*Organometallics* **2003,** *22,* 1081−1088

# Synthesis, NMR Characterization, and Cation Binding of Metallacrown Ethers with Asymmetric Bis(phosphinite) and Bis(phosphite) Ligands Derived from 2-Hydroxy-2′-(1,4,7-trisoxo-9-nonanol)-1,1′-biphenyl

Jennifer M. Butler, Michael J. Jablonsky, and Gary M. Gray*

*Department of Chemistry, The University of Alabama at Birmingham, 201 Chemistry Building, 1530 3rd Avenue South, Birmingham, Alabama 35294-1240*

*Received October 18, 2002*

Chlorodiphenylphosphine and 2,2′-biphenylylenephosphorochloridite react with 2-hydroxy-2′-(1,4,7-trisoxo-9-nonanol)-1,1′-biphenyl to yield the new α,*ω*-bis(phosphorus-donor)polyether ligands $Ph_2PO(CH_2CH_2O)_3$-2-$C_{12}H_8$-2′-$OPPh_2$ and (2,2′-$O_2C_{12}H_8$)$P(CH_2CH_2O)_3$-2-$C_{12}H_8$-2′-P(2,2′-$O_2C_{12}H_8$). These ligands react with $Mo(CO)_4$(nbd) to form the monomeric *cis*-metallacrown ethers *cis*-$Mo(CO)_4${$Ph_2PO(CH_2CH_2O)_3$-2-$C_{12}H_8$-2′-$OPPh_2$} and *cis*-$Mo(CO)_4$-{(2,2′-$O_2C_{12}H_8$)$P(CH_2CH_2O)_3$-2-$C_{12}H_8$-2′-P(2,2′-$O_2C_{12}H_8$)}. The X-ray crystal structure of *cis*-$Mo(CO)_4${(2,2′-$O_2C_{12}H_8$)$P(CH_2CH_2O)_3$-2-$C_{12}H_8$-2′-P(2,2′-$O_2C_{12}H_8$)} indicates that in the solid state three of the four metallacrown ether ring oxygens point away from the cavity in the *cis*-metallacrown ether ring. Both metallacrown ethers undergo *cis*−*trans* isomerization in the presence of catalytic amounts of $HgCl_2$ but yield quite different products, *cis*-$Mo(CO)_4$-{$Ph_2PO(CH_2CH_2O)_3$-2-$C_{12}H_8$-2′-$OPPh_2$}·$HgCl_2$ and *trans*-$Mo(CO)_4${(2,2′-$O_2C_{12}H_8$)$P(CH_2$-$CH_2O)_3$-2-$C_{12}H_8$-2′-P(2,2′-$O_2C_{12}H_8$)}·$HgCl_2$, when reacted with a stoichiometric amount of $HgCl_2$. NMR titrations of the *cis*-metallacrown ethers with lithium salts demonstrate that the *cis*-metallacrown ethers form 2:1 complexes with $Li^+$. The unexpected 2:1 ratio has been confirmed by the isolation of [*cis*-$Mo(CO)_4${$Ph_2PO(CH_2CH_2O)_3$-2-$C_{12}H_8$-2′-$OPPh_2$]$_2$$LiBPh_4$. In dichloromethane-$d_2$ solution, this complex very slowly isomerizes to form a mixture of [*trans*-$Mo(CO)_4${$Ph_2PO(CH_2CH_2O)_3$-2-$C_{12}H_8$-2′-$OPPh_2$]$LiBPh_4$ and the free *cis*-metallacrown ether, indicating that the *trans*-metallacrown ether more strongly binds $Li^+$ than does the *cis*-metallacrown ether. Neither 2:1 stoichiometries for $Li^+$ complexes of *cis*-metallacrown ethers nor complex formation by *trans*-metallacrown ethers have previously been reported.

## Introduction

Metallacrown ethers, formed by the chelation of α,*ω*-bis(phosphorus-donor)polyether ligands to transition metals and shown in Figure 1,[1−12] can bind hard metal cations.[13] Such hard−soft bimetallic complexes are of interest as catalysts for organic reactions involving carbon monoxide because the interaction of both metals with carbon monoxide can give rise to activities and selectivities that are different from those of monometallic, transition metal catalysts.[14]

An essential component in the design of catalytic processes involving complexes of metallacrown ethers with hard metal cations is an understanding of the factors that affect the coordination of hard metal cations to metallacrown ethers. Studies of symmetric *cis*-metallacrown ethers have shown that **2** and **3** form 1:1 complexes with $Li^+$ and $Na^+$ cations and that **3** forms a 1:1 complex with $HgCl_2$.[13] In contrast, the *trans* isomers of these metallacrown ethers do not bind either alkali metal cations or $HgCl_2$. Small changes in the polyether chain can have a dramatic effect on cation binding, as illustrated by the inability of the closely related *cis*-metallacrown ether **4** to bind alkali metal cations.[6]

The symmetric nature of the metallacrown ethers used in the studies discussed above limits the use of NMR spectroscopy to study cation binding because it is not possible to completely assign the $^1H$ and $^{13}C$ NMR resonances of the metallacrown ether rings. We have recently developed a new class of asymmetric metallacrown ethers, **5**, **6**, **9**, and **10**, whose NMR spectra provide significantly more information on the solution

---

(1) Gray, G. M. *Comments Inorg. Chem.* **1995**, *17*, 95.

(2) Gray, G. M.; Varshney, A.; Duffey, T. H. *Organometallics* **1995**, *14*, 238.

(3) Gray, G. M.; Duffey, C. H. *Organometallics* **1995**, *14*, 245.

(4) Stang, P. J.; Cao, D. H.; Chen, K.; Gray, G. M.; Muddiman, D. C.; Smith, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 5163.

(5) Smith, D. C., Jr.; Gray, G. M. *Inorg. Chem.* **1998**, *37*, 1791.

(6) Duffey, C. H.; Lake, C. H.; Gray, G. M. *Organometallics* **1998**, *17*, 3550.

(7) Hariharasarma, M.; Gray, G. M. *J. Chem. Crystallogr.* **1998**, *28*, 297.

(8) Smith, D. C., Jr.; Lake, C. H.; Gray, G. M. *Chem. Commun.* **1998**, 2771.

(9) Smith, D. C., Jr.; Gray, G. M. *J. Chem. Soc., Dalton Trans.* **2000**, 677.

(10) Hariharasarma, M.; Lake, C. H.; Watkins, C. L.; Gray, G. M. *J. Organomet. Chem.* **1998**, *580*, 328.

(11) Gray, G. M.; Smith, D. C., Jr.; Duffey C. H. *Inorg. Chim. Acta* **2000**, *300−302*, 581.

(12) Duffey, C. H.; Lake, C. H.; Gray, G. M. *Inorg. Chim. Acta* **2001**, *317*, 199.

(13) Gray, G. M.; Fish, F. P.; Duffey, C. H. *Inorg. Chim. Acta Special Ed. Macrocyclic Complexes* **1996**, *246*, 229.

(14) McLain, S. J.; Waller, F. J. US Patent 4432904, 1984.

10.1021/om020868t CCC: \$25.00

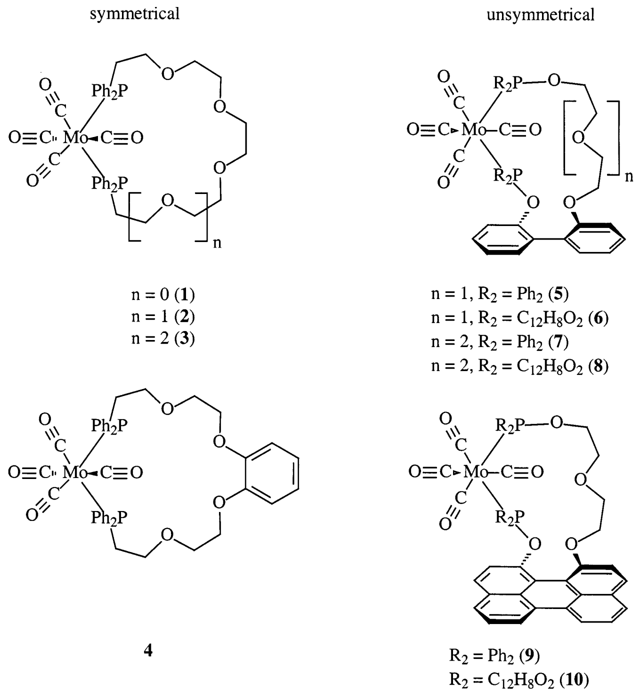

**Figure 1.** Symmetric and asymmetric metallacrown ethers.

conformations of the metallacrown ethers than do the NMR spectra of the symmetric metallacrown ethers.[10,15] Unfortunately, these metallacrown ethers do not bind alkali metal cations.

