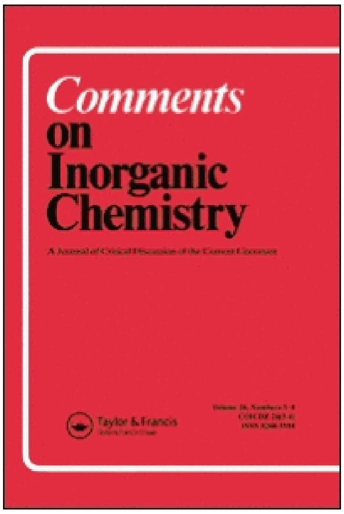

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Metallacrown Ethers: Unique Organometallic Ligands

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To cite this Article Gray, Gary M.(1995) 'Metallacrown Ethers: Unique Organometallic Ligands', Comments on Inorganic Chemistry, 17: 2, 95 — 114

To link to this Article: DOI: 10.1080/02603599508035784

URL: http://dx.doi.org/10.1080/02603599508035784

Metallacrown Ethers: Unique Organometallic Ligands

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Received September 19, 1994

Metallacrown ethers are a unique class of complexes that form when $R_2PX(CH_2CH_2O)_nCH_2CH_2XPR_2$ (X = –, O; R = Ph, alkoxy; n = 3–5) ligands chelate to transition metals. Metallacrown ethers with cis-coordinated phosphines (*cis*-metallacrown ethers) contain a crown ether-like pocket and exhibit size-selective binding of alkali metal cations similar to that observed with the crown ethers. Binding of Li^+ and Hg^{2+} to *cis*-$Mo(CO)_4\{R_2PX(CH_2CH_2O)_nCH_2CH_2XPPh_2\text{-}P,P'\}$ metallacrown ethers can, under certain circumstances, activate the carbonyl ligands cis to the phosphines to nucleophilic attack or dissociation. The *cis*-metallacrown ethers are also capable of binding water via coordination to the metal center and hydrogen bonding to the ethers. Recently, octahedral metallacrown ethers with trans-coordinated phosphines (*trans*-metallacrown ethers) have been prepared. The conformations of these complexes are quite different from those of the *cis*-metallacrown ethers with more extended metallacrown ether chains and the ether oxygens closer to the ligands on the octahedral metal center. The metal centers in the *trans*-metallacrown ethers appear to spin freely within the metallacrown ether cavity, indicating that the barriers to rotation about the P–M–P axes are low. Dimetallacrown ethers in which the $R_2PX(CH_2CH_2O)_nCH_2CH_2XPR_2$ ligands bridge two metal centers have also been isolated. These complexes contain two separate crown ether sites and may be able to coordinate two metal cations. The above results suggest that metallacrown ethers containing platinum-group metal centers could exhibit quite different catalytic activities and selectivities from those of related complexes with simple phosphorus-donor ligands.

Comments Inorg. Chem.
1995, Vol. 17, No. 2, pp. 95–114
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Printed in Malaysia

Key Words: *metallacrown ethers, Mo(O), Ru(II), Pt(II), bis(phosphine)-polyether ligands, multinuclear NMR, conformational studies, alkali metal cation coordination, size-selective reactions, carbonyl ligand activation, trans-spanning ligands, molecular gyroscopes, molecular clefts*

