Solution Conformational Features of the Unsymmetrical Metalla Crown Ether *cis*-$Mo(CO)_4\{2\text{-}(2,2'\text{-}O_2C_{12}H_8)PO(CH_2CH_2O)_2\text{-}2\text{-}C_{20}H_{12}\text{-}2'\text{-}OP(2,2'\text{-}O_2C_{12}H_8)\}$ from 2D NMR Spectroscopy and Molecular Modeling

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A new unsymmetrical metalla crown ether, *cis*-$Mo(CO)_4\{2\text{-}(2,2'\text{-}O_2C_{12}H_8)PO(CH_2CH_2O)_2\text{-}2\text{-}C_{20}H_{12}\text{-}2'\text{-}OP(2,2'\text{-}O_2C_{12}H_8)\}$, has been designed for solution conformation studies. The complex was prepared by the reaction of the α,ω-bis(phosphorus donor) polyether ligand $2\text{-}(2,2'\text{-}O_2C_{12}H_8)PO(CH_2CH_2O)_2\text{-}2\text{-}C_{20}H_{12}\text{-}2'\text{-}OP(2,2'\text{-}O_2C_{12}H_8)$ with $Mo(CO)_4(nbd)$. Separate ^1H NMR resonances were observed for six of the eight methylene protons of the metalla crown ether, indicating that the motion of the metalla crown ether ring was restricted. The ^1H, ^{13}C, and ^{31}P NMR chemical shifts of the metalla crown ether were completely assigned using a combination of ^{13}C DEPT, $^1H-^1H$ COSY, $^{13}C\{^1H\}$ HETCOR, $^{31}P\{^1H\}$ HETCOR, $^1H\{^{13}C\}$ HMBC, and $^1H-^1H$ NOESY NMR experiments. The solution conformation was analyzed using $^1H-^1H$ vicinal coupling constants and $^1H-^1H$ NOESY NMR experiments. The vicinal $^1H-^1H$ coupling constants for the ethylene protons indicated that both ethylenes were gauche. The $^1H-^1H$ NOESY NMR experiments showed a number of close contacts between aromatic protons. Good qualitative agreement was observed between the H−H distances obtained from molecular modeling studies and the intensities of the direct $^1H-^1H$ NOEs of the aromatic protons. The structure of the metalla crown ether from the molecular modeling studies also explained the unusual shieldings and deshieldings of certain aromatic protons in the molecule.

Introduction

The solution conformations of transition-metal complexes affect many of their most important properties but are very difficult to determine. This is particularly true for complexes with highly functional and potentially flexible ligands such as metalla crown ethers, formed when α,ω-bis(phosphorus donor) polyether ligands chelate soft transition metals.[1−5] Variations in both the transition-metal center and the nature of the polyether group of metalla crown ethers have significant effects on their solution conformations,[3] which in turn strongly affect their abilities to bind cations and small molecules.[2,4]

A powerful method for determining the conformation of molecules in solution is the $^1H-^1H$ NOESY NMR technique. Unfortunately, it has not been possible to use this technique to determine the solution structures of any of the metalla crown ethers that have been prepared to date. Most of these complexes have relatively flexible metalla crown ether rings, and in addition, the complete assignment of their multinuclear NMR spectra is not possible. However, unsymmetrical metalla crown ethers similar to those that we have recently synthesized (Figure 1) may be suitable for $^1H-^1H$ NOESY studies.[6,7] The chemically inequivalent phosphorus-donor groups in these metalla crown ethers simplify the assignment of their multinuclear NMR spectra, and the well-resolved ^1H NMR resonances of the methylene protons in **4** suggest that the chelate ring in this metalla crown ether has limited flexibility.

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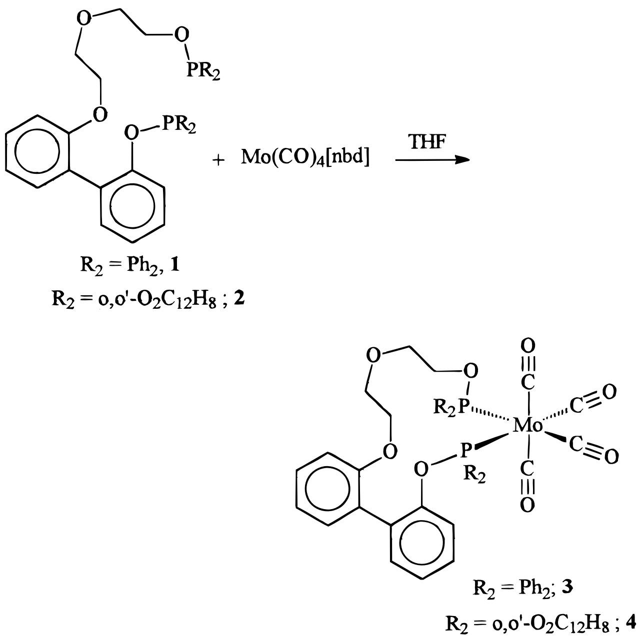

Figure 1. Synthesis of unsymmetrical *cis*-$Mo(CO)_4$ metalla crown ethers.

Although **4** has many of the properties necessary for successful $^1H-^1H$ NOESY NMR studies, it is not possible to completely assign the aromatic ^{13}C and ^1H NMR resonances, due to the similarities of the 2,2′-biphenyl groups in the metalla crown ether ring and the dibenzo[*d,f*][1,3,2]dioxaphosphepin rings. Because of this, we have synthesized a new unsymmetrical metalla crown ether, *cis*-$Mo(CO)_4\{2\text{-}(2,2'\text{-}O_2C_{12}H_8)PO(CH_2CH_2O)_2\text{-}2\text{-}C_{20}H_{12}\text{-}2'\text{-}OP(2,2'\text{-}O_2C_{12}H_8)\}$ (**7**), which contains a 1,1′-bi-2-naphthyl group in the metalla crown ether ring, for $^1H-^1H$ NOESY NMR studies. Complete ^1H, ^{13}C, and ^{31}P NMR chemical shift assignments of **7** have been made, using a combination of one- and two-dimensional multinuclear NMR spectroscopic techniques. The solution conformation of **7** has been studied by a combination of two-dimensional $^1H-^1H$ NOESY spectroscopy and molecular modeling. The results of these studies are reported in this paper.