The lack of cation binding by the asymmetric metallacrown ethers discussed above is likely due to the small size of the metallacrown ether rings. To circumvent this problem, we have prepared two new asymmetric metallacrown ethers, **7** and **8**, that have an additional $CH_2CH_2O$ group in the metallacrown ether ring. The X-ray crystal structure of **8** has been determined, and the $^1H$ and $^{13}C$ NMR resonances of the metallacrown ether rings have been assigned using a combination of 1D and 2D NMR spectroscopic experiments. The abilities of these metallacrown ethers to bind $Li^+$ and $HgCl_2$ and the $HgCl_2$-promoted *cis*−*trans* isomerizations of the metallacrown ethers have been studied.

## Experimental Section

All reactions and purification procedures were carried out under high-purity nitrogen. All starting materials were reagent grade and were used as received. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under high-purity nitrogen. Triethylamine was distilled from calcium hydride prior to use. Deuterated NMR solvents (chloroform-*d*, dichloromethane-$d_2$) were opened and handled under a nitrogen atmosphere at all times. The *cis*-$Mo(CO)_4$nbd and 2,2′-biphenylylenephosphochloridite ester were synthesized using literature procedures.[16,17]

All one-dimensional $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and $^1H$ NMR spectra of the ligands and complexes were recorded using a Bruker ARX-300 NMR spectrometer with a quad ($^1H$, $^{13}C$, $^{19}F$, $^{31}P$) 5 mm probe. The $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% phosphoric acid, and both the $^{13}C$ and the $^1H$ NMR spectra were referenced to internal $SiMe_4$. Two-dimensional $^1H-^1H$ COSY-45, $^1H\{^{13}C\}$ HMBC, $^1H\{^{13}C\}$ HMQC, and $^1H-^1H$ NOESY spectra of 0.1 M solutions of the metallacrown ethers were recorded using a Bruker DRX-400 NMR spectrometer.

Elemental analyses were performed by Atlantic Microlabs, Norcross, GA. A solvent of crystallization is included in a calculated analysis only if the solvent was observed in the $^1H$ NMR spectrum of the analytical sample.

**2-Hydroxy-2′-(1,4,7-trisoxo-9-nonanol)-1,1′-biphenyl, 11.** A solution of 21.1 g (145 mmol) of 2-[2-(2-chloroethoxy)ethoxy]-ethanol was added to a solution of 3.48 g (145 mmol) of NaH and 27.1 g (145 mmol) of 2,2′-biphenol in 100 mL of anhydrous DMF. This mixture was refluxed for 7 days. Then, the mixture was filtered through Celite, and the filtrate was evaporated to dryness to give a brown oil. The oil was purified by column chromatography on silica gel with a 4:1 mixture of ethyl acetate/hexanes as the eluent to yield 23.0 g (45.6%) of **11** as a colorless oil. $^1H$ NMR (chloroform-*d*): $\delta$ 7.16 (m, 4H, Ar), 6.91 (m, 4H, Ar), 6.70 (s, 1H, ArO*H*), 4.14 (m, 2H, $CH_2$), 3.56 (m, 10H, $CH_2$), 2.86 (s, 1H, $CH_2OH$).

**$Ph_2PO(CH_2CH_2O)_3$-2-$C_{12}H_8$-2′-$OPPh_2$, 12.** A solution of 5.85 g (26.5 mmol) of chlorodiphenylphosphine in 100 mL of THF was added to a solution of 4.22 g (13.3 mmol) of **11** and 3.68 mL (26.5 mmol) of triethylamine in 100 mL of THF at room temperature. The mixture was stirred for 18 h and then was filtered to remove the triethylamine hydrochloride precipitate. The filtrate was evaporated to dryness to give 9.46 g (74.3%) of crude **12** as a colorless oil. $^{31}P\{^1H\}$ NMR (chloroform-*d*): $\delta$ 114.90 (s, ArO*P*), 110.17 (s, $CH_2$O*P*). $^1H$ NMR (chloroform-*d*): $\delta$ 7.52 (m, 28H, Ar), 4.13 (m, 2H, $CH_2$), 4.02 (m, 4H, $CH_2$), 3.94 (m, 2H, $CH_2$), 3.45 (m, 4H, $CH_2$).

**(2,2′-$O_2C_{12}H_8$)P($CH_2CH_2O$)$_3$-2-$C_{12}H_8$-2′-P(2,2′-$O_2C_{12}H_8$), 13.** A solution of 1.22 g (3.84 mmol) of **11**, 1.92 g (7.68 mmol) of 2,2′-biphenylylenephophochloridite ester, and 1.07 mL (7.68 mmol) of triethylamine in 100 mL of freshly distilled benzene was stirred under nitrogen for 15 h. The solution was filtered through Celite, under nitrogen, and evaporated to dryness to yield 2.90 g (74.0%) of crude **13** as a viscous, colorless oil. $^{31}P\{^1H\}$ NMR (chloroform-*d*): $\delta$ 146.58 (s, ArO*P*), 140.68 (s, $CH_2$O*P*). $^1H$ NMR (chloroform-*d*): $\delta$ 7.28 (m, 24H, Ar), 4.08 (m, 4H, $CH_2$), 3.75 (m, 4H, $CH_2$), 3.67 (m, 2H, $CH_2$), 3.43 (m, 2H, $CH_2$).

***cis*-$Mo(CO)_4\{Ph_2PO(CH_2CH_2O)_3$-2-$C_{12}H_8$-2′-$OPPh_2\}$, 7.** Solutions of 1.09 g (3.62 mmol) of $Mo(CO)_4$(nbd) in 50 mL of degassed dichloromethane and 2.49 g (3.62 mmol) of **12** in 50 mL of degassed dichloromethane were added simultaneously and dropwise to 100 mL of degassed dichloromethane over a 3 h period. The mixture was stirred for 1 h and then evaporated to dryness. The residue was washed with hexanes and then with methanol to yield 1.43 g (44.8%) of crude **7** as a white powder. The crude product was purified by recrystallization from a dichloromethane/hexanes mixture to give analytically pure **7** as colorless crystals. Anal. Calcd for $C_{46}H_{40}O_9P_2Mo$: C, 61.75; H, 4.51. Found: C, 61.91; H, 4.56. $^{31}P\{^1H\}$ NMR (chloroform-*d*): $\delta$ 145.68 (d, ArO*P*, $|^2J(PP')|$ 32 Hz), 141.04 (d, $CH_2$O*P*, $|^2J(PP')|$ 32 Hz). $^{13}C\{^1H\}$ NMR (carbonyl and aliphatic carbons, chloroform-*d*): $\delta$ 215.91 (*trans* *C*O, dd, $|^2J(PC)|$ 29 Hz, $|^2J(P'C)|$ 9 Hz), 214.50 (*trans* *C*O, dd, $|^2J(PC)|$ 31 Hz, $|^2J(P'C)|$ 10 Hz), 209.49 (*cis* *C*O, dd, $|^2J(PC)|$ 13 Hz, $|^2J(P'C)|$ 13 Hz), 207.99 (*cis* *C*O, dd, $|^2J(PC)|$ 9 Hz, $|^2J(P'C)|$ 9 Hz), 71.35 (s, C3), 71.11 (s, C4), 70.13 (s, C5), 69.69 (d, C2, $|^2J(PC)|$ 7 Hz), 69.03 (s, C6), 66.35 (d, C1, $|^2J(PC)|$ 10 Hz). $^1H$ NMR (aliphatic protons, chloroform-*d*): $\delta$ 4.16 (ddd, H6, $|^2J(H6H6')|$ 11 Hz, $|^3J(H6H5')|$ 8 Hz, $|^3J(H6H5)|$ 2 Hz), 4.01 (ddd, H6′, $|^2J(H6'H6)|$ 11 Hz, $|^3J(H6'H5)|$ 5 Hz, $|^3J(H6'H5')|$ 2 Hz), 3.70 (ddd, H5, $|^2J(H5H5')|$ 11 Hz, $|^3J(H5H6')|$ 5 Hz, $|^3J(H5H6)|$ 2 Hz), 3.54 (ddd, H5′, $|^2J(H5'H5)|$ 11 Hz, $|^3J(H5'H6)|$

---

[15] Hariharasarma, M.; Watkins, C. L.; Gray, G. M. *Organometallics* **2000**, *19*, 1232.

[16] Ehrl, W.; Ruck, R.; Vahrenkamp, H. *J. Organomet. Chem.* **1973**, *56*, 285.

[17] Verizhnikov, L. V.; Kirpichnikov, P. A. *Zh. Obshch. Khim.* **1966**, *37*, 1355.

8 Hz, $|^3J(\mathrm{H5'H6'})|$ 2 Hz), 3.37 (m, H3 and H3′), 3.31 (m, H4 and H4′), 3.13 (m, H1 andH1′), 2.97 (m, H2 and H2′).