INTRODUCTION

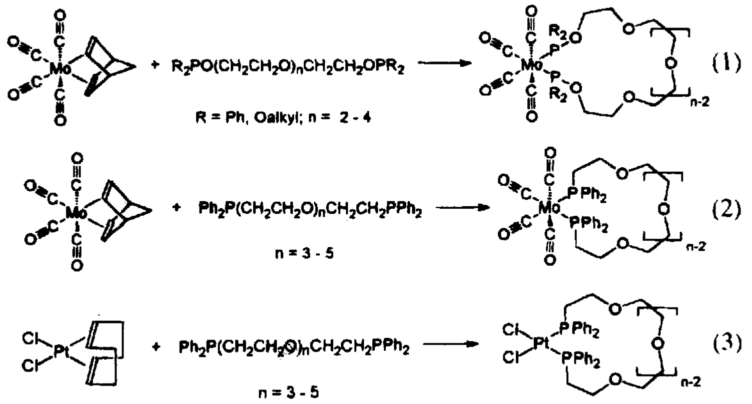
Enzymes are the most active and selective homogeneous catalysts known. Transition metal complex catalysts with enzyme-like activities and selectivities would be of enormous benefit to the chemical industry by allowing reactions to be run at lower temperatures and pressures, thereby reducing energy and equipment costs. They would also provide higher conversions of reactants into desired products, thereby resulting in lower costs for reactants, product purification and byproduct disposal. These advantages would make processes using such catalysts more environmentally benign than those using current industrial catalysts.

The primary reason for the high activities and selectivities of enzymes is that they contain a variety of functional groups arranged in optimal conformation to produce a low energy transition state and accept only a narrow range of substrates.[1] In contrast, nearly all transition metal complex catalysts contain a single metal center at which all the catalytic reactions take place.[2] A logical approach for developing transition metal complex catalysts with enzyme-like activities and selectivities is to introduce functional groups, which can interact with the reactants coordinated to the transition metal, into the coordination spheres of known transition metal complex catalysts.

Crown ethers are particularly interesting groups to introduce into the coordination environment of Pt-group metal-phosphine catalysts because of their ability to bind metal cations and small molecules.[3,4] Transition metal-phosphine complexes with crown ether functionality have been prepared using crown ether-substituted phosphine ligands,[5,6] phosphacrown ethers[7] and chelating α,ω-bis(phosphorus-donor)-polyether ligands.[8-14] The latter class of complexes, referred to as metallacrown ethers, exhibits the most interesting properties for catalytic applications and is the focus of this paper.

SYNTHESES AND CONFORMATIONS OF CIS-METALLACROWN ETHERS

The reactions of $R_2PX(CH_2CH_2O)_nCH_2CH_2XPR_2$ (X = –, O; R = Ph, alkoxy; n = 3–5) ligands with either *cis*-$Mo(CO)_4(nbd)$ (nbd = norbornadiene)[8,10] or $PtCl_2(cod)$ (cod = 1,4-cyclooctadiene)[11] under moderately high dilution conditions yield metallacrown ethers with cis-coordinated phosphorus-donor groups (Eqs. (1)–(3)). One of the most surprising aspects of this chemistry is the fact that these reactions almost exclusively yield monomeric complexes even though there are as many as 20 atoms in the metallacrown ether rings. This suggests that the ether oxygens may play a role in the formation of the chelate rings. One mechanism that could result in chelation rather than oligomerization would involve reaction of the ligand and metal precursor to form an intermediate in which the ligand is chelated via one phosphorus-donor group and the adjacent ether oxygen. The metal could then "walk" along the ligand via decomplexation/complexation of the weakly bonding ethers until it reached the second phosphorus-donor group and formed a stable monomeric product.



Few complexes with large chelate rings like those described above have been prepared. Thus little is known about the solid state and solution conformations of these large chelate rings. We have determined the X-ray crystal structures of three of these complexes, *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2\text{-}P,P'\}$, **1**,[10] and *cis*-$PtCl_2\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}$ (n = 4, **2** and 5, **3**),[11] and these are shown in Fig. 1. In all of the complexes, the metallacrown ether rings have quite asymmetric conformations due to different rotations about the metal–phosphorus bonds. These rotations are in the same directions in all three complexes but are larger in the square planar platinum complexes.