Experimental Section

Initial one-dimensional $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra of the ligand and complex were run on 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 are referenced to external 85% phosphoric acid, while both the $^{13}C\{^1H\}$ and the ^1H NMR spectra are referenced to internal $SiMe_4$. All NMR spectra for chemical shift assignments (^{13}C DEPT, $^1H-^1H$ COSY-45, $^{31}P\{^1H\}$ HETCOR, long-range $^{31}P\{^1H\}$ HETCOR, $^{13}C\{^1H\}$ HETCOR, long-range $^{13}C\{^1H\}$ HETCOR, and $^1H\{^{13}C\}$ HMBC) were run on a Bruker DRX-400 NMR spectrometer and used a 0.2 M chloroform-*d* solution of **7**. The long-range $^{13}C\{^1H\}$ HETCOR experiment was performed by modifying the delay (CNST2 parameter) to create an anti-phase magnetization in the Bruker pulse program for $^1J_{CH}$ spectroscopy (XHCORR). Similar modification of the pulse program XHCORR for $^nJ_{PH}$ (n = 4, 5) coupling constants allowed long-range $^{31}P\{^1H\}$ HETCOR experiments to be performed. Two-dimensional $^1H-^1H$ NOE experiments were performed on a Bruker DRX-400 NMR spectrometer operating at an observation frequency of 400.132 MHz in the absolute value mode and also used a 0.2 M chloroform-*d* solution of **7**. A $(\pi/2)-t_1-(\pi/2)-\tau_m-(\pi/2)-t_2$ pulse sequence was employed, and the pulse delay was maintained at 2 s. A 16-step phase cycling procedure was used to suppress J cross-peaks and double quantum coherences. Four different mixing times ranging from 600 to 1000 ms were used, but all pertinent information was obtained from the 800 and 1000 ms mixing times. All two-dimensional data were processed using standard Bruker programs.

All reactions and purifications were carried out under high-purity nitrogen. All starting materials were reagent grade and were used as received. Tetrahydrofuran was distilled from sodium/benzophenone under high-purity nitrogen. Dichloromethane and triethylamine were distilled from calcium hydride under high-purity nitrogen prior to use. Chloroform-*d* was handled under a nitrogen atmosphere at all times. The starting materials, *cis*-$Mo(CO)_4(nbd)$[8] and (2,2′-biphenylylene)phosphorochloridite ester,[9] were prepared by literature procedures. Complex **7** was stored in the dark under a nitrogen atmosphere to avoid any cis−trans isomerization.

2-Hydroxy-2′-(1,4-dioxo-6-hexanol)-1,1′-binaphthyl (5). This material was prepared by a method similar to that used to prepare 2-hydroxy-2′-(1,4-dioxo-6-hexanol)-1,1′-biphenyl.[6] A mixture of sodium hydroxide (12.0 g, 300 mmol) and 2,2′-binaphthol (25.5 g, 89.2 mmol) in *n*-butanol (300 mL) was heated at reflux as a solution of tetrahydropyranyl-protected 2-(2′-chloroethoxy)ethanol (41.7 g, 200 mmol) in *n*-butanol (100 mL) was added dropwise. The reaction mixture was refluxed for 48 h, and then additional sodium hydroxide (0.762 g, 19 mmol) was added. Refluxing was continued for 24 h, after which the solvent was removed under reduced pressure. Dichloromethane was added to the residue, the insoluble salt was removed by filtration, and the filtrate was evaporated in vacuo to yield a brown residue. Column chromatography (silica gel, 2:3 ethyl acetate−hexanes) gave 8.4 g (21%) of the tetrahydropyranyl ether of **5** eluting as the first fraction. This material was dissolved in 50 mL of methanol, and then 3 mL of concentrated hydrochloric acid in 20 mL of methanol was added. After the solution had been stirred for 1 h at room temperature, 5.0 g of sodium bicarbonate was added. The mixture was filtered, and the filtrate was evaporated in vacuo to yield 6.5 g (20%) of **5**. ^{13}C NMR (aliphatic carbons, chloroform-*d*): δ 72.22 (CH_2CH_2OH, s), 69.33 ($CH_2CH_2OC_{20}H_{12}$, s), 69.05 ($CH_2OC_{20}H_{12}$, s), 61.41 (CH_2OH, s). ^1H NMR (chloroform-*d*): δ 6.95−8.01 (m, 12H, $C_{20}H_{12}$), 4.15 (m, 1H, $CH_2OC_{20}H_{12}$), 4.05 (m, 1H, $CH_2OC_{20}H_{12}$), 3.41 (m, 2H, $CH_2CH_2OC_{20}H_{12}$), 3.25 (m, 2H, CH_2CH_2OH), 3.06 (m, 2H, CH_2CH_2OH).