***cis*-Mo(CO)$_4${(2,2′-O$_2$C$_{12}$H$_8$)P(CH$_2$CH$_2$O)$_3$-2-C$_{12}$H$_8$-2′-P-(2,2′-O$_2$C$_{12}$H$_8$)}, 8.** Solutions of 2.92 g (3.91 mmol) of Mo(CO)$_4$(nbd) in 150 mL of degassed dichloromethane and 1.17 g (3.91 mmol) of **13** in 150 mL of degassed dichloromethane were added simultaneously and dropwise to 300 mL of degassed dichloromethane over a 2 h period. This mixture was stirred for 30 min and then evaporated to dryness to give a brown oil. The oil was triturated with methanol to yield 2.61 g (63.8%) of crude **8** as an off-white powder. Recrystallization from a dichloromethane/methanol mixture yielded analytically pure **8** as colorless crystals. Anal. Calcd for $C_{46}H_{36}O_{11}P_2Mo$: C, 57.87; H, 3.80. Found: C, 57.48; H, 3.79. $^{31}$P{$^1$H} NMR (dichloromethane-$d_2$): $\delta$ 172.28 (d, ArO*P*, $|^2J(\mathrm{PP'})|$ 47 Hz), 169.60 (d, CH$_2$O*P*, $|^2J(\mathrm{PP'})|$ 47 Hz). $^{13}$C{$^1$H} NMR (aliphatic carbons, dichloromethane-$d_2$): $\delta$ 71.90 (s, C4), 71.73 (s, C3), 70.98 (d, C2, $|^2J(\mathrm{PC})|$ 7 Hz), 70.52 (s, C5), 68.99 (s, C6), 68.21 (d, C1, $|^2J(\mathrm{PC})|$ 7 Hz). $^1$H NMR (aliphatic protons, dichloromethane-$d_2$): $\delta$ 4.13 (ddd, H6, $|^2J(\mathrm{H6H6'})|$ 11 Hz, $|^3J(\mathrm{H6H5'})|$ 8 Hz, $|^3J(\mathrm{H6H5})|$ 2 Hz ), 3.93 (m, H1, H1′, and H6′), 3.65 (ddd, H5, $|^2J(\mathrm{H5H5'})|$ 11 Hz, $|^3J(\mathrm{H5H6'})|$ 5 Hz, $|^3J(\mathrm{H5H6})|$ 2 Hz), 3.51 m, H5′), 3.49 (m, H4 and H4′), 3.43 (m, H2 and H2′), 3.41 (m, H3 and H3′).

**$^{31}$P{$^1$H} NMR Study of the HgCl$_2$(s)-Catalyzed *cis*−*trans* Isomerization of *cis*-Mo(CO)$_4${Ph$_2$PO(CH$_2$CH$_2$O)$_3$-2-C$_{12}$H$_8$-2′-OPPh$_2$}, 7.** A solution of 0.011 g (0.012 mmol) of **7** in 0.6 mL of dichloromethane-$d_2$ was prepared in a 5 mm, screw-top NMR tube under nitrogen, and a $^{31}$P{$^1$H} NMR spectrum of the solution was recorded. Then solid HgCl$_2$ (two small crystals) was added to the solution. After vigorous shaking, a nonquantitative $^{31}$P{$^1$H} NMR spectrum was acquired. The complex had completely converted to *trans*-Mo(CO)$_4${Ph$_2$PO(CH$_2$CH$_2$O)$_3$-2-C$_{12}$H$_8$-2′-OPPh$_2$}, **14**. $^{31}$P{$^1$H} NMR (dichloromethane-$d_2$): $\delta$ 161.05 (d, ArO*P*, $|^2J(\mathrm{PP'})|$ 88 Hz), 152.42 (d, CH$_2$O*P*, $|^2J(\mathrm{PP'})|$ 88 Hz).

**$^{31}$P{$^1$H} NMR Study of the HgCl$_2$(s)-Catalyzed *cis*−*trans* Isomerization of *cis*-Mo(CO)$_4${(2,2′-C$_{12}$H$_8$O$_2$)P-(CH$_2$CH$_2$O)$_3$-2-C$_{12}$H$_8$-2′-P(2,2′-O$_2$C$_{12}$H$_8$)}, 8. Method 1.** A solution of 0.057 g (0.060 mmol) of **8** in 0.6 mL of chloroform-*d* was prepared in a 5 mm, screw-top NMR tube under nitrogen, and the $^{31}$P{$^1$H} spectrum of the solution was recorded. Then one drop of a dilute, aqueous HgCl$_2$ solution was added to the surface of the NMR solution. Nonquantitative $^{31}$P{$^1$H} NMR spectra were acquired 2.5, 10, 20, 30, and 40 min and both quantitive and nonquantitative $^{31}$P{$^1$H} NMR spectra were acquired 20 h after the addition. After 20 h, the ratio of *cis*-Mo(CO)$_4${(2,2′-C$_{12}$H$_8$O$_2$)P(CH$_2$CH$_2$O)$_3$-2-C$_{12}$H$_8$-2′-P(2,2′-O$_2$C$_{12}$H$_8$)}, **8**, to *trans*-Mo(CO)$_4${(2,2′-C$_{12}$H$_8$O$_2$)P(CH$_2$CH$_2$O)$_3$-2-C$_{12}$H$_8$-2′-P(2,2′-O$_2$C$_{12}$H$_8$)}, **15**, was 0.21. $^{31}$P{$^1$H} NMR for **15** (chloroform-*d*): $\delta$ 190.44 (d, ArO*P*, $|^2J(\mathrm{PP'})|$ 233 Hz), 173.09 (d, CH$_2$O*P*, $|^2J(\mathrm{PP'})|$ 233 Hz).

**Method 2.** A solution of 0.123 g (0.109 mmol) of **8** in 0.6 mL of chloroform-*d* was prepared in a 5 mm, screw-top NMR tube under nitrogen, and the $^{31}$P{$^1$H} spectrum of the solution was recorded. Then solid HgCl$_2$ (two small crystals) was added to the solution. After vigorous shaking, nonquantitative $^{31}$P{$^1$H} NMR spectra were acquired every 10 min over a 1 h and 20 min period.

***cis*-Mo(CO)$_4${Ph$_2$PO(CH$_2$CH$_2$O)$_3$-2-C$_{12}$H$_8$-2′-OPPh$_2$}·HgCl$_2$, 16.** A solution of 0.200 g (0.224 mmol) of **7** in 1.2 mL of dichloromethane was prepared, and then HgCl$_2$ (0.061 g, 0.224 mmol) was added. This mixture was stirred overnight and then was filtered through Celite and evaporated to dryness to yield 0.195 g (74.7%) of crude **16** as a dark yellow powder. Recrystallization from a dichloromethane/hexanes mixture yielded analytically pure **16** as an off-white solid. Anal. Calcd for $C_{46}H_{44}O_9P_2MoHgCl_2$ (with 0.33 mol of $C_6H_{14}$): C, 48.26; H, 3.77. Found: C, 48.25; H, 3.85. $^{31}$P{$^1$H} NMR (dichloromethane-$d_2$): $\delta$ 151.00 (d, ArO*P*, $|^2J(\mathrm{PP'})|$ 39 Hz), 127.27 (d, CH$_2$O*P*, $|^2J(\mathrm{PP'})|$ 40 Hz). $^{13}$C{$^1$H} NMR (aliphatic carbons, dichloromethane-$d_2$): $\delta$ 69.86 (s, C3 and C4), 69.23 (d, C2, $|^2J(\mathrm{PC})|$ 6 Hz), 68.26 (s, C5), 67.35 (s, C6), 65.74 (d, C1, $|^2J(\mathrm{PC})|$ 12 Hz). $^1$H NMR (aliphatic protons, dichloromethane-$d_2$): $\delta$ 4.08 (dd, H6 and H6′, $|^3J(\mathrm{H5H6}) + {}^3J(\mathrm{H5H6'})|$ 8.9 Hz), 3.68 (dd, H5 and H5′, $|^3J(\mathrm{H5H6}) + {}^3J(\mathrm{H5'H6'})|$ 8.9 Hz), 3.58 (m, H3, H3′, H4, H4′), 3.42 (bs, H1, H1′, H2, H2′).

***trans*-Mo(CO)$_4${(2,2′-C$_{12}$H$_8$O$_2$)P(CH$_2$CH$_2$O)$_3$-2-C$_{12}$H$_8$-2′-P(2,2′-O$_2$C$_{12}$H$_8$)}·HgCl$_2$, 17.** A solution of 0.100 g (0.105 mmol) of **8** in 1.2 mL of dichloromethane was prepared under nitrogen at ambient temperature, and then 0.028 g (0.10 mmol) of solid HgCl$_2$ was added. The mixture was stirred overnight and then was filtered through Celite and evaporated to dryness to yield 0.098 g (78.1%) of the crude **17** as a brown powder. Recrystallization from a dichloromethane/hexanes mixture yielded the analytically pure **17** as off-white crystals. Anal. Calcd for $C_{46}H_{36}O_{13}P_2MoHgCl_2$ (plus 0.5 mol of $C_6H_{14}$): C, 46.35; H, 3.38; Cl, 5.59. Found: C, 46.43; H, 3.63; Cl, 5.83. $^{31}$P{$^1$H} NMR-(chloroform-*d*): $\delta$ 190.67 (d, ArO*P*, $|^2J(\mathrm{PP'})|$ 233 Hz), 174.09 (d, CH$_2$O*P*, $|^2J(\mathrm{PP'})|$ 233 Hz). $^{13}$C{$^1$H} NMR (aliphatic carbons, chloroform-*d*): $\delta$ 72.14 (s, C3 or C4), 70.34 (d, C2, $|^2J(\mathrm{PC})|$ 5 Hz), 70.20 (s, C4 or C3), 69.75 (s, C5), 67.66 (s, C6), 67.18 (d, C1, $|^2J(\mathrm{PC})|$ 11 Hz). $^1$H NMR (aliphatic protons, chloroform-*d*): $\delta$ 4.23 (m, H6), 4.05 (m, H6′, H1, and H5′), 3.95 (m, H1′), 3.88 (m, H5), 3.72 (m, H3 and H3′), 3.69 (m, H4 and H4′), 3.62 (m, H2 and H2′).

