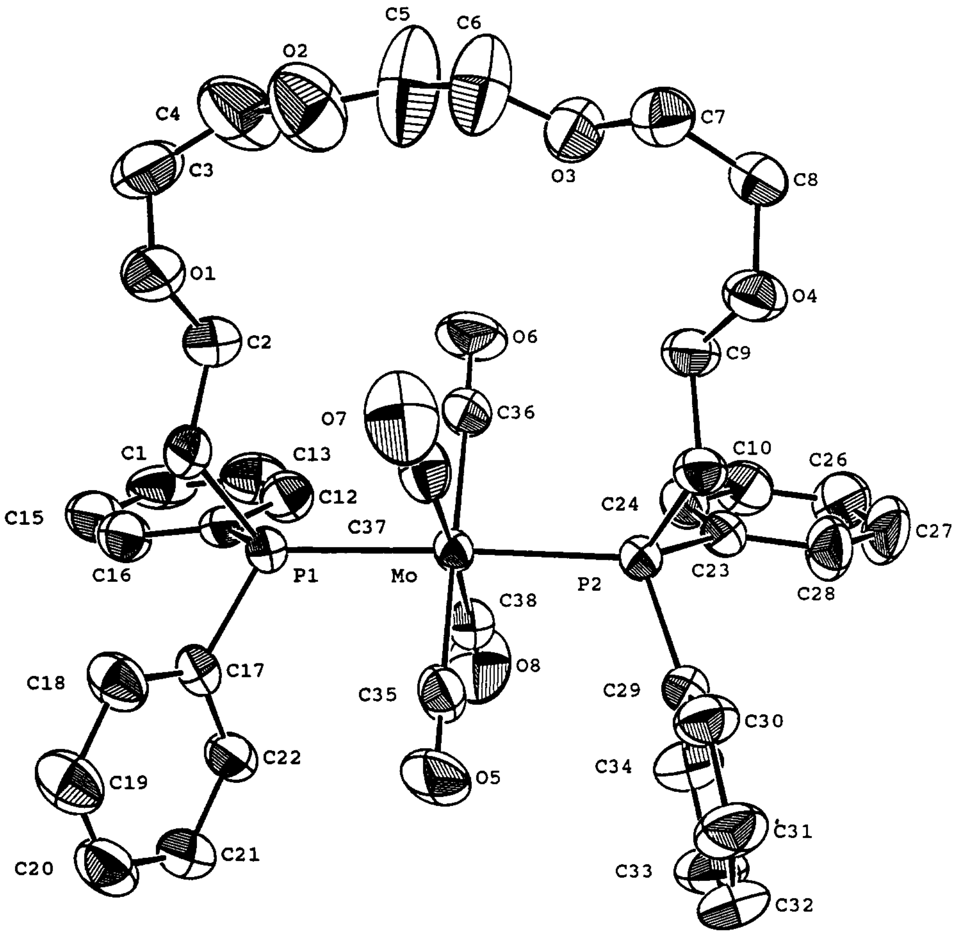

Figure 1. ORTEP[13] drawing of the molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected lengths (Å) and angles (deg): Mo–P1, 2.472(1); Mo–P2, 2.484(1); Mo–C35, 2.046(5); Mo–C36, 2.024(4); Mo–C37, 2.025(5); Mo–C38, 2.021(4); Mo–C35–O5, 178.4(4); Mo–C36–O6, 177.5(4); Mo–C37–O7, 175.5(4); Mo–C38–O8, 178.4(5). Selected torsion angles (deg): Mo–P1–C1–C2, 65.5(4); Mo–P2–C10–C9, −65.3(4); C3–O1–C2–C1, −166.4(5); C2–O1–C3–C4, −61.5(8); C5–O2–C4–C3, 157.9(7); C4–O2–C5–C6, −177.8(6); C7–O3–C6–C5, 168.9(6); C6–O3–C7–C8, 173.9(5); C9–O4–C8–C7, 82.8(5); C8–O4–C9–C10, 178.4(4); P1–C1–C2–O1, −173.4(3); O1–C3–C4–O2, −50.5(9); O2–C5–C6–O3, 142.4(6); O3–C7–C8–O4, −79.6(5); O4–C9–C10–P2, −173.5(3).

of square-planar complexes with trans-spanning bis(phosphine) ligands are known.[7] This difference arises because the group bridging the two phosphines in octahedral complexes must be much longer than that in square-planar complexes in order to wrap around the cis ligands. However, bis(phosphine) ligands with long bridging groups are statistically more likely to coordinate to a second metal and form unwanted polymers. Because of this, **3** and **4a,b** were synthesized via indirect routes that did not involve the reaction of the bis(phosphine) ligand with an octahedral metal complex precursor.

Little is known about the conformations of the flexible trans-spanning bis(phosphine) ligands in **4a,b** because no crystal structures were reported and the NMR spectra were uninformative. In contrast, both the NMR spectra[8] and the X-ray crystal structure of **2** provide important insights into the conformations of the bis(phosphine) ligand. In a 1:3 chloroform-*d*–acetone-d_6 mixture, single NMR resonances are observed for the ^{31}P nuclei and the ^{13}C nuclei of the potentially equivalent carbonyl, methylene, and phenyl carbons. Because the chemical shifts of all of these resonances are quite sensitive to asymmetry in the phosphine ligands,[9] this suggests that the trans-spanning bis(phosphine) ligand in **2** is fluxional and that the Mo(CO)$_4$ group spins freely within the chelate ring to average the environments of the four carbonyl ligands. This is supported by the results of variable-temperature NMR spectroscopic studies of **2**. As the temperature is lowered from +21 to −40 °C, no changes are observed in either the ^{31}P or ^{13}C NMR spectra. However, as the temperature is lowered from −40 to −80 °C, the carbonyl ^{13}C NMR resonances broaden ($\nu_{1/2}$ increases 50%). This broadening appears to be due to slowing of the rotation of the Mo(CO)$_4$ group about the P–Mo–P axis because the solvent ^{13}C resonances do not broaden significantly over this temperature range. The fact that the carbonyl ^{13}C NMR resonance does not even begin to broaden until the temperature is below −40 °C suggests that the energy barrier to rotation about the P–Mo–P axis is quite low.

