

cis-Mo(CO)₄{Ph₂P(CH₂CH₂O)_nCH₂CH₂PPh₂} (n = 3-5) Metallacrown Ethers. X-ray Crystal Structure of cis-Mo(CO)₄{Ph₂P(CH₂CH₂O)₃CH₂CH₂PPh₂}

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A series of Ph₂P(CH₂CH₂O)_nCH₂CH₂PPh₂ (1, n = 3; 2, n = 4; 3, n = 5) ligands and their cis-Mo(CO)₄{Ph₂P(CH₂CH₂O)_nCH₂CH₂PPh₂} (4, n = 3; 5, n = 4; 6, n = 5) complexes have been prepared. Multinuclear NMR and IR spectroscopic studies of these complexes indicate that a single Mo complex, with the ligands cis coordinated to the Mo through the PPh₂ groups, is formed with each ligand. The complexes have been titrated with LiBF₄ and NaBPh₄, and the titrations have been followed by ³¹P NMR spectroscopy. These studies indicate that **5** binds much more strongly to Li⁺ than to Na⁺, but **6** binds more strongly to Na⁺ than to Li⁺. Bimetallic complexes were isolated from the titration solutions. With **6**, 1:1 adducts were obtained with both LiBF₄ and NaBPh₄, whereas with **5**, a 1:1 adduct was obtained with LiBF₄ and a 2:1 adduct was obtained with NaBPh₄. These results demonstrate that the metallacrown ethers exhibit definite size selectivities toward the alkali-metal cations. The cis-Mo(CO)₄{Ph₂P(CH₂CH₂O)_nCH₂CH₂PPh₂} (n = 3-5) complexes react with methylolithium and phenyllithium to yield cis-Mo(CO)₄(Ph₂PCH=CH₂)₂. This result is surprising because related Mo(CO)₄ complexes of bis(phosphinite)- and bis(phosphite)-polyether ligands react with methylolithium and phenyllithium to yield acetyl and benzoyl complexes, respectively. The X-ray crystal structure of cis-Mo(CO)₄{Ph₂P(CH₂CH₂O)₃CH₂CH₂PPh₂} (**4**) is also reported. The complex crystallizes in the monoclinic space group P₂₁/n (a = 22.219 (1), b = 14.8175 (4), c = 10.680 (1) Å; β = 98.523°; V = 3477.2 Å³; z = 4). The molybdenum is in a slightly distorted octahedral coordination geometry with a P-Mo-P angle of 93.78 (2)°. The metallacrown ether ring is distorted from the symmetric solution conformation primarily due to different rotations of the diphenylphosphino groups about the molybdenum-phosphorus bonds. The three oxygens in the metallacrown ether are at the vertices of an isosceles triangle, and the plane formed by these oxygens is perpendicular to that formed by the molybdenum and the two phosphorus atoms.

Introduction

A variety of bi- and polydentate ligands with P and ether O donor atoms have been reported in the literature in the past decade. These include those with one P and one O donor site,¹⁻¹² those with one P donor site and two or more noncyclic O donor sites,¹³⁻¹⁷ those with an exocyclic phosphine on a crown ether,¹⁸⁻²⁵ those in

which one or more of the ether groups in a crown ether are replaced by phosphines,²⁶⁻²⁹ and those with α,ω-bis(phosphine), -bis(phosphinite), or -bis(phosphite) substituents on a polyether chain.³⁰⁻⁴¹ Complexes of these ligands are of interest as catalysts for several reasons. The weakly coordinating hard donor atoms of the ligands can be used to hold a coordination site open for a reactant, and thus increase the activity of the catalyst.^{5,7,9,10,15,25} The hard donor atoms can also coordinate to cations in salts, and this allows these complexes to function as phase-transfer catalysts.^{13,14,22} Heterobimetallic complexes of these ligands may also be able to activate small molecules such as carbon monoxide via coordination to both the carbon and the oxygen.^{24,29,32-34,39-41}

Chelation of α,ω-bis(phosphine)-, α,ω-bis(phosphinite)- or α,ω-bis(phosphite)-polyether ligands to a transition-metal center forms cyclic polyethers with the metal center incorporated into the ring (metallacrown ethers). If these metallacrown ethers contain a sufficient number of ether groups and a sufficiently large ring, they should exhibit the same ability to coordinate hard metal cations as do the more traditional crown ethers. Of these, the complexes of the α,ω-bis(phosphine)-polyether ligands are of most

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Table I. ^{31}P and Phenyl ^{13}C NMR Data^a

compd	P		ipso		ortho		meta		para
	$\delta(^{31}\text{P})$, ppm	$\delta(^{13}\text{C})$, ppm	$ J(\text{PC}) $, Hz	$\delta(^{13}\text{C})$, ppm	$ J(\text{PC}) $, Hz	$\delta(^{13}\text{C})$, ppm	$ J(\text{PC}) $, Hz	$\delta(^{13}\text{C})$, ppm	
1	-21.63 s	138.29 d	13 ^b	132.66 d	19 ^c	128.51 d	9 ^d	128.36 s	
2	-21.68 s	138.17 d	12 ^b	132.68 d	18 ^c	128.56 d	12 ^d	128.41 s	
3	-21.69 s	138.29 d	12 ^b	132.71 d	17 ^c	128.58 d	10 ^d	128.41 s	
4	20.36 s	137.48 aq	57 ^e	132.14 aq	9 ^f	128.30 bs		129.30 s	
5	20.11 s	136.94 aq	56 ^e	132.13 aq	9 ^f	128.35 aq	8 ^e	129.32 s	
6	20.44 s	136.17 aq	62 ^e	132.12 aq	8 ^f	128.33 bs		129.46 s	
7	20.29 s	137.63 aq	36 ^e	132.92 aq	9 ^f	129.36 aq	9 ^e	130.51 s	
8	20.64 s	137.20 aq	35 ^e	132.95 aq	8 ^f	129.46 bs		130.68 s	
9	20.32 s	137.25 aq	35 ^e	132.84 aq	11 ^f	129.35 bs		130.52 s	
10	20.11 s	137.74 aq		132.69 aq	11 ^f	129.44 bs		130.73 s	
11	29.37 s								

^a Key: b = broad, s = singlet, d = doublet, aq = apparent quintet. ^b $|^1J(\text{PC})|$. ^c $|^2J(\text{PC})|$. ^d $|^3J(\text{PC})|$. ^e $|^1J(\text{PC}) + ^3J(\text{PC})|$. ^f $|^2J(\text{PC}) + ^4J(\text{PC})|$. ^g $|^3J(\text{PC}) + ^5J(\text{PC})|$.