**[*cis*-Mo(CO)$_4${Ph$_2$PO(CH$_2$CH$_2$O)$_3$-2-C$_{12}$H$_8$-2′-OPPh$_2$}]$_2$-LiBPh$_4$, 18.** A solution of 0.050 g (0.17 mmol) of LiBPh$_4$·3dme and 0.15 g (0.17 mmol) of **7** in 8.4 mL of dichloromethane was stirred for 2 h and then evaporated to dryness. The residue was recrystallized from a dichloromethane/hexanes mixture to give 0.14 g (68%) of analytically pure **18**. Anal. Calcd for [*cis*-Mo(CO)$_4${Ph$_2$PO(CH$_2$CH$_2$O)$_3$-2-C$_{12}$H$_8$-2′-OPPh$_2$}]$_2$LiBPh$_4$: C, 58.37; H, 4.19. Found: C, 58.50; H, 4.40. $^{31}$P{$^1$H} NMR (dichloromethane-$d_2$): $\delta$ 150.22 (bs, ArO*P*), 145.50 (bs, CH$_2$O*P*). $^1$H NMR (aliphatic protons, dichloromethane-$d_2$): $\delta$ 4.03 (ddd, H6, $|^2J(\mathrm{H6H6'})|$ 11 Hz, $|^3J(\mathrm{H6H5'})|$ 8 Hz, $|^3J(\mathrm{H6H5})|$ 2 Hz), 3.95 (ddd, H6′, $|^2J(\mathrm{H6'H6})|$ 11 Hz, $|^3J(\mathrm{H6'H5})|$ 5 Hz, $|^3J(\mathrm{H6'H5'})|$ 2 Hz), 3.62 (ddd, H5, $|^2J(\mathrm{H5H5'})|$ 11 Hz, $|^3J(\mathrm{H5H6'})|$ 5 Hz, $|^3J(\mathrm{H5H6})|$ 2 Hz), 3.48 (ddd, H5′, $|^2J(\mathrm{H5'H5})|$ 11 Hz, $|^3J(\mathrm{H5'H6})|$ 8 Hz, $|^3J(\mathrm{H5'H6'})|$ 2 Hz), 3.26 (m), 3.15 (m), 2.94 (m).

**$^{31}$P{$^1$H} NMR Study of the Reaction of NaBPh$_4$ with *cis*-Mo(CO)$_4${Ph$_2$PO(CH$_2$CH$_2$O)$_3$-2-C$_{12}$H$_8$-2′-OPPh$_2$}, 7.** A 0.002 g (0.006 mmol) sample of NaBPh$_4$ was added to a solution of 0.011 g (0.012 mmol) of **7** in 0.6 mL of dichloromethane-$d_2$. The solution was stirred for 3 h, and then the $^{31}$P{$^1$H} spectrum of the solution was obtained. $^{31}$P{$^1$H} NMR (dichloromethane-$d_2$) major: $\delta$ 156.49 (vbs, ArO*P*), 148.76 (bd, CH$_2$O*P*, $|^2J(\mathrm{PP'})|$ 35 Hz); minor (**15**): $\delta$ 161.91 (d, ArO*P*, $|^2J(\mathrm{PP'})|$ 86 Hz), 154.93 (d, CH$_2$O*P*, $|^2J(\mathrm{PP'})|$ 86 Hz).

**$^{31}$P{$^1$H} NMR Titration of *cis*-Mo(CO)$_4${Ph$_2$PO(CH$_2$-CH$_2$O)$_3$-2-C$_{12}$H$_8$-2′-OPPh$_2$}, 7, with Li$_2$(DMSO)$_2$-$\mu$-(DMSO)$_2$-(OH$_2$)$_2$(BPh$_4$)$_2$.** Solutions of 0.00894 g (0.0100 mmol) of **7** in 0.5 mL of dichloromethane-$d_2$ and of 0.020 g (0.020 mmol) of Li$_2$(DMSO)$_2$-$\mu$-(DMSO)$_2$(OH$_2$)$_2$(BPh$_4$)$_2$ in 0.5 mL of dichloromethane-$d_2$ were prepared. Aliquots of the solution of the lithium salt were added to the solution of **7** using a 25 $\mu$L syringe. Both $^{31}$P{$^1$H} and $^1$H NMR spectra were taken after each addition.

**NMR Titration of *cis*-Mo(CO)$_4${Ph$_2$PO(CH$_2$CH$_2$O)$_3$-2-C$_{12}$H$_8$-2′-OPPh$_2$}, 7, with LiBPh$_4$·3dme.** Solutions of 0.00894 g (0.0100 mmol) of **7** in 0.5 mL of dichloromethane-$d_2$ and of 0.020 g (0.033 mmol) in 0.5 mL of LiBPh$_4$·3dme in dichloromethane-$d_2$ were prepared, and $^{31}$P{$^1$H} and $^1$H NMR spectra of the solution were obtained. Aliquots of the solution of the lithium salt were added to the solution of **7** using a 25 $\mu$L syringe. Both $^{31}$P{$^1$H} and $^1$H NMR spectra were taken after each addition.

**NMR Titration of *cis*-Mo(CO)$_4${(2,2′-C$_{12}$H$_8$O$_2$)P(CH$_2$-CH$_2$O)$_3$-2-C$_{12}$H$_8$-2′-P(2,2′-O$_2$C$_{12}$H$_8$)}, 10, with LiBPh$_4$·3dme.** Solutions of 0.00954 g (0.0100 mmol) of **8** in 0.5 mL of dichloromethane-$d_2$ and of 0.02 g (0.033 mmol) in 0.5 mL of

$LiBPh_4$·3dme in dichloromethane-$d_2$ were prepared, and $^{31}P\{^1H\}$ and $^1H$ NMR spectra of the solution were obtained. Aliquots of the solution of the lithium salt were added to the solution of **8** using a 25 $\mu$L syringe. Both $^{31}P\{^1H\}$ and $^1H$ NMR spectra were taken after each addition.

**Variable-Temperature $^{31}P\{^1H\}$ NMR (VT-NMR) Study of [*cis*-Mo(CO)$_4$\{$Ph_2PO(CH_2CH_2O)_3$-2-$C_{12}H_8$-2′-$OPPh_2$\}]$_2$-$LiBPh_4$, 18.** A solution was prepared by dissolving 0.003 g (0.005 mmol) of $LiBPh_4$·3dme and 0.0045 g (0.0050 mmol) of **7** in 0.5 mL of dichloromethane-$d_2$ in a 5 mm, screw-top NMR tube under nitrogen. $^{31}P\{^1H\}$ NMR spectra were taken over a temperature range of 305−192 K, which was calibrated using a methanol thermometer.

***Cis*−*trans* Isomerization of [*cis*-Mo(CO)$_4$\{$Ph_2PO(CH_2CH_2O)_3$-2-$C_{12}H_8$-2′-$OPPh_2$\}]$LiBPh_4$, 18.** A solution was prepared by dissolving 0.016 g (0.028 mmol) of $LiBPh_4$·3dme and 0.050 g (0.056 mmol) of **7** in 6.0 mL of dichloromethane. The solution was stirred overnight and then evaporated to dryness. The residue was dissolved in dichloromethane-$d_2$ to form a saturated solution. This solution was placed in an NMR tube and stored at ambient temperature under nitrogen. The slow *cis*−*trans* isomerization and lithium cation coordination to two metallacrown ethers, **7** and **14**, were followed by $^{31}P\{^1H\}$ NMR spectroscopy over a period of several months.

**X-ray Data Collection and Solution.** A suitable single crystal of **8** was mounted on a glass fiber with epoxy cement and aligned on an Enraf Nonius CAD4 single-crystal diffractometer under aerobic conditions. Standard peak search and automatic indexing routines followed by least-squares fits of 25 accurately centered reflections resulted in accurate unit cell parameters that indicated that the crystal belongs to the monoclinic crystal system. Systematic absences indicated that the space group was *P*2(1)/*c*. The analytical scattering factors of the complex were corrected for both $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion. All of the heavy atom positions were located using direct methods, and the remainder of the non-hydrogen atoms were located in difference Fourier maps. Positional and anisotropic displacement parameters for all non-hydrogen atoms were refined. Hydrogen atoms were not located directly but were input in calculated positions with $d(C-H) = 0.96$ Å. The isotropic displacement parameter of each hydrogen atom was set equal to 1.2 times the $U_{eq}$ value of the carbon atom to which it was bonded. The Siemens SHELXTL-PC program package was used for all crystallographic calculations.[18] The experimental details of the data collection and refinement are summarized in Table 1. Selected bond lengths and angles are given in Table 2, and selected torsion angles are given in Table 3.