In the solid state, the metallacrown ether rings in all of the complexes are relatively planar. This means that the approximate metallacrown ether cavity size can be determined by measuring the distances between nonadjacent ether oxygens (**1**, 4.480 Å; **2**, 4.66 Å; **3**, 5.32 Å). These distances suggest that the cavity in **1** is too small to bind even Li^+ while that in **2** is large enough to bind Li^+ but not Na^+ and that in **3** is large enough to bind both Li^+ and Na^+. These conclusions are consistent with the results from the alkali metal cation binding studies that are discussed below.

The solution conformations of the metallacrown ethers are quite different from the solid state conformations. As expected, the metallacrown ether rings are conformationally mobile and exhibit symmetric average conformations. For the *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$-P,P′} (n = 3–5) complexes, this mobility decreases with increasing ring size. This trend is seen in ^1H NMR spectra. The spectra of the n = 3 and 4 complexes are sharp and detailed at 21°C but that of the n = 5 complex is broad and featureless.[16] The ^1H NMR spectrum of the n = 5 complex sharpens as the temperature is raised and reaches its high temperature exchange limit at 55°C.

The ^{31}P and ^{13}C NMR coordination chemical shifts ($\delta_{complex}-\delta_{ligand}$) for the *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$-P,P′} and *cis*-$PtCl_4\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$-P,P′} metallacrown ethers, shown in Table I suggest that the average solution conformations for the metallacrown ether rings in octahedral molybdenum complexes are quite different from those in the square planar platinum complexes. As the ring size increases, the coordination chemical shifts of the *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$-P,P′} metallacrown ethers approach those of *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_2Me\}_2$.[17] This suggests that, as n increases, ring induced conformational changes decrease and the average conformations of methylene carbons in the metallcrown ether approach those of similar methylene carbons in the monodentate ligand. Similar behavior is not observed with the *cis*-$PtCl_2\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$-P,P′}

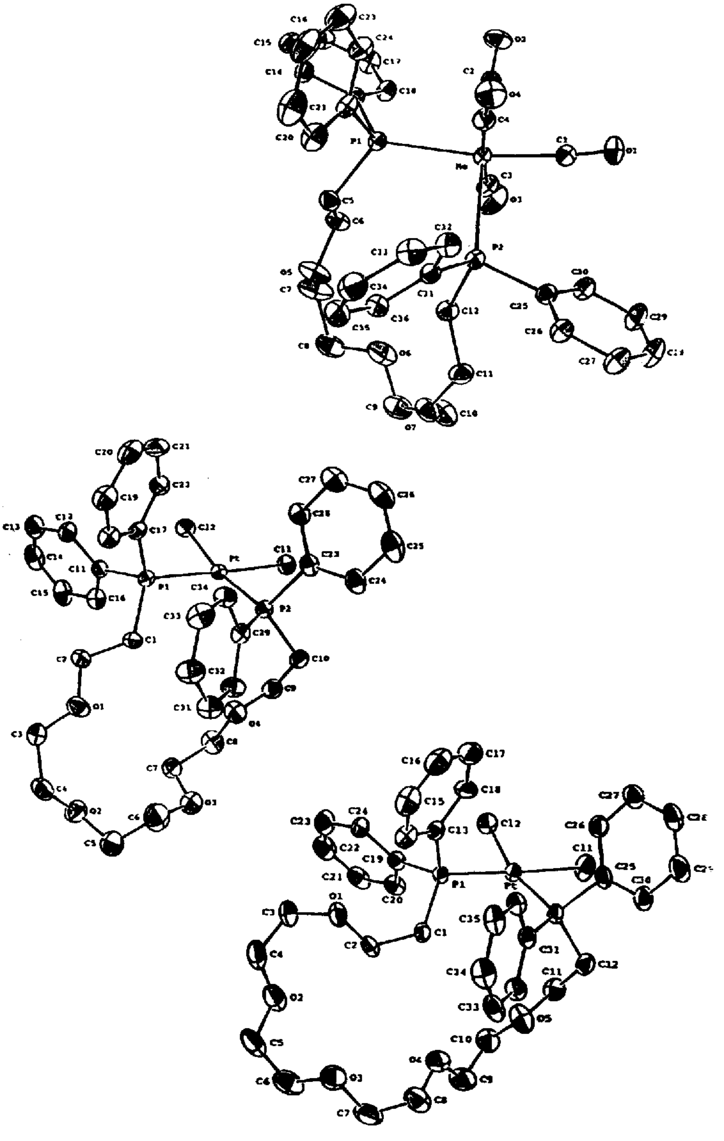
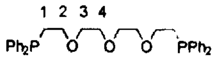
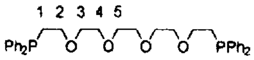