$2\text{-}(2,2'\text{-}O_2C_{12}H_8)PO(CH_2CH_2O)_2\text{-}2\text{-}C_{20}H_{12}\text{-}2'\text{-}OP(2,2'\text{-}O_2C_{12}H_8)$ (6). A solution of 2.9 g (7.7 mmol) of **5**, 3.9 g (15.4 mmol) of 2,2′-biphenylylenephosphochloridite ester, and 7.0 mL (50.0 mmol) of triethylamine in 100 mL of freshly distilled THF was stirred under nitrogen for 12 h. Then, the solvent was removed under reduced pressure, and 50 mL of THF was added to the residue. This mixture was stirred at room temperature for 30 min before being filtered to remove the insoluble triethylamine hydrochloride. The filtrate was evaporated to dryness to yield 5.8 g (96.1%) of crude **6** as a viscous, colorless oil that slowly solidified upon standing. $^{31}P\{^1H\}$ NMR (chloroform-*d*): δ 140.80 (s, CH_2OP), δ 145.18 (s, $C_{20}H_{12}OP$). ^{13}C NMR (aliphatic carbons, chloroform-*d*): δ 70.68 (CH_2CH_2OP, d, $|^3J(PC)|$ = 4 Hz), 63.74 (CH_2OP, d, $|^2J(PC)|$ = 5 Hz), 69.48 ($CH_2CH_2OC_{20}H_{12}$, s), 69.35 ($CH_2OC_{20}H_{12}$, s). ^1H NMR (chloroform-*d*): δ 8.22−6.08 (m, 28H, $OPO_2C_{12}H_8$ and $C_{20}H_{12}$), 4.18 (m, 2H, $CH_2OC_{20}H_{12}$), 3.76−3.35 (m, 4H, CH_2O), 3.01 (m, 1H, CH_2OP), 2.89 (m, 1H, CH_2OP).

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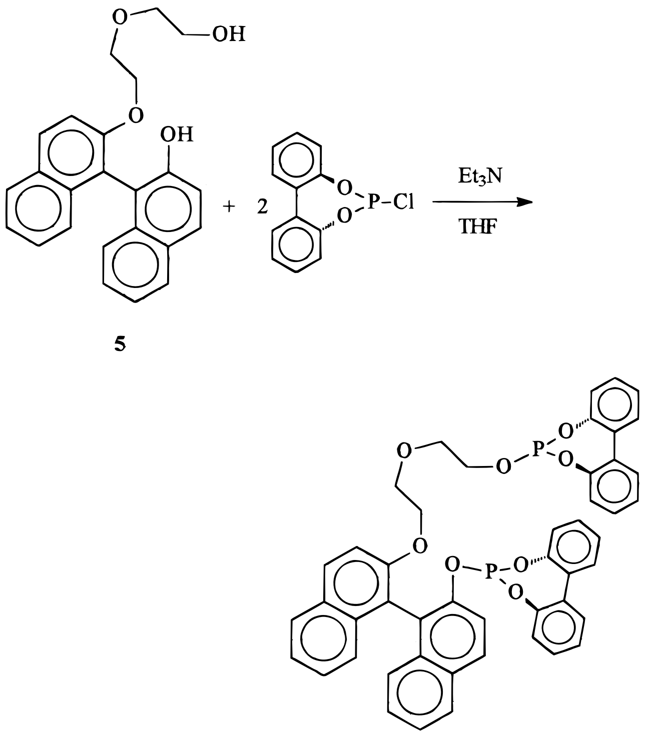

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Figure 2. Synthesis of 2-$(2,2'\text{-}O_2C_{12}H_8)PO(CH_2CH_2O)_2$-2-$C_{20}H_{12}$-2′-$OP(2,2'\text{-}O_2C_{12}H_8)$ (**6**).

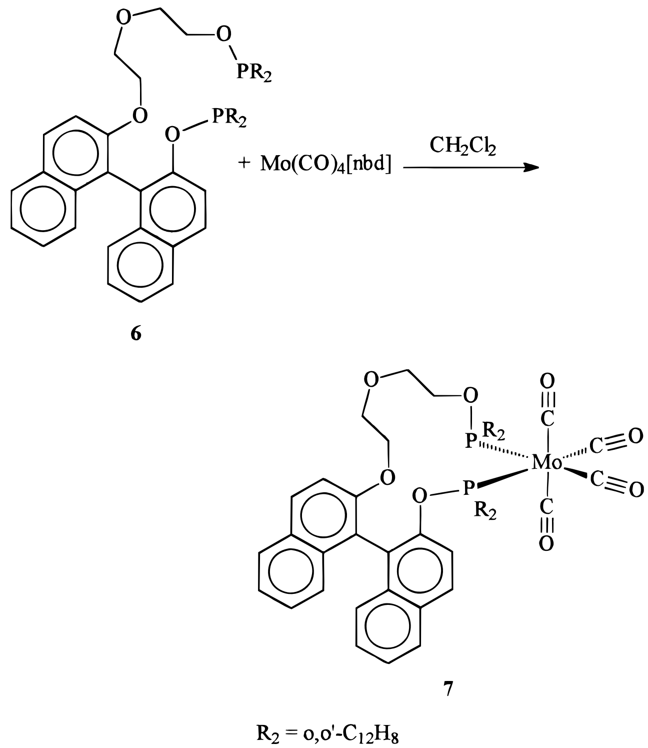

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Figure 3. Synthesis of the unsymmetrical metalla crown ether *cis*-$Mo(CO)_4${2-$(2,2'\text{-}O_2C_{12}H_8)PO(CH_2CH_2O)_2$-2-$C_{20}H_{12}$-2′-$OP(2,2'\text{-}O_2C_{12}H_8)$} (**7**).