## Results and Discussion

**Syntheses and Characterizations of the Asymmetric Bis(phosphorus-donor)polyether Ligands.** The starting material for the ligands, 2-hydroxy-2′-(1,4,7-trisoxo-9-nonanol)-1,1′-biphenyl, **11**, was prepared by the reaction of 2,2′-biphenol, sodium hydride, and 2-[2-(2-chloroethoxy)ethoxy]ethanol in anhydrous DMF and purified by column chromatography. The asymmetric bis(phosphorus-donor)polyether ligands, **12** and **13**, are viscous oils and were prepared by the reactions of **11** with chlorodiphenylphosphine and 2,2′-biphenylylenephosphochloridite ester, respectively, in the presence of triethylamine, as shown in Figure 2. The $^{31}P\{^1H\}$ and $^1H$ NMR spectra of the crude ligands contained no unexplained resonances. Because of difficulties associated with purifying the ligands either by distillation or chromatography, the crude ligands were used in the syntheses of the *cis*-metallacrown ethers, **7** and **8**.

**Table 1. Crystal Data and Structure Refinement for 8·0.25CH$_2$Cl$_2$**

| | |
|---|---|
| empirical formula | $C_{46.25}H_{36.50}Cl_{0.50}MoO_{13}P_2$ |
| fw | 975.91 |
| temperature | 293(2) K |
| wavelength | 0.71073 Å |
| cryst syst | monoclinic |
| space group | *P*2(1)/*c* |
| unit cell dimens | $a = 10.247(2)$ Å |
| | $b = 22.545(5)$ Å, $\beta = 99.27(3)°$ |
| | $c = 22.017(4)$ Å |
| volume | 5019.8(17) Å$^3$ |
| *Z* | 4 |
| density (calcd) | 1.287 Mg/m$^3$ |
| abs coeff | 0.409 mm$^{-1}$ |
| *F*(000) | 1986 |
| cryst size | 0.14 × 0.29 × 0.54 mm$^3$ |
| $\theta$ range for data collection | 1.81−22.48° |
| index ranges | $-11 \le h \le 1$, $-24 \le k \le 0$, $-23 \le l \le 23$ |
| no. of reflns collected | 7853 |
| no. of ind reflns | 6539 [$R$(int) = 0.0467] |
| completeness to $\theta = 22.48°$ | 100.0% |
| abs corr | empirical |
| max. and min. transmn | 0.2782 and 0.2528 |
| refinement method | full-matrix least-squares on $F^2$ |
| no. of data/restraints/params | 6539/0/615 |
| goodness-of-fit on $F^2$ | 1.020 |
| final *R* indices [$I > 2\sigma(I)$] | R1 = 0.0554, wR2 = 0.1423 |
| *R* indices (all data) | R1 = 0.1596, wR2 = 0.1827 |
| extinction coeff | 0.0017(2) |
| largest diff peak and hole | 0.762 and −0.473 e Å$^{-3}$ |

**Table 2. Bond Lengths [Å] and Angles [deg] for 8**

| | | | |
|---|---|---|---|
| C1−C6 | 1.392(11) | C43−Mo | 2.020(10) |
| C1−O1 | 1.398(8) | C44−O11 | 1.129(10) |
| C6−C7 | 1.496(11) | C44−Mo | 2.021(11) |
| C7−C12 | 1.386(11) | C45−O12 | 1.143(10) |
| C12−O2 | 1.378(10) | C45−Mo | 2.043(11) |
| C13−O2 | 1.436(10) | C46−O13 | 1.136(10) |
| C13−C14 | 1.503(12) | C46−Mo | 2.016(10) |
| C14−O3 | 1.400(9) | Mo−P1 | 2.425(2) |
| C15−O3 | 1.404(9) | Mo−P2 | 2.439(3) |
| C15−C16 | 1.521(11) | O1−P1 | 1.612(5) |
| C16−O4 | 1.402(9) | O5−P2 | 1.559(6) |
| C17−O4 | 1.414(10) | O6−P1 | 1.619(5) |
| C17−C18 | 1.488(11) | O7−P1 | 1.612(5) |
| C18−O5 | 1.461(9) | O8−P2 | 1.621(6) |
| C43−O(10) | 1.134(10) | O9−P2 | 1.621(5) |
| O2−C13−C14 | 111.4(7) | C43−Mo−P2 | 89.6(3) |
| O3−C14−C13 | 110.1(8) | C44−Mo−P2 | 175.4(3) |
| O3−C15−C16 | 110.7(7) | C45−Mo−P | 295.5(3) |
| O4−C16−C15 | 114.5(8) | P1−Mo−P2 | 89.27(8) |
| O4−C17−C18 | 110.3(8) | C1−O1−P1 | 122.0(5) |
| O5−C18−C17 | 108.1(7) | C12−O2−C13 | 120.7(7) |
| O10−C43−Mo | 178.2(10) | C14−O3−C15 | 112.7(7) |
| O11−C44−Mo | 177.5(10) | C16−O4−C17 | 114.0(7) |
| O12−C45−Mo | 176.0(8) | C18−O5−P2 | 129.3(5) |
| O13−C46−Mo | 175.5(9) | O1−P1−Mo | 121.79(19) |
| C46−Mo−P1 | 93.6(2) | O7−P1−Mo | 120.7(2) |
| C43−Mo−P1 | 177.5(3) | O6−P1−Mo | 113.3(2) |
| C44−Mo−P1 | 90.0(3) | O5−P2−Mo | 114.5(2) |
| C45−Mo−P1 | 88.7(3) | O9−P2−Mo | 110.7(2) |
| C46−Mo−P2 | 87.1(3) | O8−P2−Mo | 122.8(2) |

The $^{31}P\{^1H\}$ NMR spectra of **12** and **13** exhibit two singlets due to their chemically inequivalent phosphorus nuclei. The resonances were assigned on the basis of $^1H$-coupled $^{31}P$ NMR spectra and by comparison with the chemical shifts of the $^{31}P$ NMR resonances of **12** and **13** with those of ligands with similar phosphorus environments. No attempt was made to completely assign the $^1H$ NMR spectra chemical shifts of **12** and **13**.[10]

---

[18] Sheldrick, G. M. *SHELXTL NT* ver. 5.10; Bruker AXS, Inc.: Madison, WI, 1999.

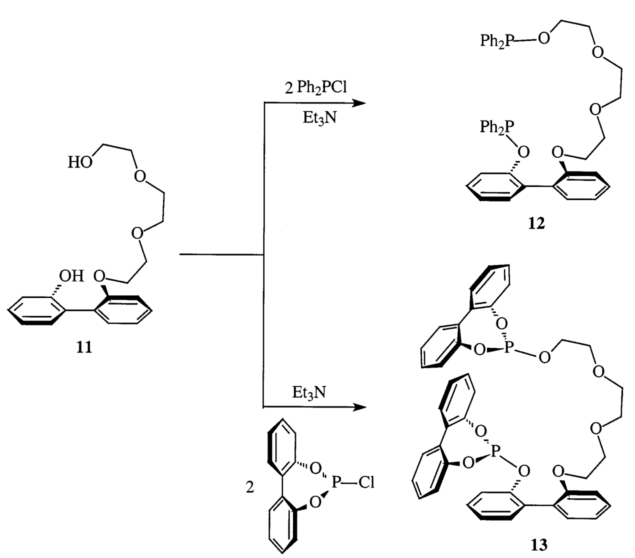

**Figure 2.** Scheme for the syntheses of the bis(phosphorus-donor)polyether ligands.

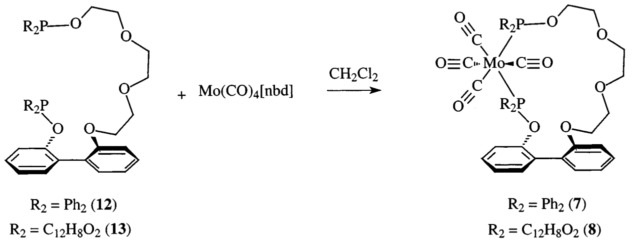

**Figure 3.** Scheme for the syntheses of the *cis*-metallacrown ethers.

**Table 3. Torsion Angles [deg] for 8 and for Comparable Groups in *cis*-Mo(CO)$_4${2,2′-($C_{12}H_8O_2$)-PO($CH_2CH_2O$)$_2$-2-$C_{12}H_8$-2′-OP(2,2′-$C_{12}H_8O_2$)}, 6**

| | 8 | 6 |
|---|---|---|
| C1−O1−P1−Mo | −45.3(6) | 130.6 |
| C6−C1−O1−P1 | 137.6(6) | 101.3 |
| C1−C6−C7−C12 | 65.9(11) | 63.6 |
| C7−C12−O2−C13 | −167.5(7) | 179.4 |
| C14−C13−O2−C12 | 83.7(10) | |
| O2−C13−C14−O3 | −75.9(10) | |
| C(13)−C(14)−O(3)−C(15) | −175.7(7) | |
| C(16)−C(15)−O(3)−C(14) | −175.1(7) | −171.0 |
| O(3)−C(15)−C(16)−O(4) | 76.6(9) | −68.2 |
| C(15)−C(16)−O(4)−C(17) | −83.9(10) | −100.6 |
| C(18)−C(17)−O(4)−C(16) | −178.3(7) | 166.9 |
| O(4)−C(17)−C(18)−O(5) | −78.9(9) | −68.4 |
| C(17)−C(18)−O(5)−P(2) | 165.3(6) | 145.5 |
| C(18)−O(5)−P(2)−Mo | −175.7(6) | 165.9 |
| P(1)−Mo−P(2)−O(5) | 9.7(3) | |
| P(2)−Mo−P(1)−O(1) | −77.0(3) | |

