Conformationally Restrained Octahedral Metallacrown Ethers with 1,2-($Ph_2P(CH_2CH_2O)_2)_2C_6H_4$ Ligands. X-ray Crystal Structure of *cis*-$Mo(CO)_4\{1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4\text{-}P,P'\}$

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A new α,ω-bis(phosphine)−polyether ligand, 1,2-($Ph_2P(CH_2CH_2O)_2)_2C_6H_4$, has been synthesized and used to prepare a number of conformationally restrained metallacrown ethers. The reaction of 1,2-($Ph_2P(CH_2CH_2O)_2)_2C_6H_4$ and $Mo(CO)_4(nbd)$ gives a good yield of *cis*-$Mo(CO)_4\{1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4\text{-}P,P'\}$. This complex has been isomerized to *trans*-$Mo(CO)_4\{1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4\text{-}P,P'\}$ using both UV light and $HgCl_2$ catalysis. The reaction of 1,2-($Ph_2P(CH_2CH_2O)_2)_2C_6H_4$ with *fac*-$RuCl_2(CO)_3(THF)$ initially yields a mixture of monomeric and oligomeric *cis,cis,trans*-$[RuCl_2(CO)_2\{1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4\text{-}P,P'\}]_n$ metallacrown ethers. Surprisingly, the oligomeric metallacrown ethers slowly convert into the monomeric metallacrown ether at ambient temperature in a chloroform-*d* solution. This does not occur with the conformationally mobile [*cis,cis,trans*-$RuCl_2(CO)_2\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}]_n$ metallacrown ethers. The X-ray crystal structure of *cis*-$Mo(CO)_4\{1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4\text{-}P,P'\}$ has also been determined. The four ether oxygens lie in a plane, and the average cross-ring oxygen−oxygen distance is slightly larger than those in metallacrown ethers containing $Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$ ligands.

Introduction

Metallacrown ethers are a unique class of transition-metal complexes that are formed when α,ω-bis(phosphorus donor)−polyether ligands chelate transition metals.[1−9] Metallacrown ethers that contain the conformationally mobile $Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$ (**1**) ligand exhibit a variety of phosphine coordination geometries. These geometries include cis-octahedral (*cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}$ (**2**)[4]), trans-octahedral (*trans*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}$ (**3**)[6] and *cis,cis,trans*-$RuCl_2(CO)_2\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}$ (**4**)[7]), and cis-square planar (*cis*-$PtCl_2\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}$ (**5**)[5]). Complex **2** binds alkali metal cations, methanol, and water[9] and also rapidly isomerizes into **3** in the presence of $HgCl_2$.[8] This isomerization may involve an intermediate in which the $HgCl_2$ coordinates to both the metallacrown ether and a carbonyl oxygen atom.[8]

In view of the range of coordination geometries that can be accommodated by the conformationally mobile ligand **1**, we were interested in determining if the introduction of conformational restraints into the ligand backbone would limit the types of metallacrown ethers that could be formed. In this paper, we report the synthesis of octahedral metallacrown ethers derived from the new, conformationally restricted ligand 1,2-($Ph_2P(CH_2CH_2O)_2)_2C_6H_4$, **6**. This ligand is identical to **1** with the exception that the central ethylene fragment in **1** has been replaced with a 1,2-phenylene fragment. The new ligand and several of its complexes have been characterized by multinuclear NMR spectroscopy, and the X-ray crystal structure of *cis*-$Mo(CO)_4\{1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4\text{-}P,P'\}$ has been determined.

Experimental Section

The starting materials, free ligands, complexes, and solvents were handled under dry nitrogen. All solvents and starting materials were of reagent grade, and the water was deionized.

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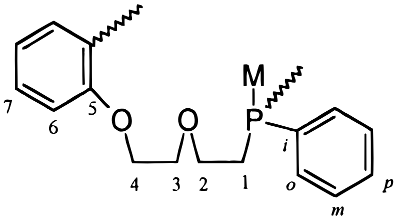
Table 1. ^{31}P and Aliphatic and Carbonyl ^{13}C NMR Data[a]

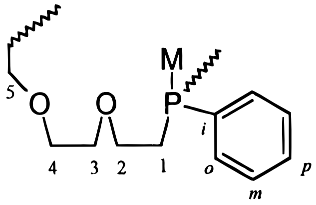
	P	C1		C2			cis CO		trans CO	
compd	$\delta(^{31}P)$ (ppm)	$\delta(^{13}C)$ (ppm)	$\lvert J(PC)\rvert$ (Hz)	$\delta(^{13}C)$ (ppm)	$\lvert J(PC)\rvert$ (Hz)	C3, C4, C5 $\delta(^{13}C)$ (ppm)	$\delta(^{13}C)$ (ppm)	$\lvert J(PC)\rvert$ (Hz)	$\delta(^{13}C)$ (ppm)	$\lvert J(PC)\rvert$ (Hz)
1[b]	−21.68 s	28.73 d	12[e]	68.53 d	26[f]	70.10 s, 70.53 s, 70.58 s				
2[b]	20.11 s	31.32 aq	15[g]	66.95 bs		70.16 s, 70.25 s, 70.65 s	215.08 aq	16[h]	209.69 t	8[f]
3[c]	32.57 s	34.38 aq	11[g]	66.96 aq	12[i]	70.24 s, 71.03 s, 71.07 s			210.59 t	8[f]
4[d]	9.74 s	27.05 aq	29[g]	65.18 s		69.07 s, 69.98 s, 70.46 s			191.67 t	11[f]
6	−21.71 s	28.54 d	13[e]	68.23 d	26[f]	68.40 s, 68.85 s				
7	20.41 s	31.36 aq	16[g]	67.17 aq	6[i]	68.96 s, 69.65 s	215.06 aq	15[h]	209.69 t	18[f]
8	34.23 s	33.96 aq	19[g]	67.21 bs		69.05 s, 69.90 s			210.48 t	18[f]
9	9.05 s	24.01 aq	28[g]	65.82 s		68.65 s, 68.12 s			192.05 t	20[f]