Table II. Aliphatic ^{13}C NMR Data^a

compd	C1		C2		C3	C4	C5	C6
	$\delta(^{13}\text{C})$, ppm	$ J(\text{PC}) $, Hz	$\delta(^{13}\text{C})$, ppm	$ J(\text{PC}) $, Hz	$\delta(^{13}\text{C})$, ppm	$\delta(^{13}\text{C})$, ppm	$\delta(^{13}\text{C})$, ppm	$\delta(^{13}\text{C})$, ppm
1	28.77 d	13 ^b	68.53 d	25 ^c	70.10 s	70.57 s		
2	28.73 d	12 ^b	68.53 d	26 ^c	70.10 s	70.58 s	70.53 s	
3	28.73 d	13 ^b	68.49 d	25 ^c	70.07 s	70.55 s	70.51 s	70.51 s
4	31.83 aq	14 ^d	67.71 bs		71.54 s	70.66 s		
5	31.32 aq	15 ^d	66.95 bs		70.16 s	70.25 s	70.65 s	
6	32.87 aq	20 ^d	66.94 bs		69.96 s	70.34 s	70.47 s	70.47 s
7	31.69 aq	16 ^d	67.40 bs		70.61 s	70.45 s	70.38 s	
8	31.99 aq	15 ^d	67.33 s		70.08 s	70.08 s	70.08 s	
9	31.24 aq	15 ^d	67.68 bs		70.54 s	70.30 s	70.30 s	70.30 s
10	31.22 aq	15 ^d	67.57 aq	9 ^e	69.81 s	69.99 s	69.99 s	69.99 s

^a Key: b = broad, s = singlet, d = doublet, aq = apparent quintet. ^b $|^1J(\text{PC})|$. ^c $|^2J(\text{PC})|$. ^d $|^1J(\text{PC}) + ^3J(\text{PC})|$. ^e $|^2J(\text{PC}) + ^4J(\text{PC})|$.

Table III. Carbonyl ^{13}C NMR and IR Data^a

compd	trans CO		cis CO		$\nu(\text{CO})$, cm^{-1}
	$\delta(^{13}\text{C})$, ppm	$ ^2J(\text{PC}) + ^2J(\text{P}'\text{C}) $, Hz	$\delta(^{13}\text{C})$, ppm	$ ^2J(\text{PC}) $, cm^{-1}	
4	214.96 aq	16	209.79 t	9	2022 m, 1920 s, 1905 s, 1885 sh
5	215.08 aq	16	209.69 t	8	2020 m, 1920 s, 1906 s, 1885 sh
6	215.05 aq	14	209.55 t	9	2023 m, 1920 s, 1905 s, 1885 sh
7	216.23 aq	16	210.56 t	9	2023 w, 1917 s, 1905 s
8	216.11 aq	15	210.55 t	9	2022 m, 1929 s, 1883 vs
9	216.22 aq	17	210.54 t	9	2023 w, 1915 s, 1905 s
10	215.68 aq	16	210.42 t	9	2023 m, 1922 s, 1900 bs

^a Key: aq = apparent quintet, t = triplet, s = strong, m = medium, sh = shoulder, b = broad, v = very.

interest from a catalytic standpoint because the ligands are hydrolytically stable and cannot undergo Arbusov dealkylations.⁴²⁻⁴⁴ However, with one exception, all of the α,ω -bis(phosphine)-polyether ligands that have been studied have contained three or fewer ether groups. The cavities in the metallacrown ether complexes of such ligands do not appear to be sufficiently large to incorporate an alkali-metal cation into the ring.

In this paper, we describe our initial studies of the coordination chemistry of a series of $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{PPh}_2$ ($n = 3-5$) ligands. Syntheses of the ligands and their $\text{cis-Mo}(\text{CO})_4$ complexes are described, and multinuclear NMR data for the ligands and complexes are presented. The coordination of alkali-metal cations to the cis complexes and the reactions of methyl- and phenyllithium with these complexes are discussed. The X-ray crystal structure of $\text{cis-Mo}(\text{CO})_4\{\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{PPh}_2\}$ (4) has been determined, and pertinent features of the structure are described.

Experimental Section

The $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a GE NT-300, wide-bore, multinuclear NMR spectrometer (Table I-III and V and Supplementary Table 1). The ^{31}P NMR spectra were referenced to external 85% phosphoric acid, and the ^{13}C NMR spectra were referenced to internal TMS. Chemical shifts downfield from those of the reference

Table IV. Analytical Data and Melting Points

compd	color	% C		% H		mp, °C
		calcd	found	calcd	found	
4-0.5H ₂ O	white	57.83	57.80	4.95	4.92	150-152 dec
5	white	58.31	58.24	5.12	5.18	119-122 dec
6	white	56.87	56.93	5.45	5.43	sinters ~50
7-0.5H ₂ O	white	51.54	51.45	4.63	4.76	92-95
8	white	62.95	62.99	5.25	5.42	102-108
9-1.0H ₂ O	white	51.19	50.97	4.91	5.20	78-80
10	pale yellow	65.74	65.57	5.48	5.75	138

compounds are reported as positive. The IR spectra of dilute dichloromethane solutions of the complexes in 0.2-mm KBr solution cells versus pure dichloromethane in matched cells were run from 2200 to 1800 cm^{-1} either on a Perkin Elmer 283B spectrometer or on a Nicolet IR44 spectrometer (Table III). Elemental analyses of the compounds were performed by Atlantic Microlab, Inc., Norcross, GA (Table IV).

All of the starting materials, free ligands, complexes, and solvents were handled under N_2 . All solvents were of reagent grade. Benzene was distilled from CaH_2 prior to use, and tetrahydrofuran (THF) and diethyl ether were distilled from Na-benzophenone. All starting materials were reagent grade. Triethylamine was distilled from calcium hydride prior to use. The $\text{cis-Mo}(\text{CO})_4(\text{nbd})$ (nbd = norbornadiene)⁴⁵ complex was prepared by literature procedures. Phenyllithium (PhLi) and methyl-lithium (MeLi) solutions were used from newly opened bottles. The

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Table V. ^{31}P NMR Data for the Titrations of **5** and **6** with LiBF_4 and NaBPh_4^a

mole ratio 5: LiBF_4	$\delta(^{31}\text{P})$, ppm	mole ratio 6: LiBF_4	$\delta(^{31}\text{P})$, ppm	mole ratio 5: NaBPh_4	$\delta(^{31}\text{P})$, ppm	mole ratio 6: NaBPh_4	$\delta(^{31}\text{P})$, ppm
0.00	20.00	0.00	20.64	0.00	20.00	0.00	20.64
0.19	20.09	0.20	20.52	0.32	20.28	0.28	20.42
0.36	20.24	0.40	20.43	0.65	20.55	0.46	20.28
0.60	20.41	0.60	20.39	0.97	20.77	0.57	20.18
0.85	20.55	0.80	20.37	1.62	20.98	0.79	20.09
0.95	20.60	1.00	20.35	1.72	21.01	0.96	20.07
1.42	20.60	1.50	20.32			1.41	20.07
		2.00	20.31				

^a ^{31}P NMR spectra taken of CD_3CN solutions of the complexes and the salts.

cis- $\text{Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{PPh}_2]$ ($n = 3-5$) complexes were stored in the dark.

$\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{PPh}_2$ (1). **Method I.** (i) **Preparation of $\text{Br}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{Br}$.** Bromine (5.8 mL, 210 mmol) was added dropwise to a solution of 9.7 g (50 mmol) of $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{OH}$ and 28 g (110 mmol) of PPh_3 in 100 mL of dry *N,N*-dimethylformamide at 5 °C until the solution remained yellow. This mixture was stirred for 2 h and then was evaporated to dryness. The residue was taken up in 200 mL of diethyl ether and 100 mL of water. The organic layer was separated and washed with six 50-mL portions of water. It was then dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated to 50 mL and then was cooled to -5 °C to precipitate the OPPh_3 by-product. This precipitate was removed by filtration, and the filtrate was evaporated to dryness. The oily residue was vacuum distilled (127–129 °C at 0.10 mmHg) to yield 5.5 g (35%) of $\text{Br}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{Br}$.