**Syntheses and Characterizations of the *cis*-Metallacrown Ethers.** The *cis*-Mo(CO)$_4${$R_2$PO($CH_2CH_2O$)$_3$-2-$C_{12}H_8$-2′-OP$R_2$} ($R_2$ = $Ph_2$, **7**; $C_{10}H_8O_2$, **8**) metallacrown ethers were prepared by the reactions of Mo(CO)$_4$(nbd) with the ligands **12** and **13** under moderate dilutions as shown in Figure 3.

The $^{31}$P{$^1$H} NMR resonances of **7** and **8** are AX patterns due to the chemically inequivalent phosphorus nuclei. Both the |$^2J$(PP′)| coupling constants (32 Hz for **7** and 47 Hz for **8**) and the chemical shifts of the resonances are consistent with the *cis* geometry of the complexes.

The $^{13}$C{$^1$H} and $^1$H NMR spectra of **7** and **8** exhibit a number of interesting features. As has previously been observed for other asymmetric *cis*-metallacrown ethers,[10] a well-resolved resonance is observed for each of the four carbonyls in **7**. The magnitudes of the phosphorus−carbon coupling constants of these resonances are consistent with the *cis* geometry of the complex. The carbonyls *trans* to the phosphorus-donor groups are chemically inequivalent because the two phosphorus-donor groups in the ligands are different. The inequivalence of the carbonyls *cis* to both phosphorus-donor groups cannot be due to this and instead must be due to an asymmetric arrangement of the metallacrown ether ring relative to the plane containing the molybdenum and the two phosphorus-donor groups.

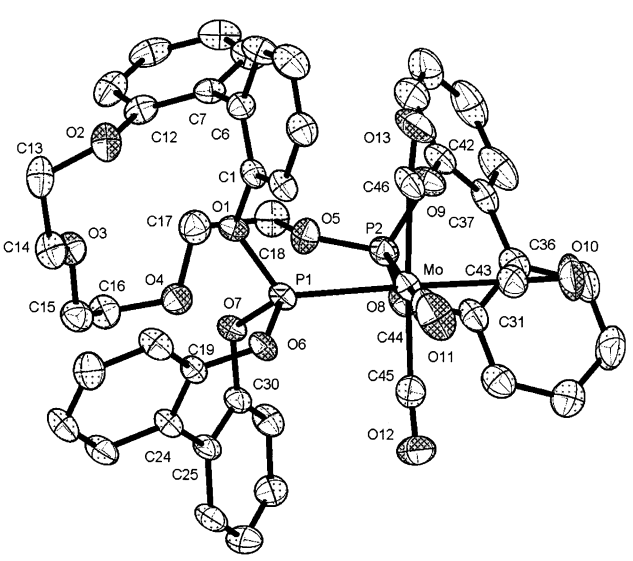

**Figure 4.** ORTEP drawing of the X-ray crystal structure of **8**. The thermal ellipsoids are drawn at 50%, and the hydrogen atoms are omitted for clarity.

All of the resonances of the aliphatic carbons and hydrogens in **7** and **8** can be assigned using 2D NMR spectroscopy.[15] A $^1$H−$^1$H COSY-45 NMR experiment was run to determine the $^1$H−$^1$H coupling, and the $^1$H−$^{13}$C connectivity was determined using a $^1$H{$^{13}$C} HMBC NMR experiment. A $^1$H{$^{13}$C} HMQC was used to assign protons to their respective carbons, and a high-resolution $^1$H−$^1$H NOESY experiment was used to assign the methylene protons adjacent to the biphenyl group.

The presence of diastereotopic protons for the ethylene groups adjacent to the biphenyl groups in **7** and **8** allows the magnitudes of the geminal, |$^2J$(H,H)|, and vicinal, |$^3J$(H,H)|, coupling constants to be determined for this group. These coupling constants are the same in **7** and **8** (geminal: 11 Hz for each methylene; vicinal: 8, 5, 2, and 2 Hz), suggesting that the ethylene groups in the two metallacrown ethers have the same conformations. Unfortunately, the magnitudes of the vicinal coupling constants are not totally consistent with either a gauche (three small and one large) or an anti (two large and two small) configuration, and it is not possible to determine the solution conformation of the ethylene groups in these metallacrown ethers. The ethylene group adjacent to the biphenyl group in **8** has a gauche conformation in the solid state.

**X-ray Crystal Structure of *cis*-Mo(CO)$_4${(2,2′-$C_{12}H_8O_2$)P($CH_2CH_2O$)$_3$-2-$C_{12}H_8$-2′-P(2,2′-$O_2C_{12}H_8$)}, 8.** The molecular structure of **8** is shown in Figure 4. The coordination environment of the molybdenum is a

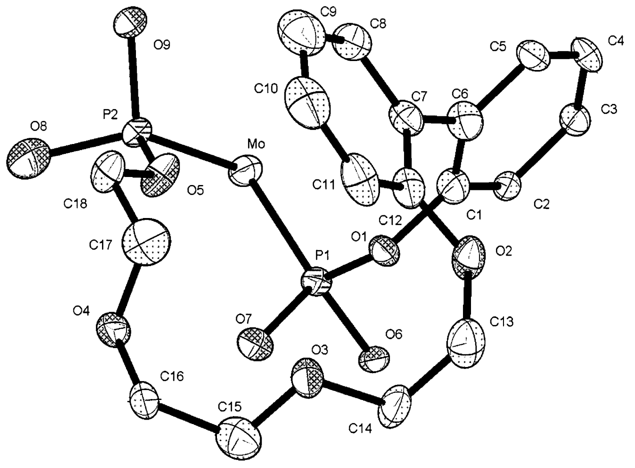

**Figure 5.** ORTEP drawing of the metallacrown ether ring in **8**. The thermal ellipsoids are drawn at 50%, and the hydrogen atoms are omitted for clarity.

slightly distorted octahedron with a P2–Mo–P1 angle of 89.27(8)°. This is similar to that in other *cis*-$Mo(CO)_4$-(phosphite)$_2$ complexes. There is also little difference between the Mo–C and C–O bonds for the carbonyls *trans* to the phosphites and those of carbonyls *trans* to carbonyls. This suggests that replacing a carbonyl with a phosphite has little effect on the ability of the Mo to $\pi$-donate electron density to the carbonyl.

The most interesting feature of the molecular structure of **8** is the conformation of the metallacrown ether ring, shown in Figure 5. The biphenyl group in the ring prevents a planar arrangement of the oxygen atoms, as has been previously observed in crystal structures of symmetric metallacrown ethers.[1] The conformation of the ring is quite similar to that of the smaller asymmetric metallacrown ether, **6**, as seen by the very similar torsion angles for the two ethylene oxide groups closest to P2. This conformation results in three of the ether oxygens (O2, O3, and O4) pointing away from the metallacrown ether cavity. This suggests that, if the solution conformation of **8** is similar to that of the solid state conformation, as appears to be the case for the closely related asymmetric metallacrown ether, **10**,[15] cation binding will be quite different from that observed for the symmetric metallacrown ethers **2** and **3**. As discussed below, this is indeed the case.