[a] b = broad, s = singlet, t = triplet, at = apparent triplet, aq = apparent quintet, w = weak. [b] Data from ref 2. [c] Data from ref 6. [d] Data from ref 7. [e] $|^1J(PC)|$. [f] $|^2J(PC)|$. [g] $|^1J(PC) + ^3J(P'C)|$. [h] $|^2J(PC) + ^2J(P'C)|$. [i] $|^2J(PC) + ^4J(P'C)|$.

Table 2. ^{31}P and ^{13}C Coordination Chemical Shifts



7 M = Mo, *cis*-P
8 M = Mo, *trans*-P
9 M = Ru, *trans*-P



2 M = Mo, *cis*-P
3 M = Mo, *trans*-P
4 M = Ru, *trans*-P

no.	$\Delta\delta^{31}P$	$\Delta\delta^{13}C$			
		1	2	3, 4	5
cis-$Mo(CO)_4$					
(2)	41.79	2.59	-1.58	0.06, -0.27	0.07
(7)	42.12	2.71	-0.89	0.56, 0.80	0.63
trans-$Mo(CO)_4$					
(3)	54.25	5.65	-1.54	0.14, 0.50	0.49
(8)	55.94	5.42	-0.85	0.65, 1.05	0.63
*cis,cis,*trans-$RuCl_2(CO)_2$					
(4)	31.42	-1.68	-3.35	-1.03, -0.55	-0.12
(9)	30.75	-4.53	-2.41	0.20, -0.28	-0.09

Chloroform-*d* was opened and handled under a dry nitrogen atmosphere. Other solvents were distilled under a dry nitrogen atmosphere prior to their use: dichloromethane and benzene from calcium hydride, tetrahydrofuran (THF) from sodium−benzophenone, and triethylamine first from potassium hydroxide and then from calcium hydride. The metal complex precursors, *cis*-$Mo(CO)_4$(nbd) (nbd = norbornadiene)[10] and *fac*-$RuCl_2(CO)_3$(THF),[11] and the ligand precursor, 1,2-bis[2-(2-hydroxyethoxy)ethoxy]benzene,[12] were prepared by literature procedures.

The NMR spectra were recorded on a Bruker ARX 300 MHz 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% H_3PO_4, and the $^{13}C\{^1H\}$and ^1H NMR spectra were referenced to internal $SiMe_4$ with positive chemical shifts downfield from those of the references. The ^{31}P and carbonyl and methylene ^{13}C NMR data for the compounds in this study are given in Table 1. Coordination chemical shifts for the ^{31}P and methylene and phenylene ^{13}C NMR resonances of **2**−**4** and those for the metallacrown ethers in this study are given in Table 2. Quantitative ^{31}P NMR spectra were acquired with an inverse-gated, 30° pulse sequence and a 20 s delay between pulses. Infrared spectra of dilute dichloromethane solutions of the complexes in a 0.2 mm KBr solution cell were run on a Perkin-Elmer Paragon 1000 FTIR or a Nicolet IR44 FTIR spectrometer using pure dichloromethane in the same cell as the background. Elemental analyses of the compounds were performed by Atlantic Microlab, Inc., Norcross, GA.

1,2-($Ph_2P(CH_2CH_2O)_2]_2)C_6H_4$ (6). (i) Preparation of 1,2-($MsO(CH_2CH_2O)_2)_2C_6H_4$. A solution of 6.4 g (0.022 mol) of 1,2-bis[2′-(2"-hydroxyethoxy)ethoxy]benzene and 6.9 mL (0.045 mol) of triethylamine in 60 mL of dichloromethane was stirred at ambient temperature while a solution of 3.5 mL (0.045 mol) of methanesulfonyl chloride in 50 mL of dichloromethane was added dropwise over a period of 2 h. After the addition was completed, the reaction mixture was stirred for 1 h and then evaporated to dryness on a rotary evaporator to yield a white oily residue. This residue was extracted with three 50-mL portions of benzene. The washes were combined and filtered to remove the triethylammonium chloride byproduct. The solvent was removed from the filtrate first on a rotary evaporator and then under high vacuum to yield 9.3 g (94%) of 1,2-$(MsO(CH_2CH_2O)_2)_2C_6H_4$ as a clear oil. The crude product was characterized by its ^1H NMR spectrum and its successful use in the next step of the ligand synthesis. ^1H

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NMR (chloroform-*d*), δ: 6.91 (phenylene, broad singlet, 4); 4.40 (methylene, multiplet, 4); 4.14 (methylene, multiplet, 4); 3.87 (two methylenes, multiplets, 8); 3.06 (methyl, sharp singlet, 6).