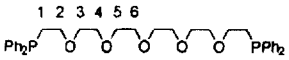
FIGURE 1 X-ray crystal structures of *cis*-Mo(CO)$_4${Ph$_2$P(CH$_2$CH$_2$O)$_3$CH$_2$CH$_2$PPh$_2$-P,P'}, **1**, (Ref. 10) and *cis*-PtCl$_2${Ph$_2$P-(CH$_2$CH$_2$O)$_n$CH$_2$CH$_2$PPh$_2$-P,P'} (n = 4 (**2**) and 5 (**3**)) (Ref. 11).

TABLE I

^{31}P and ^{13}C NMR coordination chemical shifts for the *cis*-$\mathrm{Mo(CO)_4\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}}$ and *cis*-$\mathrm{PtCl_4\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}}$ metallacrown ethers.







Complex	P	C1	C2	C3	C4	C5	C6
Mo (n = 3)	41.99	3.06	-0.82	1.44	0.97		
Mo (n = 4)	41.79	3.10	-1.58	0.06	-0.33	-0.07	
Mo (n = 5)	42.13	4.14	-1.55	-0.11	-0.23	-0.04	-0.04
cis-$\mathrm{Mo(CO)_4\{Ph_2P(CH_2CH_2O)_2Me\}_2}$[17]	42.19	4.11	-1.59	-0.11	-0.16		
Pt (n = 3)	27.32	-0.90	0.06	1.84	0.01		
Pt (n = 4)	26.87	-0.94	-0.80	1.29	0.22	0.27	
Pt (n = 5)	27.01	-1.10	-0.96	0.90	0.15	0.09	0.09
Pt (n = 5) oligomer (?)	26.15	1.69	-1.59	-0.20	0.12	0.11	0.11
cis-$\mathrm{PtCl_2\{Ph_2P(CH_2CH_2O)_2Me\}_2}$[17]	26.25	1.66	-1.60	-0.20	-0.16		

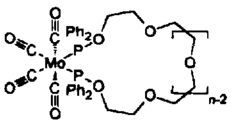
metallacrown ethers. The coordination chemical shifts for the methylene carbons in these complexes are quite different from those of similar methylene carbons in *cis*-$PtCl_2\{Ph_2P(CH_2CH_2O)_2Me\}_2$,[17] and the differences do not decrease as n increases.[17] It is not clear why this should be the case, but it is interesting that a minor product in the synthesis of *cis*-$PtCl_2\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}$, which may be an oligomer of this complex, has coordination chemical shifts quite similar to those of *cis*-$PtCl_2\{Ph_2P(CH_2CH_2O)_2Me\}_2$. These results suggest that it may be possible to tune the solution conformations of the *cis*-metallacrown ethers by changing the metal center. This could allow metallacrown ethers with the same ligands to have quite different coordinating abilities.

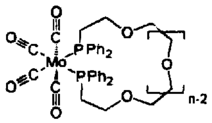
COORDINATION OF METAL CATIONS BY *CIS*-METALLACROWN ETHERS

One of the most interesting properties of metallacrown ethers is their ability to form hard–soft bimetallic complexes. Both John Powell's group[8] and our group[10] have shown that metallacrown ethers selectively bind alkali metal cations. This selectivity appears to be a function of the size of the metallacrown ether ring and not the number of oxygens in the ring, as shown by the data in Table II. This behavior

TABLE II

Metallacrown ether selectivity for alkali metal cations.