***Cis–trans* Isomerization Equilibria of the Metallacrown Ethers Catalyzed by $HgCl_2$.** As discussed above, the reactions of $Mo(CO)_4(nbd)$ with **12** and **13** in degassed $CH_2Cl_2$ under dilute conditions yield only the *cis*-metallacrown ethers **7** and **8**, respectively. When catalytic amounts of solid $HgCl_2$ are added to chloroform-*d* solutions of **7** and **8**, isomerizations to the corresponding *trans*-metallacrown ethers, **14** and **15**, are observed as shown in Figure 6. The isomerization of **7** to **14** is extremely rapid, occurring within the time needed to add the solid $HgCl_2$ to the NMR tube and obtain a nonquantitative $^{31}P\{^1H\}$ spectrum (2.5 min). The isomerization of **8** to **15** is somewhat slower, requiring several hours. These results are consistent with those obtained with the smaller, asymmetric *cis*-metallacrown ethers, **5** and **6**, in that the *cis–trans* isomerization was much more rapid for the *cis*-metallacrown ether with phosphinite P-donor groups, **5**, than for the *cis*-metallacrown ether with phosphite P-donor groups, **6**.[10]

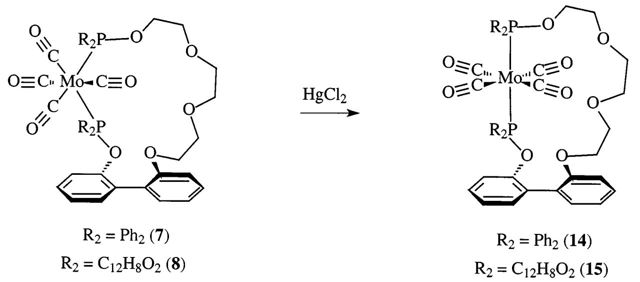

**Figure 6.** Isomerization of *cis*-metallacrown ethers catalyzed by $HgCl_2$.

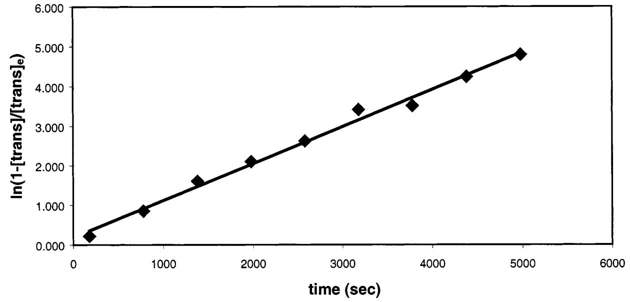

**Figure 7.** Kinetics of the *cis–trans* isomerization of **8**.

The *cis–trans* isomerization of **8** is even slower when aqueous $HgCl_2$ is layered on a chloroform-*d* solution of **8** in a 5 mm NMR tube and could be followed by quantitative $^{31}P$ NMR spectroscopy. The *cis–trans* isomerization of the bis(phosphite) complex obeys reversible first-order kinetics ($k_f = 7.7 \times 10^{-4}$ s$^{-1}$, $k_r = 1.6 \times 10^{-4}$ s$^{-1}$) (Figure 7). The difference in the rates of *cis–trans* isomerization of **8** in the solid/chloroform and aqueous/chloroform biphasic mixtures is most likely due to inefficient phase transfer of the $HgCl_2$ from the water to the organic phase in the latter reaction.

**Complexation of $HgCl_2$ by Asymmetric Metallacrown Ethers.** Stoichiometric reactions of the *cis*-metallacrown ethers, **7** and **8**, with $HgCl_2$ yield very different complexes. The 1:1 reaction of $HgCl_2$ and **7** yields *cis*-$Mo(CO)_4\{Ph_2PO(CH_2CH_2O)_3\text{-}2\text{-}C_{12}H_8\text{-}2'\text{-}OPPh_2\}\cdot HgCl_2$, **16**, as indicated by the magnitude of the $^2J(PP')$ coupling constant (40 Hz) and the elemental analyses. The large shifts in the $^{31}P$ NMR resonances of **7** upon $HgCl_2$ coordination (5 ppm downfield for the aromatic phosphinite shifts and 14 ppm upfield for the aliphatic phosphinite) suggest that significant conformation changes occur upon complexation. In contrast, the 1:1 reaction of $HgCl_2$ and **8** yields *trans*-$Mo(CO)_4\{(2,2'\text{-}C_{12}H_8O_2)P(CH_2CH_2O)_3\text{-}2\text{-}C_{12}H_8\text{-}2'\text{-}P(2,2'\text{-}O_2C_{12}H_8)\}\cdot HgCl_2$, **17**, as indicated by the magnitude of the $^2J(PP')$ coupling constant (233 Hz) and the elemental analyses. This is the first example of cation binding by a *trans*-metallacrown ether. The very similar chemical shifts of the $^{31}P$ NMR resonances of **17** and the free *trans*-metallacrown ether, **15** (aromatic phosphite: 190.67 ppm for **17** vs 190.44 ppm for **15**; aliphatic phosphite: 174.09 ppm for **17** vs 173.09 ppm for **15**), suggest that $HgCl_2$ coordination to **15** does not cause a significant change in the conformation of the metallacrown ether ring near the $^{31}P$ nuclei.

The very different reactions of $HgCl_2$ with **7** and **8** demonstrate that the phosphorus substituents can have

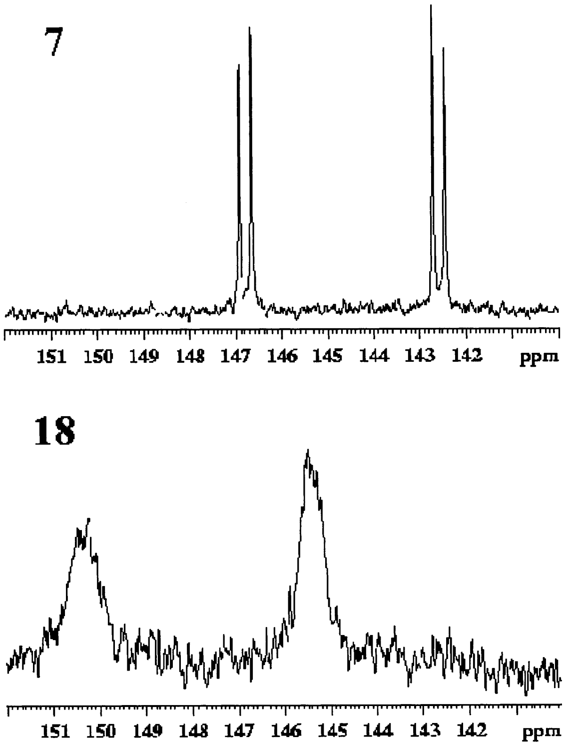

**Figure 8.** $^{31}P$ $\{^{1}H\}$ NMR spectra of the asymmetric metallacrown ether, **7** (top), and the 2:1 metallacrown ether:$LiBPh_4$ complex, **18** (bottom).

significant effects upon the cation-binding abilities of the metallacrown ethers, perhaps because the phosphite oxygens are involved in complexation of the metal cation. This result may be related to previous observations that carbonyl ligands in certain *cis*-metallacrown ethers with bis(phosphinite)polyether ligands are activated toward nucleophilic attack by phenyllithium, while those in bis(phosphite)polyether ligands with the same metallacrown ether ring are not.[10,18] The activation of carbonyls in a metallacrown ether occurs only when the metallacrown ether has one too few oxygens to effectively coordinate the $Li^+$.

**Complexation of Alkali Metal Cations by Asymmetric Metallacrown Ethers.** The asymmetric metallacrown ether **7** was reacted with $LiBPh_4$·3dme in a 1:1 mole ratio in dichloromethane. However, after recrystallization, the 2:1 [*cis*-$Mo(CO)_4\{Ph_2PO(CH_2CH_2O)_3$-2-$C_{12}H_8$-2′-$OPPh_2\}]_2LiBPh_4$ complex, **18**, was obtained in good yield. This complex also precipitates when solid $LiBPh_4$·3dme is added to a chloroform-*d* solution of **4**. As shown in Figure 8, the $^{31}P\{^{1}H\}$ NMR spectrum of **18** in dichloromethane-$d_2$ contains two broad singlets with chemical shifts downfield of those of **7**. The shifts in the $^{31}P\{^{1}H\}$ resonances of **18** relative to those of **7** suggest that the $Li^+$ is coordinated to the *cis*-metallacrown ether. The formation of the 2:1 complex, **18**, was surprising because $HgCl_2$ forms a 1:1 complex with **7**.

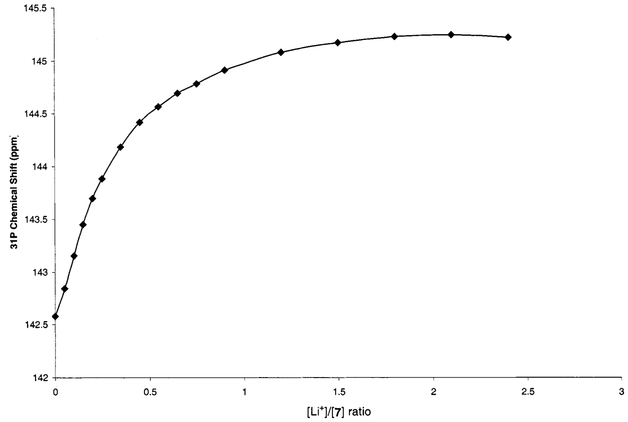

**Figure 9.** Titration of **7** with $LiBPh_4$·3dme. The $^{31}P\{^{1}H\}$ NMR chemical shift of the aliphatic phosphinite is plotted versus the $[Li^+]/[\mathbf{7}]$ ratio.