***cis*-$\mathbf{Mo(CO)_4}$\{2-$\mathbf{(2,2'\text{-}O_2C_{12}H_8)PO(CH_2CH_2O)_2}$-2-$\mathbf{C_{20}H_{12}}$-2′-$\mathbf{OP(2,2'\text{-}O_2C_{12}H_8)}$\} (7).** A mixture of 0.45 g (1.5 mmol) of $Mo(CO)_4$(nbd) and 1.20 g (1.50 mmol) of **6** in 50 mL of dichloromethane was stirred at room temperature for 3 h and then evaporated to dryness to yield a light brown, oily residue. Column chromatography (silica gel, 4:1 ethyl acetate−hexanes) gave 1.2 g (80.0%) of **7** as a white powder. Anal. Calcd for $C_{52}H_{36}O_{12}P_2Mo$: C, 61.79; H, 3.59. Found: C, 61.89; H, 3.64. $^{31}P\{^1H\}$ NMR (chloroform-*d*): δ 166.96 (d, CH_2OP, $|^2J(PP')| = 49$ Hz), δ 170.26 (d, ArO*P*, $|^2J(PP')| = 49$ Hz). ^{13}C NMR (carbonyl and aliphatic carbons, chloroform-*d*): δ 210.59 (trans *C*O, dd, $|^2J(PC)| = 60$ Hz, $|^2J(P'C)| = 40$ Hz), 210.48 (trans *C*O, dd, $|^2J(PC)| = 41$ Hz, $|^2J(P'C)| = 34$ Hz), 206.68 (cis *C*O, dd, $|^2J(PC)| = 13$ Hz, $|^2J(P'C)| = 13$ Hz), 205.11 (cis *C*O, dd, $|^2J(PC)| = 14$ Hz, $|^2J(P'C)| = 14$ Hz), 70.37 (CH_2CH_2OP, d, $|^3J(PC)| = 6$ Hz), 67.92 (CH_2OP, d, $|^2J(PC)| = 11$ Hz), 69.76 ($CH_2CH_2OC_{20}H_{12}$, s), 69.70 ($CH_2OC_{20}H_{12}$, s). ^1H NMR (400 MHz, chloroform-*d*): δ 8.01−7.00 (m, 24H, $OPO_2C_{12}H_8$ and $C_{20}H_{12}$), 4.12 (ddd, 1H, CH_2OAr), 3.85 (ddd, 1H, CH_2OAr), 3.80 (m, 2H, CH_2OP), 3.71 (ddd, 1H, CH_2CH_2OAr), 3.46 (ddd, 1H, CH_2CH_2OAr), 3.24 (ddd, 1H, CH_2CH_2OP), 3.13 (ddd, 1H, CH_2CH_2OP).

Results and Discussion

Synthesis and Characterization of 2-$\mathbf{(2,2'\text{-}O_2C_{12}H_8)PO(CH_2CH_2O)_2}$-2-$\mathbf{C_{20}H_{12}}$-2′-$\mathbf{OP(2,2'\text{-}O_2C_{12}H_8)}$ (6). The α,ω-bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin) polyether ligand 2-$(2,2'\text{-}O_2C_{12}H_8)P(CH_2CH_2O)_2$-2-$C_{20}H_{12}$-2′-$P(2,2'\text{-}O_2C_{12}H_8)$ (**6**) was prepared by the reaction of 2-hydroxy-2′-(1,4-bisoxo-6-hexanol)-1,1′-binaphthyl (**5**) with (2,2′-biphenylylene)phosphorochloridite ester in the presence of triethylamine (Figure 2). The ligands were characterized by $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectroscopy (vide infra).

The ^1H NMR spectrum of **6** contains four resonances in the 3.3−4.1 ppm region. These are assigned to the protons from the four methylene groups. The protons attached to each methylene carbon are chemically equivalent. These protons become diastereotopic when **6** chelates a *cis*-$Mo(CO)_4$ group as discussed below.

The $^{31}P\{^1H\}$ NMR spectrum of **6** contains two singlets because the phosphorus nuclei are chemically inequivalent. The chemical shifts were assigned to respective phosphorus environments on the basis of ^1H-coupled ^{31}P NMR spectra. The chemical shifts of the ^{31}P NMR resonances are close to those reported for other ligands with similar phosphorus environments.[7,10]

As expected, the ^{13}C NMR spectrum of **6** shows well-resolved resonances for all of the methylene carbons. The resonances of the carbons two and three bonds from the phosphorus (CH_2OP and CH_2CH_2OP, respectively) are doublets and are readily assigned by their chemical shifts and the relative values of the $|^nJ(PC)|$ coupling constants. No attempts were made to assign the resonances for the carbons five and six bonds from the phosphorus ($CH_2CH_2OC_{20}H_{12}$ and $CH_2OC_{20}H_{12}$, respectively).

Synthesis and Characterization of *cis*-$\mathbf{Mo(CO)_4}$\{2-$\mathbf{(2,2'\text{-}O_2C_{12}H_8)PO(CH_2\text{-}CH_2O)_2}$-2-$\mathbf{C_{20}H_{12}}$-2′-$\mathbf{OP(2,2'\text{-}O_2C_{12}H_8)}$\} (7). The metalla crown ether *cis*-$Mo(CO)_4${2-$(2,2'\text{-}O_2C_{12}H_8)PO\text{-}(CH_2CH_2O)_2$-2-$C_{20}H_{12}$-2′-$OP(2,2'\text{-}O_2C_{12}H_8)$} (**7**) was prepared in good yield by the reaction of $Mo(CO)_4${nbd} with the ligand **6** (Figure 3) and was characterized using ^{31}P, ^{13}C, and ^1H NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of **7** displays a single AX spectral pattern as expected. The ^{31}P NMR resonances

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for **7** are approximately 25 ppm downfield of those of the free ligand **6**, indicating that only the cis isomer of **7** is present.[7] The $|^2J(PP')|$ coupling constant of 49 Hz is also consistent with the cis arrangement of phosphorus-donor groups at the molybdenum.

Well-resolved resonances are observed for the four carbonyls in the ^{13}C NMR spectrum of **7**, which is quite unusual for *cis*-$Mo(CO)_4$(P-donor ligand)$_2$ complexes.[7] 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 is instead due to an asymmetric arrangement of the metalla crown ether ring relative to the plane containing the molybdenum and the two phosphorus-donor groups.