(ii) Preparation of 1,2-($Ph_2P(CH_2CH_2O)_2)_2C_6H_4$ (6). A solution of 50 mL of THF and 9.3 g (0.021 mol) of 1,2-(MsO-$(CH_2CH_2O)_2)_2C_6H_4$ in a 200 mL Schlenk flask was cooled to −78 °C in dry ice/acetone and then titrated to a persistent rose color with a 0.5 M solution of potassium diphenylphosphide in THF. After the addition was completed, the reaction mixture was stirred for 2 h and then allowed to warm to room temperature. Water (15 mL) was then added to neutralize the residual potassium diphenylphosphide, causing the solution to turn yellow. The solution was evaporated to dryness using a rotary evaporator, and the residue was extracted with four 50-mL portions of dichloromethane. The extracts were combined and evaporated to dryness first on a rotary evaporator and then under high vacuum to yield 10.6 g (81.0%) of the product as a clear, pale yellow oil. The ligand was characterized by its ^1H NMR spectrum and its successful use in the synthesis of the metallacrown ether complexes. ^1H NMR (chloroform-*d*), δ: 7.40 (phenyl, multiplet, 20); 7.27 (phenylene, singlet, 4); 4.07 (methylene, multiplet, 4); 3.71 (methylene, multiplet, 4); 3.64 (methylene, multiplet, 4); 2.39 (methylene, multiplet, 4).

***cis*-$Mo(CO)_4\{1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4\text{-}P,P'\}$ (7).** Solutions of 0.579 g (1.93 mmol) of *cis*-$Mo(CO)_4$(nbd) in 200 mL of dichloromethane and of 1.20 g (1.93 mmol) of **6** in 200 mL of dichloromethane were added simultaneously and dropwise to 500 mL of dichloromethane over a period of 3 h. This mixture was stirred for 18 h, and then its volume was reduced to 50 mL by rotary evaporation. The dark brown concentrate was filtered through 10 g of silica gel, and the light golden filtrate was evaporated to dryness on a rotary evaporator. This gave 1.27 g (78.6% yield) of the product as an off-white solid. Analytically pure product was obtained by preparative chromatography on silica gel plates using a 2:5 ethyl acetate: hexanes solvent system. Anal. Calcd for $C_{42}H_{40}O_8MoP_2\cdot H_2O$: C, 59.06; H, 4.78. Found: C, 59.44; H, 4.95. IR (chloroform solution): ν(CO) 2021 (m), 1922 (s, br), 1904 (s, br), 1880 (s, br) cm^{-1}.

***trans*-$Mo(CO)_4\{1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4\text{-}P,P'\}$ (8). (i) Preparation Using UV Irradiation.** A solution of 0.14 g (1.1 mmol) of **7** in 150 mL of THF was irradiated in an Ace concentric photochemical reactor with a 350-W mercury vapor lamp for 5 min. During this time, water was circulated in a jacket located between the lamp and solution chambers to cool the solution. The murky, dark golden reaction mixture was then evaporated to dryness. The residue was dissolved in dichloromethane, and this solution was filtered through silica gel. The filtrate was reduced in volume to 10 mL using a rotary evaporator and then streaked onto a preparative TLC plate. A 2:5 ethyl acetate:hexanes solvent system was used to develop the plate. Bands for both **7** and **8** were observed and were scraped off the plate. The metallacrown ethers were eluted from the silica gel with methanol, and the methanol solutions were evaporated to dryness on a rotary evaporator. The solid residues were dried for 2 h under high vacuum to yield 0.011 g (8% recovery) of **7** and 0.005 g (4%) of **8** as an off-white solid. Anal. Calcd for $C_{42}H_{40}O_8MoP_2\cdot H_2O$: C, 59.06; H, 4.78. Found: C, 59.12; H, 4.88.

(ii) ^{31}P NMR Study of the Isomerization of 7 to 8 Catalyzed by $HgCl_2$. A solution of 0.090 g (0.11 mmol) of **7** in 0.51 mL of chloroform-*d* was prepared in a 5 mm screw-top NMR tube. The headspace of the tube was flushed with nitrogen, and then the tube was carefully sealed with a septum cap. Both ^{13}C and ^{31}P NMR spectra of this solution were recorded. Then 6.7 μL (0.11 μmol) of an aqueous 45 mg/mL solution of $HgCl_2$ was injected under the surface of the chloroform-*d* solution. After vigorous shaking, a quantitative ^{31}P NMR spectrum was acquired, and the integration of the cis and trans peaks was used as a direct indication of the degree of isomerization. Several additional ^{31}P NMR spectra were taken at longer times after mixing, but no further change in the ratio of the isomers was observed.