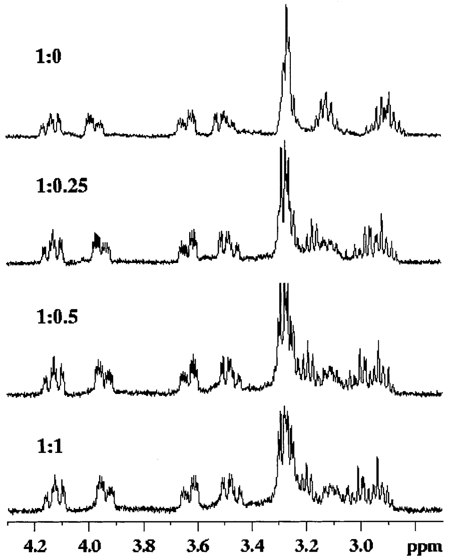

**Figure 10.** Stacked plot of the aliphatic portion of the $^{1}H$ NMR spectrum of **7** during the titration with $[Li_2(\mu\text{-}DMSO)_2(DMSO)_2(H_2O)_2][BPh_4]_2$. The four distinct resonances to the left are those of the oxyethylene group adjacent to the biphenoxy group. The overlapped resonances to the right are those of the other oxyethylene groups.

To gain more insight into the coordination of $Li^+$ to the asymmetric metallacrown ethers, NMR titrations of **7** and **8** with both $LiBPh_4$·3dme and $[Li_2(\mu\text{-}DMSO)_2(DMSO)_2(H_2O)_2][BPh_4]_2$ were carried out. A titration curve for **7** with $LiBPh_4$·3dme is shown in Figure 9, and a stacked plot of the aliphatic proton spectra of a titration of **7** with $[Li_2(\mu\text{-}DMSO)_2(DMSO)_2(H_2O)_2][BPh_4]_2$ is shown in Figure 10. The titration indicates that the binding is indeed 2:1, consistent with the elemental analyses of the isolated complex, **18**. The proton spectrum of the complex, shown in Figure 10, suggests that conformational changes in the metallacrown ether ring of **7** do occur upon $Li^+$ coordination and that these changes are primarily in the two oxyethylene groups closest to the aliphatic phosphinite. In contrast, the diastereotopic oxyethylene group adjacent to the biphenoxy group in the metallacrown ether ring does not appear to undergo significant conformational change upon $Li^+$ coordination.

The broad $^{31}P\{^{1}H\}$ resonances of **18** suggested that an exchange process is occurring on the NMR time scale. To determine if this was indeed the case, a variable-temperature NMR experiment was carried out, and the results are available in the Supporting Information. The spectra indeed suggest that several dynamic processes are occurring but unfortunately do not conclusively indicate the type of process that is occurring.

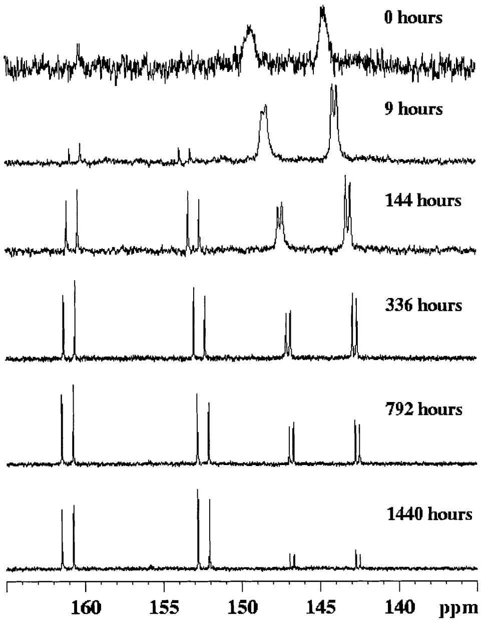

**Figure 11.** *Cis*−*trans* isomerization of **18** in dichloromethane-$d_2$.

Perhaps the most interesting aspect of the interactions of the metallacrown ethers with alkali metal salts is the slow isomerization of **18** in dichloromethane-$d_2$. This reaction was followed by quantitative $^{31}P\{^1H\}$ NMR spectroscopy, and selected spectra are shown in Figure 11. As the isomerization begins to occur, the $^{31}P\{^1H\}$ NMR resonances of **18** begin to sharpen and shift in position toward those of **7**. This indicates that the $Li^+$ is binding preferentially to the *trans* isomer, **14**, and that the free *cis*-metallacrown ether, **7**, is being formed. This conclusion is confirmed by the fact that the chemical shifts of the *trans*-metallacrown ether are significantly different from those of **14**. When the isomerization has proceeded to the point at which equal amounts of *cis*- and *trans*-metallacrown ethers are in solution, the chemical shifts of the $^{31}P$ resonances of the *cis*-metallacrown ether are identical with those of **7**. This suggests that the *trans*-metallacrown ether, **14**, is both binding the $Li^+$ significantly more strongly than is the *cis*-metallacrown ether, **7**, and is binding the $Li^+$ in a 1:1 ratio. This conclusion is confirmed by the fact that, as the isomerization continues past the halfway point, the $^{31}P$ resonances of the *cis*-metallacrown ether do not shift, but those of the *trans*-metallacrown ether move toward those of the free *trans*-metallacrown ether, **14**. This is as expected if the **14** forms a 1:1 complex with $Li^+$, because after the halfway point, the isomerization is forming free **14**.

A final point of interest is that the larger asymmetric *cis*-metallacrown ether, **7**, does not react with phenyllithium, in contrast to the previously reported reaction of the smaller asymmetric *cis*-metallacrown ether, **5**, with phenyllithium.[10] These results are consistent with Powell's conclusion that carbonyl activation occurs only in *cis*-metallacrown ethers in which the phosphorus-donor groups are phosphinites and the metallacrown ether ring has one too few oxyethylene groups to strongly bind $Li^+$.[19]

## Conclusions

Unlike the smaller asymmetric *cis*-metallacrown ethers, **5** and **6**, the newly synthesized larger asymmetric metallacrown ethers, **7** and **8**, are capable of binding $HgCl_2$ and $Li^+$. The variety of binding modes that are observed with the larger asymmetric metallacrown ethers is surprising in light of earlier research with symmetric metallacrown ethers. The *cis*-metallacrown ethers, **7** and **8**, form 2:1 adducts with $Li^+$. The 2:1 adduct of **7** with $Li^+$ slowly isomerizes to form a equimolar mixture of the *trans*-metallacrown ether, **14**, and the 1:1 adduct of **14** with $Li^+$. In contrast, although both *cis*-metallacrown ethers, **7** and **8**, isomerize to the *trans*-metallacrown ethers, **14** and **15**, in the presence of catalytic amounts of $HgCl_2$, the reaction of **7** and a stoichiometric amount of $HgCl_2$ yields a 1:1 complex of **7** and $HgCl_2$, but the reaction of **8** and a stoichiometric amount of $HgCl_2$ under the same conditions yields a 1:1 complex of **15** and $HgCl_2$. The reasons for the formation of the various complexes are not clear; however it is obvious that the products depend both on the hard metal cation and on the phosphorus substituents. The very different abilities of symmetric, smaller asymmetric, and larger asymmetric metallacrown ethers to bind metal cations and active carbonyl ligands could allow them to exhibit quite different catalytic activities and selectivies for catalytic reactions involving carbon monoxide, and studies of metallacrown ethers as catalysts for some of these reactions are currently underway.

**Acknowledgment.** The authors thank the NSF-REU Summer Research Program (CHE-9820282) at UAB and the Petroleum Research Fund of the American Chemical Society (35349-AC3) for funding of the research. J.M.B. thanks the Chemistry Department of the University of Alabama at Birmingham for a graduate teaching assistantship.

**Supporting Information Available:** This material (complete X-ray crystallography data and one figure of the variable-temperature NMR study of **18**) is available free of charge via the Internet at http://pubs.acs.org.

OM020868T

---

[19] (a) Powell, J.; Kuksis, A.; May, C. J.; Nyberg, S. C.; Smith, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 5941. (b) Powell, J.; Nyberg, S. C.; Smith, S. J. *Inorg. Chim. Acta* **1983**, *76*, L75. (c) Powell, J.; Ng, K. S.; Ng, W. W.; Nyberg, S. C. *J. Organomet. Chem.* **1983**, *243*, C1. (d) Powell, J.; Gregg, M. R.; Kuskis, A.; Meindl, P. *J. Am. Chem. Soc.* **1983**, *105*, 1064. (e) Powell, J.; Gregg, M. R.; Kuksis, A.; May, C. J.; Smith, S. J. *Organometallics* **1989**, *8*, 2918. (f) Powell, J.; Kuskis, A.; May, C. J.; Meindl, P. E.; Smith, S. J. *Organometallics* **1989**, *8*, 2933. (g) Powell, J.; Gregg, M. R.; Meindl, P. E. *Organometallics* **1989**, *8*, 2942. (h) Powell, J.; Lough, A.; Wang, F. *Organometallics* **1992**, *11*, 1, 2289.