(ii) **Preparation of $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{PPh}_2$ (1).** A solution of 21.5 mL (34 mmol) of 1.6 M Bu^nLi in 100 mL of diethyl ether was added dropwise to a solution of 6.0 mL (34 mmol) of Ph_2PH in 100 mL of diethyl ether at -78 °C over a 90-min period. The initially clear and colorless solution turned bright yellow, and a yellow precipitate formed. This solution was stirred for 1 h at -78 °C, and then a solution of 5.5 g (17 mmol) of $\text{Br}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{Br}$ in 100 mL of diethyl ether was added dropwise over a period of 1 h at -78 °C. This solution was stirred overnight at room temperature and then was evaporated to dryness. The residue was washed with four 50-mL portions of a degassed 1:1 dichloromethane–hexanes mixture, and the washes were evaporated to dryness to give 7.4 g (28%) of **1** as a colorless oil.

$\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{PPh}_2$ (1). **Method II.** (i) **Preparation of $\text{TsO}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{OTs}$.** A solution of 16 g (84 mmol) of *p*-toluenesulfonyl chloride in 100 mL of THF was added dropwise to a solution of 7.2 mL (42 mmol) of $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{OH}$ and 12 mL (84 mmol) of triethylamine in 100 mL of THF at room temperature. This mixture was stirred for 15 h and then was filtered to remove the triethylammonium chloride precipitate. The filtrate was evaporated to dryness to give 8.5 g (46%) of $\text{TsO}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{OTs}$ as a colorless oil.

(ii) **Preparation of $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{PPh}_2$ (1).** A solution of lithium diphenylphosphide was prepared as described above from 6.7 mL (39 mmol) of PPh_2H and 24.2 mL (38.7 mmol) of 1.6 M Bu^nLi in 300 mL of THF. A solution of 8.5 g (20 mmol) of $\text{TsO}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{OTs}$ in 100 mL of THF was added dropwise to this solution at -78 °C over a 1-h period, and the mixture was stirred at room temperature overnight. It was then evaporated to dryness, and the residue was washed with two 100-mL portions of diethyl ether. The extracts were evaporated to dryness to yield 9.1 g (41%) of **1**.

$\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{CH}_2\text{PPh}_2$ (2). (i) **Preparation of $\text{MsO}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{CH}_2\text{OMs}$.** A solution of 6.5 mL (84 mmol) of methanesulfonyl chloride in 100 mL of THF was added dropwise to a solution of 8.9 mL (42 mmol) of pentaethylene glycol and 11.7 mL (82.9 mmol) of triethylamine in 300 mL of THF at 5 °C over a 90-min period. This mixture was stirred overnight and then filtered. The filtrate was evaporated to dryness to give a viscous oil. This oil was taken up in 100 mL of a 6:1 mixture of dichloromethane and hexanes, and the solution was filtered through Celite. The filtrate was evaporated to dryness to yield 16.5 g (100%) of $\text{MsO}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{CH}_2\text{OMs}$ as a colorless oil.

(ii) **Preparation of $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{CH}_2\text{PPh}_2$ (2).** A solution of lithium diphenylphosphide was prepared as described above from 18.5 mL (83.7 mmol) of PPh_2H and 55 mL (88 mmol) of 1.6 M Bu^nLi in 400 mL of diethyl ether at -78 °C. A solution of 16.5 g (41.8 mmol) of $\text{MsO}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{CH}_2\text{OMs}$ in 250 mL of THF at -78 °C was then added dropwise to this solution over a 60-min period. The orange reaction mixture was stirred at room temperature overnight during which time it turned pale yellow and a white precipitate formed. The reaction mixture was then filtered, and the filtrate was evaporated to dryness to yield an off-white oil. The oil was treated with 200 mL of a 1:1 mixture

of dichloromethane and water. The organic layer was separated, dried over anhydrous Na_2SO_4 , and filtered. The filtrate was evaporated to dryness to yield 17.2 g (71.0 %) of **2** as a colorless oil.

$\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_2\text{CH}_2\text{PPh}_2$ (3). (i) **Preparation of $\text{MsO}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_2\text{CH}_2\text{OMs}$.** With use of the procedure for the preparation of $\text{MsO}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{CH}_2\text{OMs}$, 10.0 mL (39.9 mmol) of hexaethylene glycol, 11.1 mL (79.8 mmol) of triethylamine, and 6.18 mL (79.8 mmol) of methanesulfonyl chloride yielded 17.1 g (98.0%) of $\text{MsO}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_2\text{CH}_2\text{OMs}$.

(ii) **Preparation of $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_2\text{CH}_2\text{PPh}_2$ (3).** By use of the procedure for the preparation of **2**, 13.6 mL (78.3 mmol) of Ph_2PH , 52.0 mL of 1.6 M Bu^nLi , and 17.1 g of $\text{MsO}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_2\text{CH}_2\text{OMs}$ yielded 22.0 g (91.0%) of **3**.

***cis*- $\text{Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{PPh}_2]$ (4).** Solutions of 1.00 g (3.33 mmol) of $\text{Mo}(\text{CO})_4(\text{nb})$ in 500 mL of dichloromethane and 1.77 g (3.33 mmol) of **1** in 500 mL of dichloromethane were added dropwise to 1000 mL of dichloromethane over a period of 5 h. The mixture was stirred for an additional 18 h and then was evaporated to dryness to give a light brown, oily residue. The residue was taken up in 50 mL of a 1:1 dichloromethane–hexanes mixture, and this solution was treated with 10 g of silica gel before being filtered. The silica gel was washed with two 50-mL portions of a 1:1 dichloromethane–hexanes mixture, and then the filtrate was evaporated to dryness to yield 1.60 g (65.0%) of crude **4** as an off-white powder. Recrystallization from dichloromethane–hexanes gave analytically pure **4**·0.5H₂O as colorless crystals.

***cis*- $\text{Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{CH}_2\text{PPh}_2]$ (5).** With use of the procedure for the preparation of crude **4**, 1.00 g (3.33 mmol) of $\text{Mo}(\text{CO})_4(\text{nb})$ and 1.91 g (3.33 mmol) of **2** yielded 1.70 g (65.0%) of analytically pure **5** as an off-white solid after trituration of the residue with hexanes.

***cis*- $\text{Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_2\text{CH}_2\text{PPh}_2]$ (6).** By use of the procedure for the preparation of crude **4**, 0.500 g (1.67 mmol) of $\text{Mo}(\text{CO})_4(\text{nb})$ and 1.03 g (1.67 mmol) of **3** yielded 0.23 g (17%) of analytically pure **6** as a colorless oil.

Titrations of the *cis*- $\text{Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{PPh}_2]$ Complexes. (i) ***cis*- $\text{Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{CH}_2\text{PPh}_2]$ (5) with LiBF_4 .** Aliquots of solid LiBF_4 were added to a solution of 0.15 g (0.19 mmol) of **1** in 3 mL of acetonitrile-*d*₃. Following each addition of LiBF_4 , ^{31}P and ^{13}C NMR spectra were recorded (the ^{31}P NMR data are given in Table V). Then, the NMR solution was evaporated to dryness, and the residue was washed with three 10-mL portions of dichloromethane. The washes were evaporated to dryness, and the residue was trituated with hexanes to give 0.12 g (71%) of *cis*- $\text{Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{CH}_2\text{PPh}_2]\cdot\text{LiBF}_4\cdot 0.5\text{H}_2\text{O}$ (7·0.5H₂O) as an off-white powder.