As is the case for the free ligand, the ^{13}C NMR spectrum of **7** shows well-resolved resonances for all of the methylene carbons. The resonances of the carbons two and three bonds from the phosphorus (CH_2OP and CH_2CH_2OP, respectively) are doublets, while the resonances of the carbons five and six bonds from the phosphorus (CH_2CH_2OAr and CH_2OAr, respectively) are singlets.

Unlike the ^1H NMR spectra of the free ligand **6**, individual NMR resonances for all but two methylene protons are observed in the ^1H NMR spectra of **7**. The diastereotopism in the methylene protons is apparently due to reduction in the conformational flexibility of the ligand upon chelation to the $Mo(CO)_4$ group. The 2,2′-binaphthyl group forces the metalla crown ether ring to be asymmetric in relation to a plane that passes through the two phosphorus atoms and the molybdenum. This conclusion is consistent with our observation that the carbonyls cis to both phosphorus-donor groups show separate ^{13}C NMR resonances.

Complete ^1H, ^{13}C, and ^{31}P NMR Chemical Shift Assignments for *cis*-$Mo(CO)_4$-{2-(2,2′-$O_2C_{12}H_8$)PO-$(CH_2CH_2O)_2$-2-$C_{20}H_{12}$-2′-OP(2,2′-$O_2C_{12}H_8$)} (7). To probe the solution conformation of **7** using NMR spectroscopy, it is necessary to completely and unambiguously assign its ^1H, ^{13}C, and ^{31}P NMR resonances. This complete assignment is not straightforward because, as shown in Figure 4, **7** has a large number of similar aromatic carbons and hydrogens. We have successfully carried out the assignment of the ^1H and ^{13}C NMR spectra of **7** using a combination of one- and two-dimensional multinuclear NMR spectroscopic techniques. The details of these studies are discussed below, and we refer to the numbering scheme in Figure 4 in the subsequent discussion.

The assignment of the NMR resonances of the two phosphorus nuclei, P1 and P2, was done on the basis of the ^1H-coupled ^{31}P NMR spectra. The assignment of the P1 resonance was confirmed using a $^{31}P-^1H$ HETCOR NMR experiment that demonstrated that the P1 resonance is *J*-coupled to the H36 and H36′ methylene protons.

The assignment of the methylene protons and carbons involved several experiments. The H36 and H36′ methylene protons were unambiguously located using the $^{31}P-^1H$ HETCOR NMR experiment, and the H33 and H33′ protons were assigned by the fact that they are the only aliphatic protons to have strong NOE contacts with an aromatic proton (H31). The aliphatic proton−proton connectivity in the metalla crown ether ring was determined with a $^1H-^1H$ COSY-45 NMR experiment, and the one-bond proton−carbon connectivity was determined with a $^{13}C-^1H$ HETCOR NMR experiment.

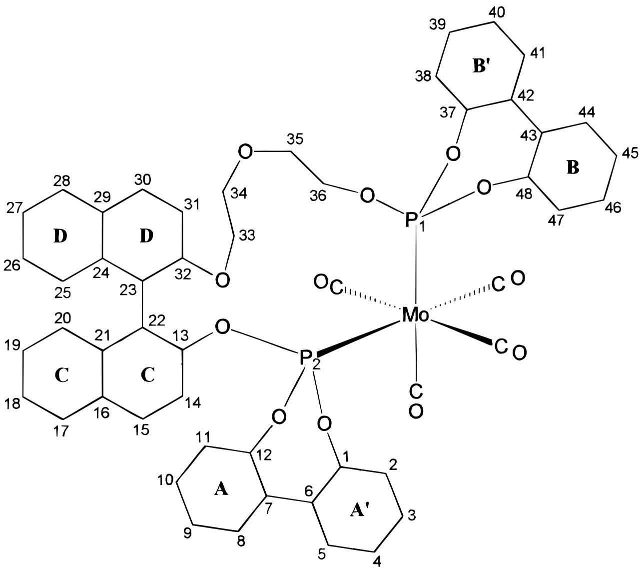
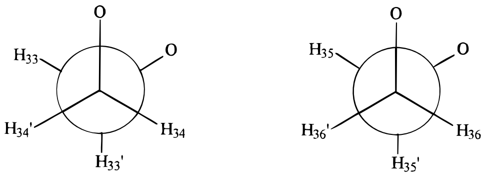


Figure 4. Molecular structure and atom-numbering scheme for the unsymmetrical metalla crown ether *cis*-$Mo(CO)_4$-{2-(2,2′-$O_2C_{12}H_8$)PO$(CH_2CH_2O)_2$-2-$C_{20}H_{12}$-2′-OP(2,2′-$O_2C_{12}H_8$)} (**7**). The letters A, A′, B, B′, C, and D refer to the notation for aromatic rings.

Assignment of the aromatic ^1H and ^{13}C NMR resonances was challenging because of the numbers of resonances within a restricted chemical shift range. Fortunately, however, both the phosphorus−proton and the proton−proton coupling networks in the aromatic rings are straightforward. The first step in the assignment procedure was to unambiguously determine at least one proton on each of the phenylene rings (A, A′, B, B′) and at least one proton on each of the naphthylene rings (C, D)). The protons on the phenylene rings and on naphthylene ring C were located using a long-range $^{31}P-^1H$ HETCOR experiment by taking advantage of the phosphorus−proton coupling networks in the aromatic rings. A proton (H31) on the other naphthylene ring (D) was located, as described previously, by its strong NOESY contacts to the H33 and H33′ methylene protons. Using these aromatic proton assignments as the starting point, the proton−proton coupling networks in the aromatic rings were then determined with a $^1H-^1H$ COSY-45 experiment. These aromatic proton assignments were then confirmed with a $^1H-^1H$ NOESY experiment. The one-bond carbon−hydrogen connectivities of the aromatic rings were determined with a $^{13}C-^1H$ HETCOR experiment. The quaternary carbons were first located using a DEPT-45 experiment and then assigned using a heteronuclear multiple bond correlation (HMBC) experiment. This experiment related their chemical shifts to those of previously assigned aromatic protons and provided significantly better information than did a long-range $^{13}C-^1H$ HETCOR experiment. The ^1H and the ^{13}C NMR chemical shift assignments for **7** are given in Table 1.