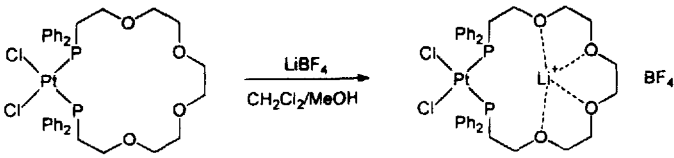




n	atoms in ring	Li^+	Na^+	n	atoms in ring	Li^+	Na^+
2	13	no	no				
3	16	weak	no	4	17	yes	weak
4	19	yes	yes	5	20	yes	yes

is consistent with the predictions based on the structural studies discussed above.

We have found that the reactions of the *cis*-$PtCl_2\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$-P,P'$\}$ (n = 3, 4, 5) metallacrown ethers with alkali metal cations are more complicated than are those of the *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$-P,P'$\}$ (n = 3, 4, 5) metallacrown ethers.[11] In a dichloromethane–methanol mixture, *cis*-$PtCl_2\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-P,P'$\}$ forms a 1:1 $LiBF_4$ complex (Eq. 4). Unlike the free metallacrown ether, which is soluble in chloroform-*d*$_1$ and insoluble in acetonitrile-*d*$_3$, the bimetallic complex is insoluble in chloroform-*d*$_1$ and soluble in acetonitrile-*d*$_3$. However, when the same reaction is run in a two phase chloroform-*d*$_1$/water mixture, the product appears to be [*cis*-$PtCl\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-P,P',O$\}]BF_4$ based upon its NMR spectra (Eq. (5)). This complex is in equilibrium with the free metallacrown ether and $LiBF_4$ and could not be isolated from these solutions. When *cis*-$PtCl_2\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-P,P'$\}$ reacts with NaCN in a dichloromethane–methanol mixture, the product is *trans*-$Pt(CN)_2\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-P,P'$\}$ (Eq. (6)). No binding of Na^+ by this *trans*-metallacrown ether is observed.



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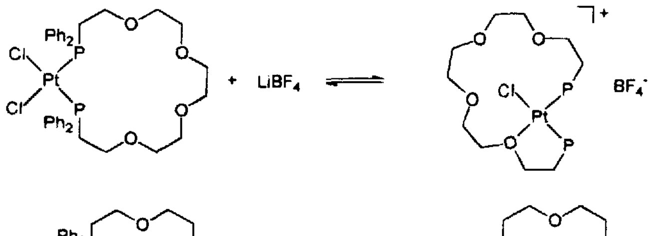

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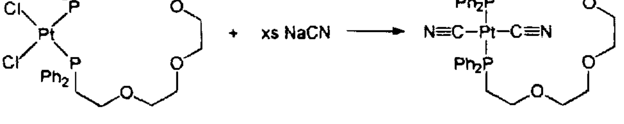
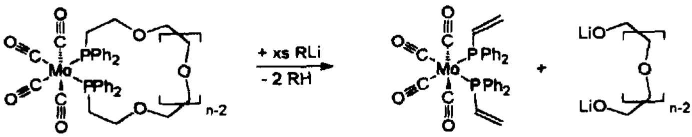


(6)