(ii) ***cis*- $\text{Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_2\text{CH}_2\text{PPh}_2]$ (5) with NaBPh_4 .** With use of the above procedure, 0.080 g (0.10 mmol) of **1** and NaBPh_4 gave 0.050 g (42%) of *cis*- $\text{Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_2\text{CH}_2\text{PPh}_2]\cdot 0.5\text{NaBPh}_4$ (8) as an off-white powder.

(iii) ***cis*- $\text{Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{PPh}_2]$ (6) with LiBF_4 .** By use of the above procedure, 0.15 g (0.18 mmol) of **2** and LiBF_4 gave 0.10 g (59%) of *cis*- $\text{Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{PPh}_2]\cdot\text{LiBF}_4\cdot \text{H}_2\text{O}$ (9·H₂O) as an off-white powder.

(iv) ***cis*- $\text{Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_2\text{CH}_2\text{PPh}_2]$ (6) with NaBPh_4 .** The previous procedure was repeated by using 0.26 g (0.32 mmol) of **1** and NaBPh_4 to yield 0.10 g (27%) of *cis*- $\text{Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_2\text{CH}_2\text{PPh}_2]\cdot\text{NaBPh}_4$ (10) as a pale yellow powder that precipitated from a chloroform-*d* solution.

Reactions of *cis*- $\text{Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{PPh}_2]$ with RLi. A solution of 0.13 mmol of *cis*- $\text{Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{PPh}_2]$ (**4**, $n = 3$; **5**, $n = 4$; **6**, $n = 6$) in 20 mL of dry benzene was stirred under N_2 at ambient temperature as a solution containing 0.52 mmol of RLi ($\text{R} = \text{Ph}, \text{Me}$) was added. The solution gradually became dark brown and cloudy. After 18 h, the mixture was evaporated to dryness. The residue was treated with dichloromethane,

Table VI. Experimental Data for Crystallographic Studies of *cis*-Mo(CO)₄[Ph₂P(CH₂CH₂O)₃CH₂CH₂PPh₂] (4)

formula	C ₃₆ H ₃₆ MoO ₇ P ₂
MW	738.57
space group	<i>P</i> ₂ ₁ / <i>n</i>
<i>a</i> , Å	22.2190
<i>b</i> , Å	14.8174
<i>c</i> , Å	10.6798
β, deg	98.5247
<i>V</i> , Å ³	3477.2
<i>Z</i>	4
<i>d</i> _{calc} , g/cm ³	1.495
cryst dimens, mm	0.10 × 0.41 × 0.40
abs coeff, cm ⁻¹	44.016
extinction coeff	1.6307 × 10 ⁻⁷
θ limits, deg	0.10–70.00
no. of reflns measd	6748
scan width, deg	1.14
no. of reflns with <i>I</i> ≥ 3σ(<i>I</i>)	5695
no. of variables	416
<i>R</i> , %	3.53
<i>R</i> _w , %	5.27
GOF	1.314

Table VII. Fractional Coordinates for *cis*-Mo(CO)₄[Ph₂P(CH₂CH₂O)₃CH₂CH₂PPh₂] (4)

atom	<i>x</i>	<i>y</i>	<i>z</i>
Mo	0.38880 (1)	0.26484 (1)	0.14346 (2)
P1	0.35345 (3)	0.16526 (5)	-0.04740 (6)
P2	0.34672 (3)	0.40960 (5)	0.03220 (7)
O1	0.4535 (1)	0.3633 (2)	0.3844 (3)
O2	0.4433 (1)	0.0952 (2)	0.2924 (3)
O3	0.2706 (1)	0.2435 (2)	0.2718 (3)
O4	0.5185 (1)	0.2870 (2)	0.0590 (3)
O5	0.1815 (1)	0.2305 (2)	-0.1855 (3)
O6	0.1157 (1)	0.3627 (2)	-0.0614 (3)
O7	0.1809 (1)	0.5248 (2)	-0.0891 (2)
C1	0.4276 (2)	0.3316 (2)	0.2949 (3)
C2	0.4224 (1)	0.1560 (2)	0.2354 (3)
C3	0.3119 (2)	0.2512 (2)	0.2224 (3)
C4	0.4704 (2)	0.2798 (2)	0.0809 (3)
C5	0.2866 (1)	0.1949 (2)	-0.1637 (3)
C6	0.2280 (1)	0.1834 (2)	-0.1096 (3)
C7	0.1229 (2)	0.2161 (3)	-0.1493 (5)
C8	0.0881 (2)	0.3037 (3)	-0.1542 (4)
C9	0.0896 (2)	0.4504 (3)	-0.0666 (4)
C10	0.1374 (2)	0.5149 (3)	-0.0073 (4)
C11	0.2422 (2)	0.5208 (2)	-0.0289 (3)
C12	0.2634 (1)	0.4228 (2)	-0.0010 (3)
C13	0.3350 (1)	0.0481 (2)	-0.0139 (3)
C14	0.3358 (2)	-0.0191 (2)	-0.1060 (3)
C15	0.3198 (2)	-0.1072 (2)	-0.0814 (4)
C16	0.3022 (2)	-0.1296 (2)	0.0328 (3)
C17	0.3001 (2)	-0.0646 (2)	0.1222 (3)
C18	0.3161 (2)	0.0245 (2)	0.0993 (3)
C19	0.4137 (1)	0.1533 (2)	-0.1450 (3)
C20	0.4132 (2)	0.2005 (3)	-0.2566 (3)
C21	0.4630 (2)	0.1952 (3)	-0.3225 (4)
C22	0.5118 (2)	0.1428 (3)	-0.2763 (4)
C23	0.5138 (2)	0.0967 (3)	-0.1651 (4)
C24	0.4645 (2)	0.1019 (2)	-0.0986 (3)
C25	0.3648 (1)	0.5123 (2)	0.1257 (3)
C26	0.3863 (1)	0.5915 (2)	0.0787 (3)
C27	0.3943 (2)	0.6676 (2)	0.1540 (4)
C28	0.3805 (2)	0.6662 (2)	0.2754 (4)
C29	0.3591 (2)	0.5884 (3)	0.3227 (3)
C30	0.3515 (2)	0.5114 (2)	0.2485 (3)
C31	0.3718 (1)	0.4339 (2)	-0.1206 (3)
C32	0.4342 (1)	0.4460 (2)	-0.1219 (3)
C33	0.4556 (2)	0.4606 (3)	-0.2349 (3)
C34	0.4163 (2)	0.4602 (3)	-0.3480 (3)
C35	0.3550 (2)	0.4476 (3)	-0.3476 (3)
C36	0.3328 (2)	0.4352 (2)	-0.2337 (3)

and the mixture was filtered through Celite. The filtrate was evaporated to dryness to give *cis*-Mo(CO)₄[Ph₂PCH=CH₂]₂ (11) as a colorless oil.