$\|^2J(H_{33},H_{33'})\|$ = 10.6 Hz	$\|^2J(H_{35},H_{35'})\|$ = 11.9 Hz
$\|^2J(H_{34},H_{34'})\|$ = 12.2 Hz	$\|^2J(H_{36},H_{36'})\|$ = not observed
$\|^3J(H_{33},H_{34})\|$ = 9.0 Hz	$\|^3J(H_{35},H_{36})\|$ = 5.7 Hz
$\|^3J(H_{33},H_{34'})\|$ = 2.7 Hz	$\|^3J(H_{35},H_{36'})\|$ = 5.7 Hz
$\|^3J(H_{33'},H_{34})\|$ = 3.0 Hz	$\|^3J(H_{35'},H_{36})\|$ = 2.8 Hz
$\|^3J(H_{33'},H_{34'})\|$ = 2.9 Hz	$\|^3J(H_{35'},H_{36'})\|$ = 2.8 Hz

Figure 5. Magnitudes of geminal $|^2J(H,H)|$ and vicinal coupling constants $|^3J(H,H)|$ of the diastereotopic OCH_2-CH_2O fragments of the unsymmetrical metalla crown ether *cis*-$Mo(CO)_4\{2\text{-}(2,2'\text{-}O_2C_{12}H_8)PO(CH_2CH_2O)_2\text{-}2\text{-}C_{20}H_{12}\text{-}2'\text{-}OP(2,2'\text{-}O_2C_{12}H_8)\}$ (**7**).

Solution Conformation of *cis*-$Mo(CO)_4\{2\text{-}(2,2'\text{-}O_2C_{12}H_8)PO(CH_2CH_2O)_2\text{-}2\text{-}C_{20}H_{12}\text{-}2'\text{-}OP(2,2'\text{-}O_2C_{12}H_8)\}\}$ (7). Two primary NMR methods of analysis were employed to probe key solution-state conformational features of the unsymmetrical metalla crown ether **7**. The first method was a complete ^1H NMR spectral analysis of the diastereotopic OCH_2CH_2O fragments, as was previously done for these fragments in **4**.[7] The second method involved the use of two-dimensional $^1H-^1H$ NOESY NMR spectroscopy to qualitatively measure inter-ring distances between various aromatic protons.

The magnitudes of the geminal (H−C−H, $|^2J(H,H)|$) and vicinal (H−C−C−H, $|^3J(H,H)|$) coupling constants of the diastereotopic OCH_2CH_2O fragments in **7** have been evaluated to determine the average solution conformations about the C−C bonds. The magnitudes of the geminal coupling constants are approximately 12 Hz and are consistent with the tetrahedral geometry around each methylene carbon. One moderate vicinal coupling constant (9 and 5.7 Hz) and three smaller vicinal coupling constants (3−4 Hz) are observed for each of the diastereotopic OCH_2CH_2O groups. The magnitudes of the vicinal coupling constants indicate that the average solution conformation about the C−C bonds in each of the OCH_2CH_2O groups in the metalla crown ether ring is gauche, as shown in Figure 5. It is interesting that the average solution conformation about the C−C bonds in each of the OCH_2CH_2O groups of **4** is also gauche and similar gauche conformations are also present in the solid-state structure of **4**. These results strongly suggest that replacing the 2,2′-biphenyl group (**4**) in the metalla crown ether ring with a 1,1′-bi-2-naphthyl group (**7**) has little effect on the average solution conformations of the ethylene groups in the metalla crown ether rings. This result is consistent with those from the molecular modeling studies that are discussed below.

Table 1. Aromatic ^1H and ^{13}C NMR Chemical Shift Assignments for the Unsymmetrical Metalla Crown Ether *cis*-$Mo(CO)_4\{2\text{-}(2,2'\text{-}O_2C_{12}H_8)\text{-}PO(CH_2CH_2O)_2\text{-}2\text{-}C_{20}H_{12}\text{-}2'\text{-}OP(2,2'\text{-}O_2C_{12}H_8)\}$ (7) in Chloroform-*d* at Observation Frequencies of 400.132 and 100.623 MHz, Respectively, at 293 K

carbon	$\delta(^{13}C)$ (ppm)	proton	$\delta(^1H)$ (ppm)	carbon	$\delta(^{13}C)$ (ppm)	proton	$\delta(^1H)$ (ppm)
C1	149.57			C23	118.62		
C2	121.98	H2	7.025	C24	134.02		
C3	128.92	H3	7.026	C25	125.05	H25	6.578
C4	125.10	H4	7.049	C26	126.10	H26	6.737
C5	129.95	H5	7.181	C27	123.06	H27	7.018
C6	129.93			C28	127.62	H28	7.623
C7	129.73			C29	128.88		
C8	129.13	H8	7.110	C30	129.53	H30	7.790
C9	125.05	H9	6.890	C31	114.35	H31	7.289
C10	128.81	H10	6.721	C32	154.31		
C11	122.28	H11	6.237	C37	149.85		
C12	148.00			C38	122.33	H38	7.327
C13	147.66			C39	129.50	H39	7.274
C14	121.06	H14	7.925	C40	125.57	H40	7.169
C15	128.56	H15	7.808	C41	130.14	H41	7.350
C16	130.65			C42	130.19		
C17	127.78	H17	7.741	C43	129.59		
C18	124.74	H18	7.254	C44	129.95	H44	7.360
C19	126.15	H19	7.091	C45	125.45	H45	7.160
C20	126.13	H20	6.989	C46	129.50	H46	7.176
C21	134.08			C47	122.26	H47	7.060
C22	123.88			C48	150.22		