Table 3. X-ray Parameters for *cis*-$Mo(CO)_4\{1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4\text{-}P,P'\}$, 7

empirical formula	$C_{42}H_{40}MoO_8P_2$
cryst size	0.30 × 0.30 × 0.10 mm
cryst syst, space group	monoclinic, $P2_1/c$
unit cell dimens	$a = 18.7844(33)$, $b = 18.0198(33)$, $c = 23.6283(24)$ Å; $\beta = 90.086(13)°$
V	77998(4) $Å^3$
Z	8
fw	830.6
d (calcd)	1.380 Mg/m^3
abs coeff	0.459 mm^{-1}
F(000)	3424
T	298 K
monochromator	highly oriented graphite crystal
index ranges	$-24 < h < 24$, $-23 < k < 0$, $-30 < l < 0$
no. of reflns collected	18 789
no. of indep reflns	18 340 ($R_{int} = 2.92\%$)
obsd reflns	6911 ($F \geq 6.0\sigma(F)$), 8173 ($F \geq 3.0\ \sigma(F)$)
abs cor	semiempirical
min/max transm	0.7027/0.8014
system used	Siemens SHELXTL PLUS (PC version)
solution/refinement method	Patterson methods/full-matrix least-squares
quantity minimized	$\sum w(F_o - F_c)^2$
hydrogen atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0021F^2$
no. of params refined	956
final R indices (6σ data/3σ data)	$R = 6.01\%$, $R_w = 6.45\%$/$R = 7.01\%$, $R_w = 8.70\%$
goodness-of-fit	1.01
largest and mean Δ/σ	0.001, 0.000
largest diff peak/hole	0.71/−0.54 e $Å^{-3}$

***cis,cis,trans*-$RuCl_2(CO)_2\{1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4\text{-}P,P'\}$ (9).** Solutions of 0.164 g (0.498 mmol) of *fac*-$RuCl_2(CO)_3$(THF) in 200 mL of dichloromethane and of 0.310 g (0.248 mmol) of **6** in 200 mL of dichloromethane were added simultaneously and dropwise to 500 mL of dichloromethane over a period of 2 h. This reaction mixture was stirred for 18 h, and then the yellow solution was evaporated to dryness to yield 0.43 g (100% yield) of **9** as a pale yellow solid. Anal. Calcd for $C_{42}H_{40}O_6Cl_2RuP_2$: C, 56.60; H, 4.82. Found: C, 56.48; H, 4.74. IR (chloroform): ν(CO) 2058 (s), 1994 (s) cm^{-1}.

X-Ray Structural Analysis for *cis*-$Mo(CO)_4\{1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4\text{-}P,P'\}$. A crystal with dimensions 0.35 × 0.30 × 0.10 mm was mounted upon a glass fiber under aerobic conditions. It was then mounted and aligned upon an Enraf-Nonius CAD4 single-crystal diffractometer. Details of the data collection are collected in Table 3.

The unit cell parameters suggest that the crystal belongs to the orthorhombic crystal system ($a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$), but upon examination of equivalent reflections, it is clear that the crystal belongs to the monoclinic crystal system ($+h,+k,+l = +h,-k,+l = -h,-k,-l = -h,+k,-l \neq -h,+k,+l = +h,-k,-l = -h,-k,+l = +h,+k,-l$). This was confirmed by analyzing the merging statistics (monoclinic $R_{int} = 2.92\%$ vs orthorhombic $R_{int} = 54.9\%$). Upon correct assignment of the crystal system, the space group was determined unequivocally by the systematic absences, $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, to be the centrosymmetric space group $P2_1/c$.

All crystallographic calculations were accomplished with the Siemens SHELXTL-PC program package.[13] The analytical

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[13] *Siemens SHELXTL-PC Manual*, Release 4.1; Siemens Analytical Instruments: Madison, WI, 1990.

Table 4. Selected Bond Lengths (Å) for *cis*-$Mo(CO)_4\{1,2-(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$-*P,P′*}, 7

molecule 1		molecule 2	
Mo(1)−P(1)	2.543(2)	Mo(1′)−P(1′)	2.554(2)
Mo(1)−P(2)	2.569(2)	Mo(1′)−P(2′)	2.574(3)
P(1)−C(1)	1.824(9)	P(1′)−C(1′)	1.862(10)
P(2)−C(18)	1.829(9)	P(2′)−C(18′)	1.837(9)
O(3)−C(2)	1.362(14)	O(3′)−C(2′)	1.410(12)
O(3)−C(4)	1.405(14)	O(3′)−C(4′)	1.395(12)
O(6)−C(5)	1.388(13)	O(6′)−C(5′)	1.394(13)
O(6)−C(7)	1.383(13)	O(6′)−C(7′)	1.362(12)
O(13)−C(12)	1.375(14)	O(13′)−C(12′)	1.378(14)
O(13)−C(14)	1.411(15)	O(13′)−C(14′)	1.434(13)
O(16)−C(15)	1.480(17)	O(16′)−C(15′)	1.422(12)
O(16)−C(17)	1.319(16)	O(16′)−C(17′)	1.404(11)
C(1)−C(2)	1.512(15)	C(1′)−C(2′)	1.529(13)
C(4)−C(5)	1.472(16)	C(4′)−C(5′)	1.476(15)
C(7)−C(12)	1.395(16)	C(7′)−C(12′)	1.388(15)
C(14)−C(15)	1.496(19)	C(14′)−C(15′)	1.484(16)
C(17)−C(18)	1.459(18)	C(17′)−C(18′)	1.499(13)

Table 5. Selected Bond Angles (deg) for *cis*-$Mo(CO)_4\{1,2-(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$-*P,P′*}, 7