The coordination of metal ions to the metallacrown ether rings in *cis*-$Mo(CO)_4\{R_2PX(CH_2CH_2O)_nCH_2CH_2XPR_2\text{-}P,P'\}$ (X = –, R = Ph; X = O, R = Ph, alkoxy) metallacrown ethers can have a significant effect upon the reactivity of the carbonyl ligands. Powell has noted that the carbonyl ligands in *cis*-$M(CO)_4\{Ph_2PO(CH_2CH_2O)_nCH_2CH_2OPPh_2\text{-}P,P'\}$ (M = Cr, Mo, W; n = 2) metallacrown ethers react readily with methyllithium, phenyllithium and lithium amides to form the corresponding acetyl, benzoyl and aminocarbonyl complexes (Eq (7)).[8] Similar reactions do not occur with the n = 0, 1, 3 or 4 complexes. Apparently these reactions only occur when the metallacrown ether contains one fewer oxygen than is needed to fill the coordination sphere of Li^+. Powell proposes that the key step in the nucleophilic attack on the carbonyl ligand is coordination of Li^+ to both the metallacrown ether oxygens and the oxygen of the carbonyl ligand. We have found that the *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}$ (n = 3, 4, 5) metallacrown ethers do not react with either phenyllithium or methyllithium to form benzoyl or acetyl complexes. Instead, the methylene adjacent to the phosphorus is deprotonated and *cis*-$Mo(CO)_4\{Ph_2PCH=CH_2)_2$ is formed (Eq (8)).[10] This type of reaction cannot occur with the *cis*-$M(CO)_4\{Ph_2PO(CH_2CH_2O)_nCH_2CH_2OPPh_2\text{-}P,P'\}$ metallacrown ethers because they lack alpha methylene protons.

(7)



(8)

We have demonstrated that *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}$ metallacrown ethers undergo size-selective reactions with $HgCl_2$ in dichloromethane.[13] When the ring is sufficiently large to hold Hg^{2+} (n = 5), the expected bimetallic complex [*cis*-$Mo(CO)_4\{\mu\text{-}(Ph_2P(CH_2CH_2O)_5CH_2CH_2PPh_2\text{-}P,P',O,O',O'',O''',O'''')\}HgCl_2$] is obtained. The X-ray crystal structure of this complex, shown in Fig. 2, contains a molecular cleft between the Mo and the Hg and an open coordination site on the Hg. This suggests that it should be possible to bridge a bifunctional ligand between the two metals in these complexes.

When the ring in the *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$-P,P′} metallacrown ether is too small to hold the Hg^{2+} (n = 4), isomerization to *trans*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-P,P′}, **4,** occurs. A possible mechanism is suggested by the cleft observed in the bimetallic MoHg complex. Coordination of Hg^{2+} to both the metallacrown ether oxygens and a carbonyl oxygen would weaken the molybdenum–carbonyl bond. This would facilitate dissociation of the carbonyl and isomerization of the complex.[18] This mechanism is similar to that proposed for the activation of carbonyls towards nucleophilic attack by Li^+.

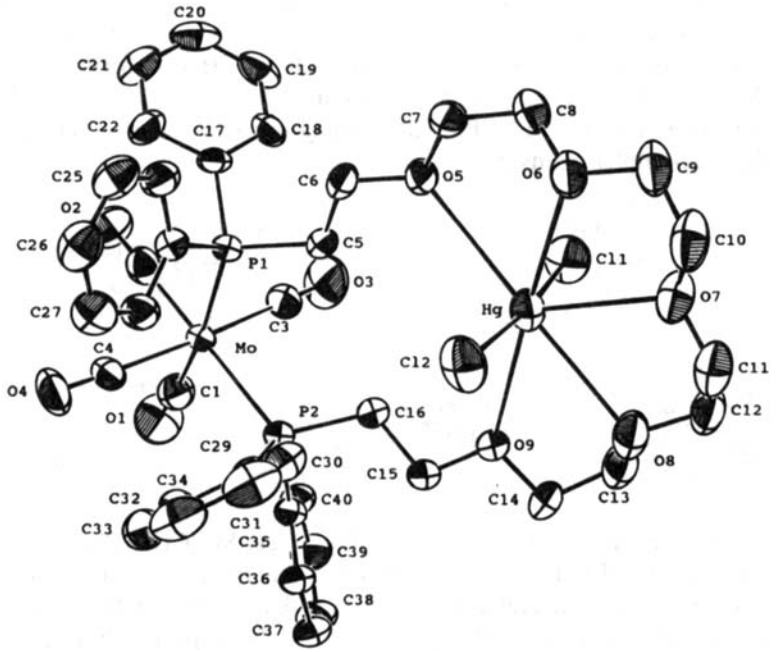


FIGURE 2 X-ray crystal structure of [*cis*-$Mo(CO)_4\{\mu$-$(Ph_2P(CH_2CH_2O)_5CH_2CH_2$-$PPh_2$-P,P′,O,O′,O″,O‴,O⁗)}$HgCl_2$].