One of the most interesting structural features of the unsymmetrical metalla crown ether complex **7** is the relative spatial orientation of the aromatic rings in the molecule. The 2,2′-biphenyl groups in the seven-membered dibenzo[*d*,*f*][1,3,2]dioxaphosphepin rings as well as the 1,1′-bi-2-naphthyl group in the backbone assume twisted nonplanar conformations and thus are axially chiral. This combination of structural elements results in high stereoselectivities in the asymmetric hydroformylation of olefins with rhodium catalysts containing related α,ω-bis(dibenzo[*d*,*f*][1,3,2]dioxaphosphepin) ligands.[11]

The limited conformational mobility of the metalla crown ether ring in **7** means that two-dimensional $^1H-^1H$ NOESY spectroscopy could provide insight into the solution conformation of **7** if the distance between protons on different rings is less than 5 Å.[12] The inter-ring proton−proton NOE networks in **7** were determined using a phase-sensitive $^1H-^1H$ NOESY experiment. One large, positive, direct NOE between H14 and H47 was observed, and thus, these protons are very close in space. Four weak inter-ring NOE's, between H11 and H14, H11 and H15, H11 and H25, and H11 and H47 were also observed.

Two protons involved in the inter-ring proton−proton NOE networks in **7**, H11 (δ 6.23 ppm) and H14 (δ 7.93 ppm), exhibit unusual chemical shifts. The upfield chemical shift of H11 suggests that it is located in the shielding region of an aromatic ring, and the downfield chemical shift of H14 suggests that it is located in the deshielding region of an aromatic ring. We would have liked to obtain the X-ray crystal structure of **7** to confirm

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(11) Recent examples with Rh(I)−chiral α,ω-bis(dibenzo[*d*,*f*][1,3,2]-dioxaphosphepin) complexes: (a) Wink, D. J.; Kwok, T. J. Yee, A. *Inorg. Chem.* **1990**, *29*, 5006. (b) Kwok, J.; Wink, D. J. *Organometallics* **1993**, *12*, 1954. (c) Buisman, G. J. H..; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1993**, *4*, 1625. (d) Buisman, G. J. H.; van der Veen, L. A.; Klootwijik, A.; de Lange, W. G. J.; Kramer, P. C. J.; van Leeuwen, P. W. N. M.; Vogt, D. *Organometallics* **1997**, *16*, 2929. (e) Babin, J. E.; Whiteker, G. T. WO 93/03839, U. S. Patent 911,518, 1992; *Chem. Abstr.* **1993**, 119, 159872h. (f) Buisman, G. J. H.; Martin, M. E.; Vos, E. J.; Klootwijik, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1995**, *6*, 719.

(12) (a) Friebolin. H. *Basic One- and Two-Dimensional NMR Spectroscopy*, 3rd ed.; VCH: Weinheim, Germany, 1998. (b) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*, 2nd ed.; Oxford University Press: Oxford, U.K., 1993.

Table 2. C−C Torsion Angles for the OCH_2CH_2O Fragments and for the Axially Chiral Biaryl Groups for the X-ray Crystal Structure of *cis*-$Mo(CO)_4\{2\text{-}(2,2'\text{-}O_2C_{12}H_8)PO(CH_2CH_2O)_2\text{-}C_{12}H_8\text{-}2'\text{-}OP(2,2'\text{-}O_2C_{12}H_8)\}$ (4) and in the Minimized Molecular Conformation of 4 and *cis*-$Mo(CO)_4\{2\text{-}(2,2'\text{-}O_2C_{12}H_8)PO(CH_2CH_2O)_2\text{-}2\text{-}C_{20}H_{12}\text{-}2'\text{-}OP(2,2'\text{-}O_2C_{12}H_8)\}$ (7)[a]

	torsion angle (deg)		
atoms	solid-state conformn, **4**	minimized conformn, **4**	minimized conformn, **7**
C37−C42−C43−C48	−45.1	−50.2	−49.9
C1−C6−C7−C12	43.5	48.5	45.4
C13−C22−C23−C32	63.6	69.4	75.6
C32−O−C33−C34	−171.0	−179.7	−178.4
O−C33−C34−O	68.2	63.4	62.4
C33−C34−O−C35	−84.4	−82.4	−80.6
C34−O−C35−C36	167.0	171.9	174.6
O−C35−C36−O	68.4	65.9	66.2

[a] The minimizations were carried out using the PCMODEL molecular modeling program with the MMX force field. In the calculations, the positions of the molybdenum atom, the phosphorus atoms, and the carbon and oxygen atoms of carbonyl ligands were fixed relative to their locations in the X-ray crystal structure of **4**.

the structural features suggested by solution NOE's; however, we were unable to obtain stable single crystals of this complex. Because of this, molecular mechanics calculations (PCMODEL with the MMX force field)[13] were performed by starting from the solid-state conformation of **4**, which was determined by X-ray crystallography.[7] In all calculations, the relative positions of the molybdenum, the phosphorus, and carbonyl carbon and oxygen atoms were fixed at the positions in which they were observed in the X-ray crystal structure.

The first step in the molecular mechanics calculations was to minimize the structure of **4** to determine whether the minimized structure differed significantly from the solid-state structure. As shown in Table 2, good agreement is observed between the torsion angles around the metalla crown ether rings in the crystal structure and in the minimized structure. This suggests that the molecular mechanics studies may provide a reasonably accurate model of the solution conformation of the ligand in **4**.