Collection and Reduction of the X-ray Data. A hot, saturated dichloromethane–hexanes solution of 4 was slowly cooled to -10 °C to yield

Table VIII. Bond Distances (Å) and Angles (deg) for *cis*-Mo(CO)₄[Ph₂P(CH₂CH₂O)₃CH₂CH₂PPh₂] (4)

Bond Distances			
Mo–P1	2.5444 (7)	O2–C2	1.147 (4)
Mo–P2	2.5608 (7)	O3–C3	1.129 (5)
Mo–C1	1.981 (3)	O4–C4	1.132 (4)
Mo–C2	1.976 (3)	O5–C6	1.400 (4)
Mo–C3	2.024 (4)	O5–C7	1.427 (5)
Mo–C4	2.036 (3)	O6–C8	1.394 (5)
P1–C5	1.842 (3)	O6–C9	1.421 (6)
P1–C13	1.831 (3)	O7–C10	1.403 (5)
P1–C19	1.823 (3)	O7–C11	1.420 (4)
P2–C12	1.843 (3)	C5–C6	1.511 (5)
P2–C25	1.832 (3)	C7–C8	1.508 (7)
P2–C31	1.837 (3)	C9–C10	1.497 (6)
O1–C1	1.141 (4)	C11–C12	1.542 (5)
Bond Angles			
P1–Mo–P2	93.78 (2)	Mo–P2–C25	114.06 (9)
P1–Mo–C1	171.5 (1)	Mo–P2–C31	115.99 (9)
P1–Mo–C2	88.51 (9)	C6–O5–C7	113.1 (3)
P1–Mo–C3	95.5 (1)	C8–O6–C9	114.4 (3)
P1–Mo–C4	89.13 (9)	C10–O7–C11	114.7 (3)
P2–Mo–C1	92.6 (1)	P1–C5–C6	111.7 (2)
P2–Mo–C2	177.71 (9)	O5–C6–C5	109.0 (3)
P2–Mo–C3	90.23 (9)	O5–C7–C8	110.3 (4)
P2–Mo–C4	92.18 (9)	O6–C8–C7	110.2 (3)
Mo–P1–C5	121.6 (1)	O6–C9–C10	107.9 (3)
Mo–P1–C13	116.40 (9)	O7–C10–C9	108.3 (3)
Mo–P1–C19	110.40 (9)	O7–C11–C12	111.8 (3)
Mo–P2–C12	117.7 (1)	P2–C12–C11	113.9 (2)
Torsion Angles			
C1–Mo–P1–C5	-166.6 (6)	C2–Mo–P2–C12	-25.8 (2)
Mo–P1–C5–C6	-71.4 (2)	Mo–P2–C12–C11	39.0 (3)
P1–C5–C6–O5	-67.0 (5)	P2–C12–C11–O7	-162.8 (2)
C5–C6–O5–C7	-174.0 (3)	C12–C11–O7–C10	-79.4 (4)
C6–O5–C7–C8	138.2 (4)	C11–O7–C10–C9	-134.7 (3)
O5–C7–C8–O6	-67.0 (5)	O7–C10–C9–O6	-71.2 (4)

crystals of the complex. A suitable crystal was mounted on a glass fiber with epoxy cement. Standard peak search and automatic indexing routines followed by least squares fits of 25 accurately centered reflections ($2\theta > 25^\circ$) gave the cell constants. An Enraf-Nonius CAD-4 diffractometer with Ni-filtered Cu K α ($\lambda = 1.5418$ Å) radiation was used for data collection. Three reflections were remeasured periodically to monitor for decay, and linear decay corrections were applied. The data were processed by using the Enraf-Nonius SDP series of programs. Variances were assigned to the *I*s on the basis of counting statistics with the addition of an instrumental uncertainty term. Lorentz, polarization, and analytical absorption corrections were made to *I*s and σ^2 s.

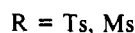
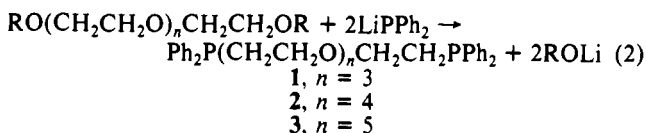
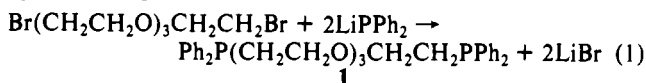
Solution and Refinement of the Structure. The cell parameters and systematic absences indicated that the space group was *P*₂₁/*n*. The positions of the Mo and P atoms were obtained from the Patterson functions, and the remainder of the non-H atoms were located by Fourier methods. The structure was refined by a full-matrix least-squares procedure that minimized $w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma(F_o))^2$. All non-H atoms were refined anisotropically, and H atoms were included in calculated positions with isotropic thermal parameters based upon those of the atoms to which they were attached and were not refined. The use of data with $I > 3\sigma(I)$ and with $0.1 < \theta < 70.0$ in the refinement gave an observation to parameter ratio of 13.7 to 1. The refinement was carried out to minimize $R(\sum(|F_o| - |F_c|)/\sum|F_o|)$ and $R_w((\sum(w(|F_o| - |F_c|)^2)/\sum w(F_o)^2)^{0.5})$ and to give the best goodness of fit $((\sum w(|F_o| - |F_c|)^2)/(\text{NO} - \text{NV}))^{0.5}$. A secondary extinction correction of the Zachariassen type⁴⁶ was made to the data, and the extinction coefficient was refined. In the last stage of refinement no parameter varied by more than 0.03 of its standard deviation. The final difference Fourier maps had no interpretable peaks (maximum 0.541 e/Å³ near the Mo). Neutral-atom scattering factors were taken from the compilations of Cromer and Weber,⁴⁷ and those for H atoms were taken from ref 48. Corrections for the real and imaginary components of anomalous dispersion were taken from the compilations of Cromer and Liberman⁴⁹ and were applied to the Mo and P atoms. Details of the data collection and

(46) Zachariassen, W. H. *Acta Crystallogr.* **1963**, *16*, 1139.(47) Cromer, D. T.; Weber, D. T. *Acta Crystallogr.* **1965**, *18*, 104.(48) *International Tables for X-ray Crystallography*, Vol. IV; Kynoch Press: Birmingham, U.K., 1974; p 72.(49) Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891.

structure solution procedures are summarized in Table VI. The values for the positional parameters are given in Table VII, and bond lengths and angles are given in Table VIII.

Results and Discussion

Syntheses of the Ligands. The α,ω -bis(phosphine)-polyether ligands have been prepared by the reaction of lithium diphenylphosphide with either the dibromo, ditosyl, or dimesyl derivatives of the corresponding glycol (eqs 1 and 2). The dimesyl derivative is the preferred starting material for these ligands because, in contrast to the dibromo and ditosyl derivatives, it reacts completely with lithium diphenylphosphide to give the ligands in high yields and no further purification of the ligand is required. The only limitation of this route is that the dimesylate must be used immediately after preparation because it slowly decomposes upon standing.



Ligands 1–3 have been characterized by ^{31}P and ^{13}C NMR spectroscopy (Tables I and II). The ^{31}P NMR resonances of the three ligands are singlets with nearly identical chemical shifts. The chemical shifts of the ^{31}P NMR resonances of these ligands are similar to those reported for other ligands of this type.^{31,35} The ^{13}C NMR resonances of the ipso, ortho, and meta carbons are doublets but those of the para carbons are singlets. The $[\text{J}(\text{PC})]$ s are similar in the three ligands and are consistent with those previously reported for similar ligands.³⁵ The assignment of the ^{13}C NMR resonances to the various methylene carbons in these ligands is more difficult. The resonances of the carbons one and two bonds from the phosphorus (C_1 and C_2 , respectively) are readily assigned because they are upfield of the resonances of the other aliphatic C's (that of C_1 is at approximately 29.75 ppm and that of C_2 is at approximately 68.55 ppm) and are doublets. The resonances for the carbons four, five, seven, and eight bonds from the phosphorus (C_3 , C_4 , C_5 and C_6 , respectively) are all found between 70.06 and 70.60 ppm and are overlapped. The assignment of the resonances due to these carbons is made by comparing the relative intensities and positions of the resonances in the 70–71 ppm region of the ^{13}C NMR spectra of the three ligands.