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(8) ^{31}P NMR (CDCl$_3$): δ 32.57 (s). ^{13}C NMR (CDCl$_3$): δ 210.59 (CO, t, $|^2J(\mathrm{PC})|$ = 8 Hz), 139.48 (ipso phenyl, at, $|^1J(\mathrm{PC}) + {}^3J(\mathrm{P'C})|$ = 34 Hz), 131.70 (ortho phenyl, at, $|^2J(\mathrm{PC}) + {}^4J(\mathrm{P'C})|$ = 11 Hz), 129.16 (para phenyl; s), 128.28 (meta phenyl, bs), 71.07 (C5, s), 71.03 (C4, s), 70.24 (C3, s), 66.96 (C2, at, $|^2J(\mathrm{PC}) + {}^4J(\mathrm{P'C})|$ = 12 Hz), 34.37 (C1, at, $|^1J(\mathrm{PC}) + {}^3J(\mathrm{P'C})|$ = 22 Hz). ^{1}H NMR (CDCl$_3$): δ 7.53 (phenyl, 2H, m), 7.36 (phenyl, 3H, m), 3.65 (C5, C4, C3, C2, 8H, m), 2.87 (C1, 2H, m). Key: s = singlet, bs = broad singlet, t = triplet, at = apparent triplet (A portion of an AXX′ spin system), m = multiplet.

(9) Gray, G. M.; Redmill, K. A. *Inorg. Chem.* **1985**, *24*, 1279.

This is the first direct experimental evidence that supports the current view that there is no significant d–d π-bonding between transition metals and the phosphine ligands.[10]

The X-ray structure of **2** is shown in Figure 1.[11] The octahedral coordination geometry of the molybdenum (P–Mo–C angles from 86.1(1) to 91.8(1)° and a P1–Mo–P2 angle of 175.69(4)°) is less distorted than is that of the iridium in **3** (P–Ir–Cl and P–Ir–C angles from 83.6(1) to 96.5(1)° and a P1–Ir–P2 angle of 170.7°). This is consistent with the larger, more flexible bis(phosphine) ligand in **2**. The four oxygens of the metalla crown ether are essentially planar, with the largest deviation from their least-squares plane being 0.106(4) Å. The metalla crown ether ring bisects the angle formed by two of the carbonyls and the molybdenum and is nearly symmetric to rotation about a 2-fold axis running from the Mo to the midpoint of the C5–C6 bond. The P1–C1–C2–O1 and P2–C10–C9–O4 torsion angles in **2** (−173.4(3) and +173.5(3)°) are quite different from those in **3** (−93(1) and +74(1)°), reflecting the different sizes and flexibilities of the ligands in the complexes. There are no close intramolecular contacts between the carbonyls and the metalla crown ether,[12] consistent with the free rotation of the $\mathrm{Mo(CO)_4}$ group in solution.

The conformation of the metalla crown ether ring in **2** is very different from those of the metalla crown ethers in *cis*-$\mathrm{Mo(CO)_4\{Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2}\text{-}P,P'\}$ (**5**)[3a] and *cis*-$\mathrm{PtCl_2(Ph_2P(CH_2CH_2O)_{\mathit{n}}CH_2CH_2PPh_2}\text{-}P,P')$ (n = 4, **6a**; n = 5, **6b**).[3b] The cis coordination of the phosphines in **5** and **6a,b** forces the metalla crown ether ring away from the metal center. In contrast, the trans coordination of the phosphines in **2** causes the metalla crown ether ring to wrap around the metal center. Thus, although the α,ω-bis(phosphine)polyether ligands are identical in **2** and **6a**, the metalla crown ether ring in **2** is more extended (the average of the O1–O3 and O2–O4 distances is 5.869(6) Å in **2** and 4.66 Å in **6a**) and is much closer to the metal center. Because of their very different conformations, **2** and **6a** should have very different abilities to bind metal cations and small molecules. Also, the proximity of the metalla crown ether ring and the metal center in **2** suggests that hard metal ions bound to trans metalla crown ethers could easily interact with the ligands on the metal.

Supplementary Material Available: X-ray crystallographic data for **2** including tables of experimental details, atomic and thermal coordinates, bond lengths and angles, torsion angles, and least-squares planes and an ORTEP[13] drawing of the metalla crown ether ring (17 pages). Ordering information is given on any current masthead page.

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[10] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 67.

[11] Crystal data: colorless needles, monoclinic space group $P2_1/n$, a = 15.000(2) Å, b = 10.398(1) Å, c = 23.132(4) Å, β = 91.01(1)°, V = 3727.6, Z = 4, d_{calc} = 1.394 g cm^{-3}, n_{obsd} = 5509, R = 4.93%, R_w = 6.26%, GOF = 1.166.

[12] Nearest intramolecular contacts between the carbonyls and the metalla crown ether ring: O6–H(C2), 2.943(4) Å; O7–H(C1), 2.809(5) Å; C36–H(C2), 2.838(4) Å; C37–H(C1), 2.829(5) Å.

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