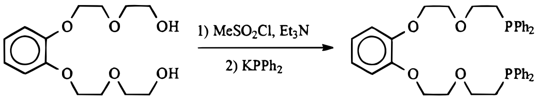
molecule 1		molecule 2	
P(1)−Mo(1)−P(2)	96.0(1)	P(1′)−Mo(1′)−P(2′)	100.8(1)
Mo(1)−P(1)−C(1)	113.0(3)	Mo(1′)−P(1′)−C(1′)	115.1(3)
Mo(1)−P(2)−C(18)	124.3(3)	Mo(1′)−P(2′)−C(18′)	123.8(3)
C(2)−O(3)−C(4)	119.2(9)	C(2′)−O(3′)−C(4′)	118.5(8)
C(5)−O(6)−C(7)	117.2(8)	C(5′)−O(6′)−C(7′)	119.5(8)
C(12)−O(13)−C(14)	119.6(9)	C(12′)−O(13′)−C(14′)	117.3(8)
C(15)−O(16)−C(17)	113.3(10)	C(15′)−O(16′)−C(17′)	113.8(7)
P(1)−C(1)−C(2)	114.8(7)	P(1′)−C(1′)−C(2′)	111.1(6)
O(3)−C(2)−C(1)	116.7(9)	O(3′)−C(2′)−C(1′)	111.6(8)
O(3)−C(4)−C(5)	115.8(10)	O(3′)−C(4′)−C(5′)	111.7(9)
O(6)−C(5)−C(4)	109.6(9)	O(6′)−C(5′)−C(4′)	110.6(8)
O(6)−C(7)−C(12)	114.5(9)	O(6′)−C(7′)−C(12′)	115.0(9)
O(13)−C(12)−C(7)	114.8(9)	O(13′)−C(12′)−C(7′)	114.1(9)
O(13)−C(14)−C(15)	107.8(10)	O(13′)−C(14′)−C(15′)	108.1(8)
O(16)−C(15)−C(14)	112.4(10)	O(16′)−C(15′)−C(14′)	113.0(8)
O(16)−C(17)−C(18)	111.6(10)	O(16′)−C(17′)−C(18′)	110.4(7)
P(2)−C(18)−C(17)	119.6(8)	P(2′)−C(18′)−C(17′)	115.4(6)

scattering factors were corrected for both $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion. The structure was solved by the use of a Patterson synthesis. Positional and anisotropic thermal parameters of 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 and with the appropriate staggered tetrahedral geometry.[14] The isotropic thermal parameter of each hydrogen atom was set equal to the U_{eq} value of the carbon atom to which it was bonded. Following refinement, the extreme features left on the difference Fourier map were a peak of height 0.71 e Å^{-3} and a negative feature of −0.54 e Å^{-3}. Refinement of the model converged with $R = 7.01\%$ and $R_w = 8.70\%$ for those 8173 reflections with $|F_o| > 3.0\sigma|F_o|$. Selected bond lengths and bond angles are listed in Tables 4 and 5, respectively.

Results and Discussion

It is well established that variations in the conformational mobility of crown ether ligands can greatly affect their ability to bind metal cations and small molecules,[15] and it seems likely that this would also be the case for metallacrown ethers. In addition, the introduction of conformational restraints into the α,ω-bis(phosphine)−polyether ligands could affect the ability of the ligand to adopt certain coordination geometries or alter the relative amounts of monomeric versus *n*-meric metallacrown ethers that are formed in certain reactions.[7,16] We have begun our study of conformationally restrained metallacrown ethers using the new ligand $1,2-(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$, **6**.

Ligand Synthesis and Characterization. The ligand, **6**, was prepared in high yield as shown in eq 1.

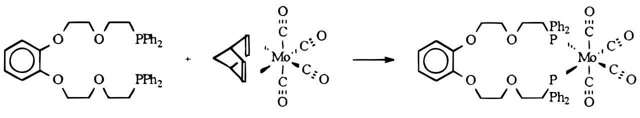


6

(1)

The ^{31}P NMR spectrum of the crude ligand indicates that, once the excess diphenylphosphine is removed, the ligand is essentially pure. The ^{31}P and ^{13}C NMR spectroscopic data for **6** are given in Table 1. The ^{31}P NMR resonance is a singlet, and its chemical shift is quite similar to that of the ^{31}P NMR resonance of **1**. The chemical shifts and carbon−phosphorus coupling constants for analogous ^{13}C NMR resonances of **1** and **6** are similar with the exception of the shifts for the two methylene carbons adjacent to the phenylene unit, C3 and C4.[4] The ^{13}C NMR resonances of these methylenes are 2 ppm upfield of those of the corresponding methylenes of **1**, as would be expected for methylenes adjacent to an aromatic ring.

Synthesis and Characterization of *cis*-$Mo(CO)_4$-{$1,2-(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$-*P,P′*},(7). Complex **7** was prepared in good yield by the high-dilution reaction of **6** and $Mo(CO)_4$(nbd), as shown in eq 2. Only the monomeric cis metallacrown ether was obtained from this reaction, as was previously observed for the reaction of **1** and $Mo(CO)_4$(nbd) under similar conditions.[4] The cis geometry in **7** is demonstrated by the presence of two carbonyl resonances in the ^{13}C NMR spectrum. As has previously been observed for other complexes of this type, the downfield resonance, due to carbonyls trans to phosphines, is an apparent quintet (A portion of an AXX′ spin system),[17] while the upfield resonance, due to carbonyls trans to carbonyls, is a 1:2:1 triplet (A portion of an AX_2 spin system).