Syntheses and Characterizations of the $\text{Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{PPh}_2]$ Complexes. The $\text{cis-Mo}(\text{CO})_4\text{-}[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{PPh}_2]$ ($4, n = 3; 5, n = 4; 6, n = 5$) complexes have been synthesized in relatively good yields by the reactions of $\text{cis-Mo}(\text{CO})_4(\text{nbd})$ and the ligands (eq 3) under relatively high-dilution conditions. Complexes 4 and 5 are obtained as powders, whereas the complex 6 remains a hard oil even after repeated attempts at trituration with hexanes. These complexes are initially colorless but become colored when stored in the air in the solid state even for a few days. This is unusual as most $\text{cis-Mo}(\text{CO})_4(\text{phosphine})_2$ complexes are relatively air stable. This suggests that the presence of the metallacrown ether ring may aid in the photochemical displacement of one of the carbonyls. Oxidation can then occur through the open coordination site. Storing these complexes in the dark under nitrogen eliminates this problem.

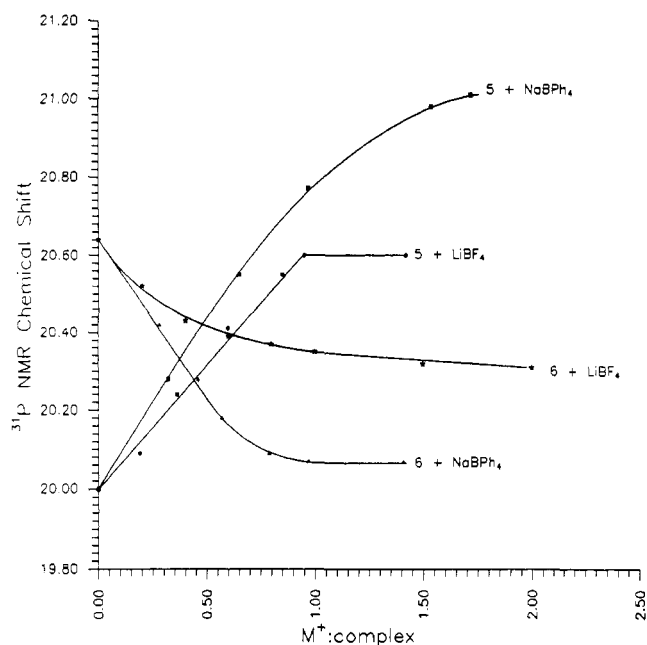
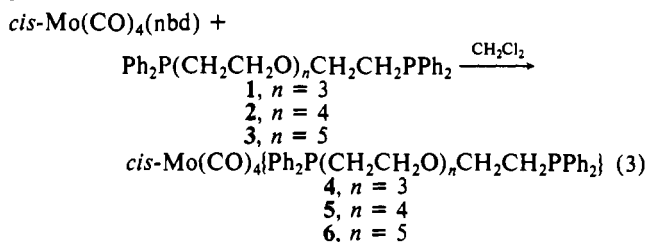


Figure 1. Plots of the ^{31}P NMR chemical shifts vs the MX:metallacrown ether ratios for the titrations of the metallacrown ethers $\text{cis-Mo}(\text{CO})_4\text{-}[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{PPh}_2]$ ($5, n = 4; 6, n = 5$), with the alkali-metal salts MX ($\text{MX} = \text{LiBF}_4, \text{NaBPh}_4$).

The ^{31}P NMR spectrum of each of these complexes contains a single resonance approximately 40 ppm downfield from that of the free ligand. This indicates that a single isomer and a single conformer of the each complex is formed (Table I). The CO regions of the IR spectra of the three complexes have bands at approximately 2022 (m) (A_1^1), 1920 (vs) (A_1^2), 1906 (vs) (B_1), and 1885 (sh) (B_2) cm^{-1} showing cis chelation of the phosphines (Table III).⁵⁰ The cis chelation is confirmed by the presence of two equal-intensity resonances below 200 ppm in the ^{13}C NMR spectra of the three complexes.

The aromatic and aliphatic ^{13}C resonances of the complexes are significantly shifted from those of the free ligands. The C_{ipso} resonances are shifted nearly 2 ppm upfield from those of the free ligands while the other phenyl C's exhibit smaller shifts. The C_{ipso} , C_o , and C_m resonances appear either as apparent quintets or as broad peaks as expected for cis phosphine complexes.⁵¹ The ^{13}C NMR resonances for the C_1 methylenes are also apparent quintets and are shifted 2–3 ppm downfield from those of the free ligands. The C_2 resonances are broad singlets, and these are shifted about 1.5 ppm upfield from those of the free ligands. The assignments for other aliphatic C's have been made on the basis of relative intensities and positions of the resonances observed for their respective free ligands.

Titration of 5 and 6 with LiBF_4 and NaBPh_4 . Titrations of the $\text{cis-Mo}(\text{CO})_4[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{PPh}_2]$ ($5, n = 4; 6, n = 5$) complexes with both LiBF_4 and NaBPh_4 in acetonitrile- d_3 have been carried out and were followed by both ^{31}P and ^{13}C NMR spectroscopy. The ^{31}P NMR data for the titrations are summarized in Table V, and a plot of this data is given in Figure 1. The ^{13}C NMR data for one of the titrations are given in supplementary Table I. No NMR data for salt:complex ratios greater than 2.0:1 are reported because the increasing ionic strengths of the solutions cause significant shifts in the positions of both the ^{31}P and ^{13}C NMR resonances, and these cannot be readily separated from the coordination chemical shifts.

The shapes of the titration curves derived from the ^{31}P NMR data (Figure 1) indicate that 5 binds strongly to Li^+ and much more weakly to Na^+ but that 6 binds Na^+ somewhat more strongly than it does Li^+ . This behavior is consistent with the fact that the cavity in 5 is significantly smaller than that in 6. This behavior

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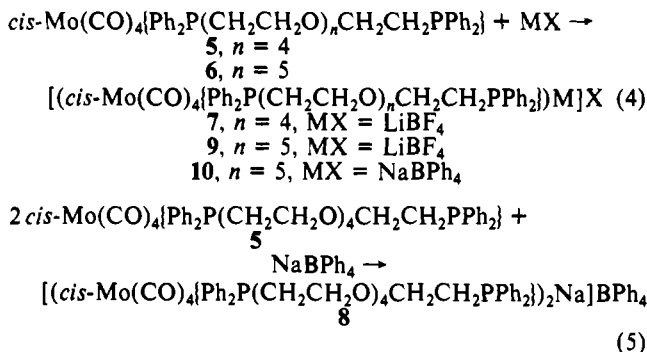
(51) Redfield, D. A.; Nelson, J. H.; Cary, L. W. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 727.

is different from that reported by Powell et. al. for the *cis*-Mo(CO)₄[Ph₂P(O)(CH₂CH₂O)_nPPh₂] (*n* = 2–5) complexes.³⁹ In this series, the *n* = 2 and 3 (three and four ether oxygen) complexes do not bind alkali-metal cations, the *n* = 4 (five ether oxygen) complex only binds Li⁺ and the *n* = 5 (six ether oxygen) complex binds Li⁺ weakly and Na⁺ strongly. Thus, the selectivity of the *n* = 4 complex is similar to that of **5** (four ether oxygens), and the selectivity of the *n* = 6 complex is similar to that of **6** (five ether oxygens). The similarities appear to be due to the similar sizes of the metallacrown ether rings in the complexes (16 atoms for the *n* = 4 complex and 17 atoms for **5**; 19 atoms for the *n* = 5 complex and 20 atoms for **6**). Thus, cavity size and not the number of ether oxygens in the metallacrown ether ring seems to be primarily responsible for determining the stability of alkali-metal cation binding by these complexes.