BINDING OF SMALL MOLECULES BY *CIS*-METALLACROWN ETHERS

From the studies discussed above it is apparent that polyfunctional ligands such as carbonyls can coordinate to both metals in *cis*-metallacrown ether complexes of hard metal cations. Bifunctional interaction of ligands with metallacrown ethers can occur in the absence of the hard metal cation if the ligand is both a Lewis base and capable of hydrogen bonding. Both Brown's group[9a,9b] and our group[11] have reported that cationic platinum-group metallacrown ethers can bind water in this manner, as shown in Fig. 3. The water is coordinated to the platinum-group metal by donation of an electron pair on the oxygen and is also hydrogen bonded to the crown ether oxygens through the hydrogens. This type of binding of water can occur with either *cis*- or *trans*-metallacrown ethers and appears to be quite favorable, as evidenced by the fact that both complexes were prepared under inert atmospheres. This suggests that hydrogen bonding of one reactant and coordination of a second reactant to a metallacrown ether could result in preorganization of these reactants that could result in unusual catalytic activities and/or selectivities.

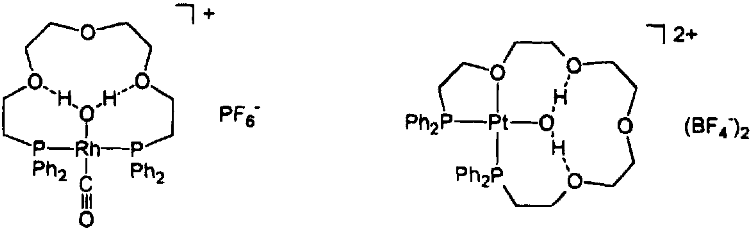


FIGURE 3 Water coordination by cationic Pt-group *cis*-metallacrown ethers.

Hydrogen bonding interactions, such as those shown in Fig. 3, are also important in solutions of metallacrown ethers. Crystallization of *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-P,P'$\}$ from dichloromethane/methanol yields crystals containing one mole of methanol per mole of the metallacrown ether. When these are dissolved in wet acetonitrile-d_3, three bond coupling between the hydroxyl proton and the methyl protons of the methanol is still observed in the ^1H NMR spectrum.[16] Thus, it appears that strong hydrogen bonding between the methanol and the metallacrown ether in the acetonitrile-d_3 solution greatly slows the exchange of the methanol hydroxyl protons and the water protons. The addition of $LiBF_4$ to this solution causes the coupling to disappear, presumably because the Li^+ displaces the methanol from the metallacrown ether and allows the typically rapid proton exchange between the hydroxyl and water protons to occur.

SYNTHESES AND CONFORMATIONS OF *TRANS*-METALLACROWN ETHERS

Before 1994, nearly all of the metallacrown ethers that were reported had cis phosphorus-donor groups. The only exceptions were the square planar Rh(I) complexes prepared by Brown's and Thewissen's groups.[9] Unfortunately, the largest ligand used in these complexes was $Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2$, which does not form a sufficiently large ring to bind metal ions. In addition, only one crystal structure was reported. Thus, nothing was known about effect of the trans coordination of the phosphines on the conformations and properties of *trans*-metallacrown ethers. We have recently prepared a variety of *trans*-metallacrown ethers with octahedral metal centers. These complexes have solution and solid state conformations that are quite different from those of the *cis*-metallacrown ethers.