6 **7**

(2)

Crystal Structure of *cis*-$Mo(CO)_4\{1,2-(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$-*P,P′*} (7). Complex **7** crystallized with two molecules per asymmetric unit. All molecules in the structure are separated by normal van der Waals distances. There are no anomalously close intermolecular contacts. The labeling of the atoms for the first molecule is shown in Figure 1 (the labeling of the second molecule is consistent with that of the first molecule with a "prime" being added to each of the labels to distinguish between the two). Selected bond distances and angles are collected in Tables 4 and 5, respectively.

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(14) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.
(15) Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: New York, 1989.
(16) Smith, D. C., Jr.; Gray, G. M. *Inorg. Chem.* **1998**, *37*, 1791.
(17) Redfield, D. A.; Nelson, J. H.; Cary, L. W. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 727.

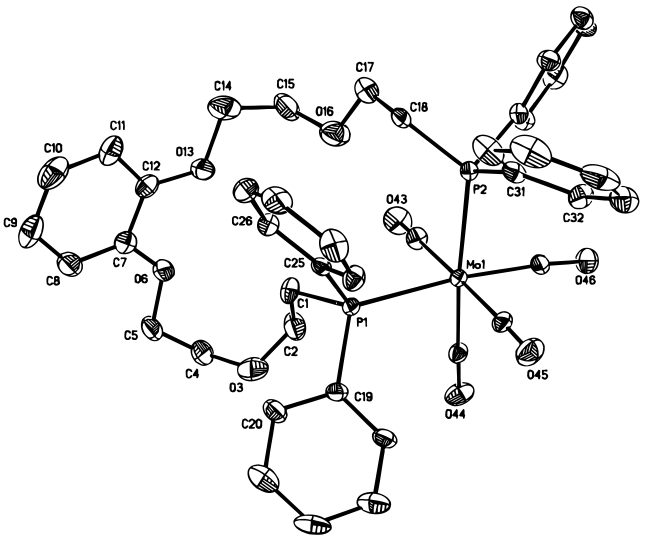


Figure 1. ORTEP drawing of one molecule in the asymmetric unit of *cis*-Mo(CO)$_4${1,2-(Ph$_2$P(CH$_2$CH$_2$O)$_2$)$_2$C$_6$H$_4$-*P*,*P*′}, **7**. The thermal ellipsoids are set at 25% for clarity.

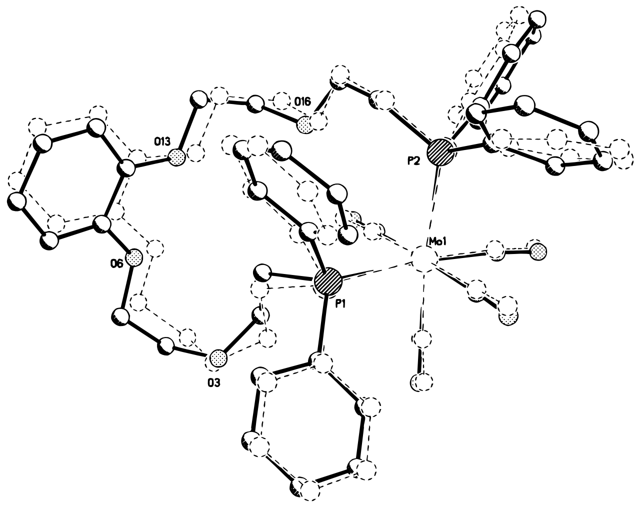


Figure 2. ORTEP drawing showing the superimposition of the two molecules in the asymmetric unit of *cis*-Mo(CO)$_4$-{1,2-(Ph$_2$P(CH$_2$CH$_2$O)$_2$)$_2$C$_6$H$_4$-*P*,*P*′}, **7**. The thermal ellipsoids are set at 25% for clarity.

The overall conformations of the two molecules in the asymmetric unit are similar but not identical. The superimposition of the two molecules, shown in Figure 2, clearly demonstrates that the molecules are not related by symmetry. The 18-membered metallacrown ether rings in both molecules are asymmetric about the molybdenum metal center. The largest conformational differences in the two molecules are associated rotations about the carbon−carbon bonds adjacent to the phosphines, C1−C2 and C17−C18 (torsion angles: P1−C1−C2−O3, 109.8°; P1′−C1′−C2′−O3′, 148.5°; O16−C17−C18−P2, 70.6°; O16′−C17′−C18′−P2′, 49.1°). The two molecules in the asymmetric unit also differ in the rotations of the phenyl groups about the phosphorus−*ipso* carbon bonds. These differences range from 17.9° for one of the phenyl substituents on P2 to 1.9° for one of the phenyl substituents on P1. The differences in the solid state conformations of the two molecules are most likely due to crystal packing forces because the average solution state conformation is symmetric.