An even more interesting feature of the alkali-metal cation binding by complexes **5** and **6** is that the direction of the shift in the ³¹P NMR resonance upon cation binding depends upon the ring size, but the magnitude of the shift depends upon the cation. The shifts in the ³¹P NMR resonances of **5** and **6** are approximately twice as large with Na⁺ as with Li⁺, and the shifts are in the opposite directions for **5** and **6**. This type of behavior has not been reported for metallacrown ethers but must be due to different conformational changes that occur when the metal ions are bound to the metallacrown ethers.

The ¹³C NMR data for these titrations are less helpful because of the difficulties in assigning the resonances due to the various methylene carbons. Only the ¹³C NMR resonances of C₁ and C₂ can be accurately assigned. However, these are the resonances that are least affected by the coordination of the alkali-metal cations, and these resonances are also broadened by coupling to the phosphorus. Thus, it is difficult to determine the coordination chemical shifts of the methylene carbons, although the general trends appear to be the same as in the ³¹P NMR data.

Bimetallic complexes can be isolated from the titration solutions. This is done by evaporating the solutions to dryness, and then treating the residues with dichloromethane. Filtration of these mixtures removes the excess free alkali-metal salts, and analytically pure bimetallic complexes are obtained when the filtrates are evaporated to dryness. As shown in eqs 4 and 5, 1:1 complexes between **5** and LiBF₄ and between **6** and both LiBF₄ and NaBPh₄ are formed, but a 2:1 complex is formed between **5** and NaBPh₄. The fact that a 2:1 complex is isolated from the reaction of **5** and NaBPh₄ is consistent with the ³¹P NMR spectroscopic data, which suggest that **5** binds very weakly to Na⁺. Apparently two molecules of the smaller metallacrown ether are needed to form a stable complex with Na⁺, but only one molecule of the larger metallacrown ether is needed to form a stable complex with Na⁺.



Reactions of the Mo Carbonyl Complexes with RLi. Powell and co-workers have previously demonstrated that *cis*-Mo(CO)₄[R₂P(O)(CH₂CH₂O)_nPR₂] (R = Ph, alkoxy) complexes react with methyl lithium and phenyllithium to form bimetallic acyl complexes in which a Li⁺ is coordinated to both the metallacrown ether oxygens and the acyl oxygen.^{32–34,39–41} The reactions of **4–6** with methyl lithium and phenyllithium are quite different. The only product that is observed for the reaction of either methyl lithium or phenyllithium with either **4–6** in either THF or benzene is *cis*-Mo(CO)₄(Ph₂PCH=CH₂)₂ (**11**) regardless of the ratio of

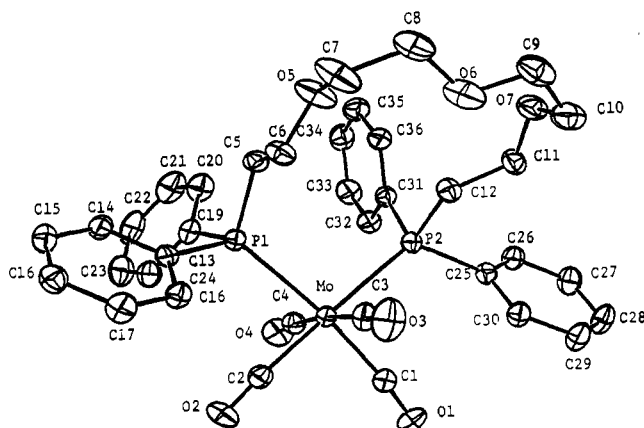
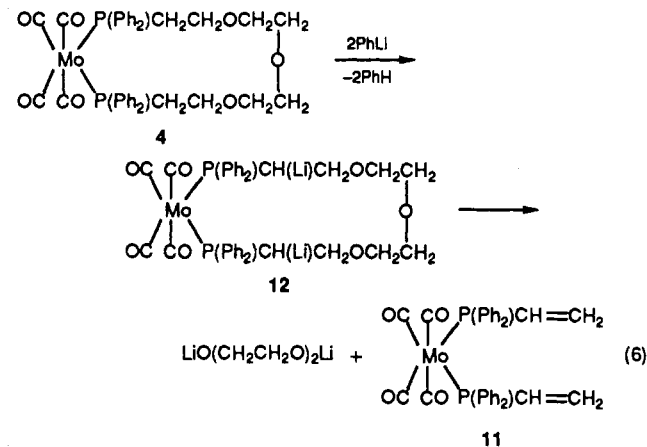


Figure 2. ORTEP⁵⁴ drawing of the molecular structure of *cis*-Mo(CO)₄[Ph₂P(CH₂CH₂O)₃CH₂CH₂PPh₂] (**4**). The H atoms are omitted for clarity, and the thermal ellipsoids are drawn at the 25% probability level.

metallacrown ether to the organolithium compound in the solution.^{52,53} This is also the only product that is observed for the reaction of *cis*-Mo(CO)₄(PPh₂CH₂CH₂OCH₂CH₂OMe)₂ and phenyllithium in benzene. This indicates that the metallacrown ether ring is not necessary for the ligand cleavage to occur.

A proposed mechanism for the formation of **11** for **4** is shown in eq 6. The first step is the removal of a proton from both C₁ methylenes by phenyl carbanions to form the dilithiated complex **12**. This step is analogous to the formation of a Wittig reagent from a phosphonium salt. This complex then rearranges to **11** via the cleavage of the C₂–O bonds, and the insoluble lithium alkoxide precipitates from the reaction solution.



X-ray Crystal Structure of 4. The molecular structure of **4** has been determined and is shown in Figure 2. This structure is of interest because nearly all of the metallacrown ether complexes of α,ω -bis(phosphine)-polyether ligands that have been reported contain three or fewer ether oxygens. Organic crown ethers with three or fewer ether oxygens do not contain sufficiently large cavities to strongly bind to metal cations, and it is important to determine if incorporation of a metal complex into a three-oxygen crown ether ring will increase the cavity size sufficiently to allow strong cation binding to occur.

In **4**, the three ether oxygens form the vertices of an isosceles triangle with an O5–O6 distance of 2.883 Å, an O6–O7 distance of 2.842 Å, and an O5–O7 distance of 4.480 Å. The calculations of the size of the cavity created by the three oxygens suggest that if, in a hypothetical situation, a Li⁺ was coordinated equidistant (2.59 Å) from all the three oxygens and in the plane of the three oxygens, it would be displaced 0.81 Å outside the O5–O7 edge

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of the triangle towards the molybdenum. This would be a sterically unfavorable position, and thus this complex would not be expected to coordinate strongly even to small cations such as Li^+ in a 1:1 complex.