The second step in the molecular mechanics studies was to minimize the structure of **7**. This was accomplished by replacing the bridging 2,2′-biphenyl group in the minimized conformation of **4** with the 1,1′-bi-2-naphthyl group of **7** and repeating the minimization. The minimized molecular conformation of **7** is shown in Figure 6. The torsion angles around the metalla crown ether rings of **4** and **7** (Table 2) are quite similar, indicating that the bridging biaryl group has little effect on the conformation. This is consistent with the conclusions drawn from the analysis of the vicinal coupling constants of the OCH_2CH_2O fragments in **4** and **7**. Further, these results suggest that the minimized conformation of **7** may also provide a reasonably accurate model of its solution conformation.

The observed inter-ring NOE's are generally consistent with the minimized conformation shown in Figure 6. The calculated inter-ring H14−H47 distance (2.7 Å) agrees with the strong direct NOE between these protons. Also, H11 is located directly over the naphthyl ring C, in the shielding region, and H14 is oriented toward the edge of ring B, in the deshielding region in the minimized structure. These orientations explain the unusually large negative and positive coordination chemical shifts of their ^1H NMR resonances. The orientations of H11 and H14 in space result in short inter-ring H11−H14, H11−H15, and H11−H15 distances (3.2, 3.4, and 3.5 Å, respectively) that agree with the NOE's observed between these protons. The only distance in the minimized conformation of **7** that does not agree with the NOE is the inter-ring H11−H47 distance of 6 Å, a distance that is too large for the observation for any NOE between the protons. The weak NOE between H11 and H47 protons may an indirect NOE "relayed" from H11 to H47 via H14. This suggestion is supported by the inter-ring distances (H11−H47 (6.0 Å), H11−H14 (3.2 Å), H14−H47 (2.7 Å)) for the minimized conformation, which are characteristic of a linear three-spin system. It seems less likely that the observation of NOE between H11 and H47 is due to a significant difference in the solution and minimized conformations of the unsymmetrical metalla crown ether because the distance between these protons in the X-ray crystal structure of **4** is also 6 Å.

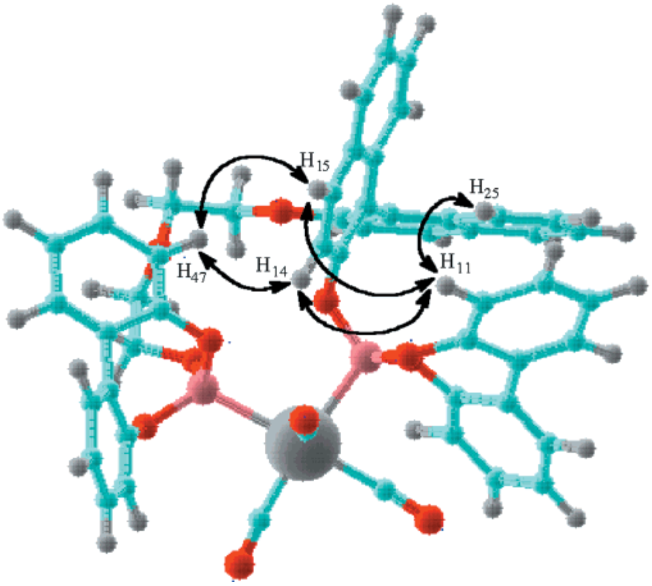

Figure 6. Molecular conformation of the unsymmetrical metalla crown ether *cis*-$Mo(CO)_4\{2\text{-}(2,2'\text{-}O_2C_{12}H_8)PO(CH_2CH_2O)_2\text{-}2\text{-}C_{20}H_{12}\text{-}2'\text{-}OP(2,2'\text{-}O_2C_{12}H_8)\}$ (**7**), as calculated with the PCMODEL molecular modeling program with the MMX force field. As expected, the most shielded H11 proton (δ 6.23 ppm) is located over the face of the naphthyl ring C, while the most deshielded H14 proton (δ 7.93 ppm) is located along the edge of the phenyl ring B. The arrows indicate the key inter-ring NOE's between various aromatic protons.

Summary

The reaction of the sterically congested ligand $2\text{-}(2,2'\text{-}O_2C_{12}H_8)PO(CH_2CH_2O)_2\text{-}2\text{-}C_{20}H_{12}\text{-}2'\text{-}OP(2,2'\text{-}O_2C_{12}H_8)$ (**6**) with $Mo(CO)_4(nbd)$ gives the unsymmetrical, monomeric metalla crown ether *cis*-$Mo(CO)_4\{2\text{-}(2,2'\text{-}O_2C_{12}H_8)PO(CH_2CH_2O)_2\text{-}2\text{-}C_{20}H_{12}\text{-}2'\text{-}OP(2,2'\text{-}O_2C_{12}H_8)\}$ (**7**) in good yields. The solution structure of **7**, obtained from molecular mechanics calculations, is consistent with the X-ray

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[13] PCMODEL, Version 6; Serena Software, P.O. Box 3076, Bloomington, IN 47402-3076.

crystal structure of the related metalla crown ether *cis*-Mo(CO)$_4${2-(2,2′-O$_2$C$_{12}$H$_8$)PO(CH$_2$CH$_2$O)$_2$-2-C$_{12}$H$_8$-2′-OP-(2,2′-O$_2$C$_{12}$H$_8$} (**4**) and with both the ^{1}H−^{1}H NOE spectral data and the vicinal ^{1}H−^{1}H coupling constants of the OCH$_2$CH$_2$O groups for **7**. The combination of molecular modeling and two-dimensional NMR studies provides a detailed picture of the solution conformation of **7**.

Supporting Information Available: Figures giving ^{31}P-{^{1}H} HETCOR, ^{1}H NOESY, ^{1}H COESY, ^{13}C{^{1}H} HETCOR (aromatic and aliphatic protons), and ^{1}H{^{13}C} HMBC NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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