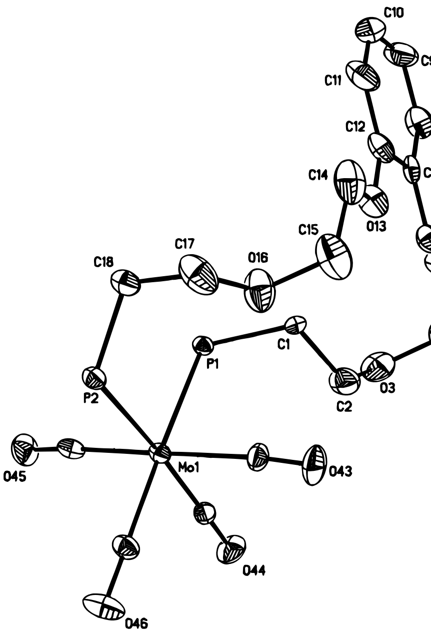
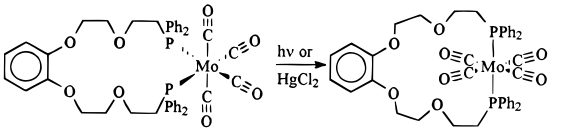


Figure 3. ORTEP drawing showing the relationship between the plane of the metallacrown ether oxygen atoms and the 1,2-phenylene ring in one molecule in the asymmetric unit of *cis*-Mo(CO)$_4${1,2-(Ph$_2$P(CH$_2$CH$_2$O)$_2$)$_2$C$_6$H$_4$-*P*,*P*′}, **7**. The thermal ellipsoids are set at 25% for clarity.

The feature of primary interest in this structure is the 17-membered metallacrown ether ring. The oxygen atoms in the rings (O3, O6, O13, O16) are in a planar arrangement with the average deviation from the least squares planes through the four oxygen atoms being 0.0328 Å for molecule 1 and 0.0697 Å for molecule 2. Because the oxygen atoms are in a planar arrangement, it is possible to estimate the cavity size by averaging the cross-ring O···O contact distances: O3···O13 and O6···O16. This gives a cavity size of 4.861 (±0.123) Å for molecule 1 and 4.927 (±0.089) Å for molecule 2. These distances are slightly larger that those observed for closely related metallacrown ethers containing the conformationally flexible Ph$_2$P(CH$_2$CH$_2$O)$_4$CH$_2$CH$_2$PPh$_2$ ligand, **1** (*cis*-Mo(CO)$_4${Ph$_2$P(CH$_2$CH$_2$O)$_4$CH$_2$CH$_2$PPh$_2$-*P*,*P*′}·MeOH, 4.642 Å; *cis*-Mo(CO)$_4${Ph$_2$P(CH$_2$CH$_2$O)$_4$-CH$_2$CH$_2$PPh$_2$-*P*,*P*′}·H$_2$O, 4.602 Å; *cis*-PtCl$_2${Ph$_2$P(CH$_2$-CH$_2$O)$_4$CH$_2$CH$_2$PPh$_2$-*P*,*P*′}, 4.66 Å).[4,9] The fact that the cavity in **7** is larger that those in the metallacrown ethers derived from **1** suggests that **7**, like *cis*-Mo(CO)$_4$-{Ph$_2$P(CH$_2$CH$_2$O)$_4$CH$_2$CH$_2$PPh$_2$-*P*,*P*′}, **2**, could bind both Li$^+$ and Na$^+$ cations.[9]

Although the cavity in **7** is sufficiently large to allow cation binding, there is another feature of the structure that could interfere with it. The 1,2-phenylene group is not coplanar with the plane through the oxygen atoms but instead intersects this plane at an angle of 42.0° for molecule 1 and 33.1° for molecule 2. This causes O3, O13, and O16 to point to the convex side of the metallacrown ether ring and O6 to point to the concave face as shown in Figure 3. If the structure of the ring in solution at all resembles that in the solid state, significant reorganization of the ring will be necessary if all four oxygens are to coordinate to a metal cation. This could greatly reduce the ability of these complexes to bind alkali metal cations.

Synthesis and Characterization of *trans*-Mo(CO)$_4${1,2-(Ph$_2$P(CH$_2$CH$_2$O)$_2$)$_2$C$_6$H$_4$-*P*,*P*′} (8). We have previously reported that the conformationally labile metallacrown ether *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P,P′*}, **2**, isomerizes to *trans*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P,P′*}, **3**, on exposure to either UV light or $HgCl_2$.[6,8] The conformationally restricted metallacrown ether *cis*-$Mo(CO)_4\{1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$-*P,P′*}, **7**, also can be isomerized to *trans*-$Mo(CO)_4\{1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$-*P,P′*}, **8**, under the same conditions; however, different degrees of isomerization are observed for **2** and **7**. The equilibrium constant for the isomerization of **7** to **8** (calculated from the integration of the quantitative ^{31}P NMR spectrum using eq 4) is 0.23 while that for the isomerization of **2** to **3** is 1.0.[18] The relative magnitudes of the equilibrium constants are consistent with the fact that the yield of **8** from the photochemical isomerization of **7** (4%) is much lower than that of **3** from **2** (45%).[6] Both observations suggest that the steric constraints imposed by the 1,2-phenylene in **7** favor the cis coordination geometry with its smaller phosphorus−phosphorus distance.