A second interesting feature in the molecular structure of **4** is the conformation of the metallacrown ether ring. The plane containing the three ether oxygens is nearly perpendicular to the plane containing P1, P2, Mo, C1 and C2 (dihedral angle $95.1(1)^\circ$). The chelate ring is distorted from the symmetric conformation observed in solution, as shown by the very different torsion angles for the two halves of the ring. This distortion appears to be primarily due to the different rotations of the diphenylphosphino groups about the molybdenum-phosphorus bonds.

The X-ray structure of **4** also confirms the coordination geometry about molybdenum inferred from the spectroscopic data. The coordination geometry at molybdenum is a slightly distorted octahedron composed of four carbonyls and two phosphine donor groups in a cis geometry. The P1-Mo-P2 angle ($93.78(2)^\circ$) is significantly distorted from the ideal 90° angle as is generally observed in *cis*-Mo(CO)₄(phosphine)₂ complexes.

Summary. Ligands of the type $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{PPh}_2$ ($n = 3-5$) can be synthesized in high yields from the reaction of LiPPh_2 with the appropriate bis(mesylate), $\text{MsO}(\text{CH}_2\text{CH}_2\text{O})_{n+1}\text{Ms}$. The ligands react with *cis*-Mo(CO)₄(*nbd*) in dilute solution to form mononuclear *cis*-Mo(CO)₄{ $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{PPh}_2$ } ($n = 3-5$) complexes in good yields. These complexes are quite different from the *cis*-Mo(CO)₄{ $\text{Ph}_2\text{PO}(\text{CH}_2\text{CH}_2\text{O})_n\text{PPh}_2$ } ($n = 1-4$) complexes reported by Powell and co-workers. The alkali-metal cation selectivities of the two types of complexes differ significantly for complexes with equal numbers of ether oxygens but are similar for complexes with

similar numbers of atoms in the metallacrown ether rings. This suggests that the alkali-metal cation selectivities exhibited by metallacrown ether complexes are primarily due to the ring size and not to the number of oxygens in the ring. The reactions of organolithium compounds with the two types of complexes are also quite different. Organolithium compounds react with the *cis*-Mo(CO)₄{ $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{PPh}_2$ } complexes to yield *cis*-Mo(CO)₄{ $\text{Ph}_2\text{PCH}=\text{CH}_2$ }₂ via an unusual C—O bond cleavage, but react with the *cis*-Mo(CO)₄{ $\text{Ph}_2\text{PO}(\text{CH}_2\text{CH}_2\text{O})_n\text{PPh}_2$ } complexes to yield acyl complexes.

The results from this and earlier studies indicate that metallacrown ethers formed from bis(P donor)-polyether ligands with sufficient numbers of oxygens and sufficiently large cavities are capable of solubilizing salts of alkali-metal cations in organic solvents, and thus these complexes may be useful as phase-transfer catalysts. The ease with which the metallacrown ethers form hard/soft bimetallic complexes suggested that related complexes may also be useful for the activation of small, bifunctional molecules. The type of bis(P donor)-polyether ligand used in these complexes will have significant effects upon the reactivities of the complexes and thus upon their usefulness in these various processes.

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Supplementary Material Available: Tables of the ¹³C data for the titration of **6** with NaBPh₄ (Table 1), the thermal parameters for **4** (Table 2), the calculated H positions for **4** (Table 3), other bond distances and angles in **4** (Table 4), and the least-squares planes for **4** (Table 5) (5 pages); a table of observed and calculated structure factors for **4** (29 pages). Ordering information is given on any current masthead page.

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Poly(pyrazolyl)borate Complexes of Tin(II). Crystal and Molecular Structures of $[\text{H}_2\text{B}(\text{pz})_2]\text{SnCl}$ and $[\text{B}(\text{pz})_4]_2\text{Sn}$ (pz = Pyrazolyl Ring)

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The complexes $[\text{H}_n\text{B}(\text{pz})_{4-n}]\text{SnCl}_{2-m}$ ($n = 0-2$; $m = 1, 2$; pz = pyrazolyl ring) have been prepared by the reaction of SnCl_2 and the ligand salts in the appropriate stoichiometries. The complexes are air stable in the solid phase with solution stability increasing with the number of poly(pyrazolyl)borate ligands and the number of pyrazolyl rings present in the ligand. The structure of $[\text{H}_2\text{B}(\text{pz})_2]\text{SnCl}$ (**1**) has been determined by X-ray crystallography: monoclinic, $P2_1/n$, $a = 4.894(5) \text{ \AA}$, $b = 27.079(23) \text{ \AA}$, $c = 7.744(6) \text{ \AA}$, $\beta = 100.32(7)^\circ$, $V = 1009.8(16) \text{ \AA}^3$, $Z = 4$, $R(F) = 5.67\%$. The basic geometry about the three-coordinate tin is trigonal pyramidal. The donor atom angles through the tin atom average 86° , and the lone pair on tin presumably occupies the fourth vertex. There are also weak tin-chlorine bridging interactions forming centrosymmetric dimeric units. In both the solution and solid phases, $[\text{H}_2\text{B}(\text{pz})_2]_2\text{Sn}$ (**2**) has a trigonal-bipyramidal geometry with each ligand spanning an axial and equatorial site. The tin lone pair presumably occupies the remaining equatorial vertex. The molecule shows two types of dynamic processes in solution. The axial and equatorial positions equilibrate with a barrier of 10.2 kcal/mol at -58°C . Also, the barrier to the boat-boat flip of the SnN_4B rings formed by each ligand is determined to be 10.3 kcal/mol at -52°C . $[\text{HB}(\text{pz})_3]\text{SnCl}$ (**3**) and $[\text{B}(\text{pz})_4]\text{SnCl}$ (**5**) are believed to have a similar trigonal-bipyramidal geometry, and both are fluxional in solution. An X-ray crystallographic study of $[\text{B}(\text{pz})_4]_2\text{Sn}$ (**6**) shows it to be four-coordinate with a highly distorted trigonal-bipyramidal structure: monoclinic, $P2_1/n$, $a = 10.754(3) \text{ \AA}$, $b = 17.109(4) \text{ \AA}$, $c = 15.566(3) \text{ \AA}$, $\beta = 91.236(20)^\circ$, $V = 2863.6(12) \text{ \AA}^3$, $Z = 4$, $R(F) = 3.63\%$. Each ligand is bidentate with one of the noncoordinated pyrazolyl rings located fairly close to the tin. Correlations from the ¹¹⁹Sn NMR chemical shifts of these complexes indicate that **6** is also four-coordinate in solution. The ¹H NMR spectra show that **6** is dynamic in solution. All of the pyrazolyl rings are equivalent at ambient temperatures with a 3/1 pattern observed at -80°C . The low-temperature spectrum can be explained by a low-energy process that equilibrates the three pyrazolyl rings in each ligand close to tin, but the fourth ring remains unique. At higher temperatures, the fourth ring also equilibrates by a boat-boat flip of the six-membered ring (10.5 kcal/mol barrier). The ¹¹⁹Sn data indicate that $[\text{HB}(\text{pz})_3]_2\text{Sn}$ (**4**) may be five-coordinate in solution.

Introduction

We have recently initiated an investigation into the synthesis and characterization of poly(pyrazolyl)borate complexes of main-group metals. In our initial publications, we have described

the preparation and characterization of an extensive series of stable group-13 complexes of gallium^{1a,b} and indium^{1c} of the general formula $[\text{H}_2\text{B}(\text{pz})_2]_m\text{MCl}_n(\text{CH}_3)_p$ ($m + n + p = 3$; pz = pyrazolyl

[†] University of South Carolina.

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