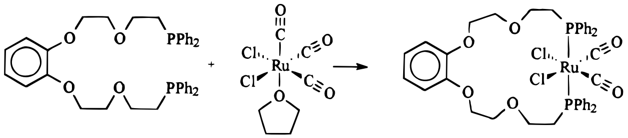


7 **8** (3)

$$K_{eq} = [\text{trans isomer}]/[\text{cis isomer}] \qquad (4)$$

It is interesting that the isomerizations of **2** to **3** and of **7** to **8** are both quite rapid. In each case, the ^{31}P NMR spectra of the reaction mixtures show that the equilibria are established within 2 min of the addition of the aqueous $HgCl_2$ solution. Given the low solubility of $HgCl_2$ in chloroform, this suggests that both **2** and **7** are capable of transferring $HgCl_2$ from the aqueous phase to the organic phase.[8] This conclusion is consistent with the X-ray crystal structure of **7**, which indicates that the cavities in metallacrown ether rings in **2** and **7** have similar sizes.

Synthesis and Characterization of *cis,cis,trans*-$RuCl_2(CO)_2\{1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$-*P,P′*} (9). The reaction of **6** and *fac*-$RuCl_2(CO)_3(THF)$, shown in eq 5, was carried out under moderately high dilution conditions. The ^{31}P NMR spectrum of the crude reaction mixture indicated that three products were formed (the ^{31}P NMR resonances at 9.05, 14.37, and 14.93 ppm are of approximately equal intensity), as was previously observed for the reaction of **1** and *fac*-$RuCl_3(CO)_2(THF)$.[7] On the basis of our earlier studies,[7] the resonance at 9.05 ppm was assigned to the monomeric *cis,cis,trans*-$Ru(CO)_2Cl_2\{1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$-*P,P′*}, **9**, while the downfield resonances were assigned to cyclic *n*-mers having the same empirical formula and ruthenium coordination geometry as the monomer. However, unlike the [*cis,cis,trans*-$Ru(CO)_2Cl_2\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P,P′*}]$_n$ metallacrown ethers, which did not interconvert and could be separated by column chromatography on silica gel,[7] the *n*-meric [*cis,cis,trans*-$RuCl_2(CO)_2\{1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$-*P,P′*}]$_n$ metallacrown ethers gradually convert into the monomeric metallacrown ether, **9**, in chloroform-*d* solution over a period of 1 week at ambient temperature. This suggests that the oligomeric metallacrown ethers are kinetically favored but the monomeric metallacrown ether, **9**, is thermodynamically favored. X-ray crystal structures of [*cis,cis,trans*-$Ru(CO)_2Cl_2\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P,P′*}], **4**, and its cyclic dimer, **10**, demonstrate that the phosphines are much closer to one another in **4** than in **10**.[7] The *n*-mer to monomer conversion of the conformationally restrained metallacrown ethers is most likely due to the steric constraints of the 1,2-phenylene that favor the monomer with its smaller phosphorus−phosphorus distance.



6 **9** (5)

NMR Coordination Chemical Shifts of Metallacrown Ethers. To gain more insight into the conformational changes that occur when the α,ω-bis(phosphine)−polyether ligands, **1** and **6**, coordinate to metals, we have calculated the ^{31}P and methylene and phenylene ^{13}C NMR coordination chemical shifts for metallacrown ethers containing these ligands. These are given in Table 2. The ^{31}P NMR coordination chemical shifts almost entirely depend on the nature of the metal center in the metallacrown ether and are consistent with those reported for related complexes with monodentate phosphine ligands.[19]

The ^{13}C NMR coordination chemical shifts of the methylene and phenylene carbons in the metallacrown ether rings are affected both by the nature of the metal center and by the nature of the ligand. Perhaps the most interesting observation is that the ^{13}C NMR coordination chemical shifts for C3, C4, and C5 are quite different for the *trans*-$Mo(CO)_4$− and *cis,cis,trans*-$RuCl_2(CO)_2$−metallacrown ethers with the same α,ω-bis(phosphine)−polyether ligand (**3** and **4** with ligand **1** and **8** and **9** with ligand **6**). This is surprising because C3, C4, and C5 are too far from the metal to be affected by through-bond interactions, and all of the complexes are octahedral with trans phosphine groups. Apparently, the ^{13}C NMR coordination chemical shifts of these carbons are quite sensitive to the different steric requirements of the ligands cis to the phosphines. This suggests that there is a significant interaction between the α,ω-bis(phosphine)−polyether ligand and the other ligands coordinated to the metal center. Such interactions could be useful in activating these ligands during catalytic processes.

Summary. Metallacrown ethers derived from the conformationally restrained $1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$ ligand are significantly different from those derived from the conformationally mobile $Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$ ligand even though they have the same numbers of atoms in the metallacrown ether rings. The 1,2-phenylene ligand favors metallacrown ethers with smaller distances between the phosphines, i.e. *cis*-Mo-

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[19] Pregosin, P. S.; Kunz, R. W. *NMR: Basic Principles in Progress*; Springer-Verlag: Berlin, 1979.

$(CO)_4\{(Ph_2P(CH_2CH_2O)_2)_2C_6H_4\text{-}P,P'\}$, **7**, over its trans isomer, **8**, and monomeric *cis,cis,trans*-$RuCl_2(CO)_2\{(Ph_2P(CH_2CH_2O)_2)_2C_6H_4\text{-}P,P'\}$ over its *n*-mers. This property may be useful in catalyst design because our results to date suggest that monomeric, cis metallacrown ethers have the best cation-binding abilities.

Supporting Information Available: Tables of aromatic ^{13}C NMR data, atomic coordinates, thermal parameters, bond lengths, bond angles, torsional angles, and O···O contact distances (14 pages). Ordering information is given on any current masthead page.

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