One route to *trans*-metallacrown ethers with octahedral metal centers is the isomerization of *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}$ metallacrown ethers using either UV light[12] or $HgCl_2$ ($n = 4$)[13] (Eq. (9)). The X-ray crystal structure of *trans*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}$, **4**, is shown in Fig. 4. The metallacrown ether ring bisects the angle formed by two of the carbonyls and the molybdenum and is nearly symmetric to rotation about a C_2 axis running from the midpoint of the ligand through the molybdenum. The conformation of the metallacrown ether ring is quite different from that of the metallacrown ether ring in the isomeric *cis*-complex. In the *trans*-metallacrown ether, the ring is more extended with longer oxygen–oxygen distances (5.87 Å versus 4.66 Å), and this causes the ether oxygens to be much closer to the carbonyls and the molybdenum. These structural differences suggest that the *cis*- and *trans*-metallacrown ethers should exhibit quite different affinities for hard metal cations and that metal ions coordinated

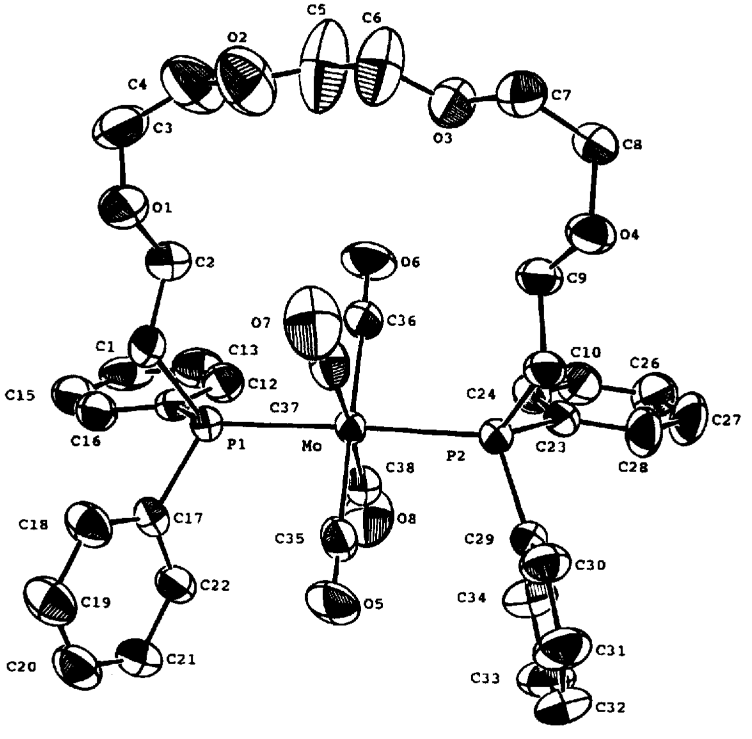
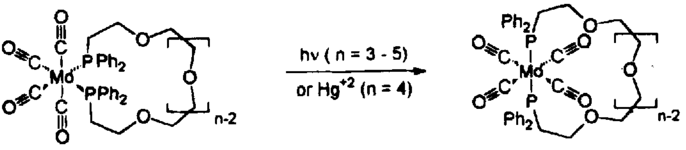


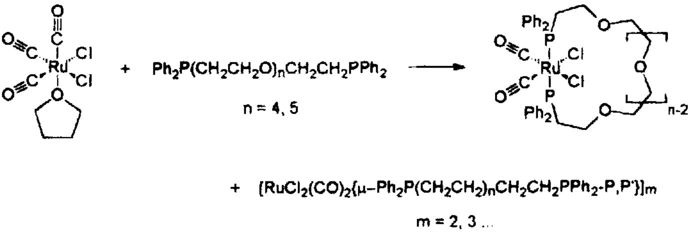
FIGURE 4 X-ray crystal structure of *trans*-Mo(CO)$_4${Ph$_2$P(CH$_2$CH$_2$O)$_4$CH$_2$CH$_2$PPh$_2$-P,P′}, 4.

to the metallacrown ether rings could more strongly interact with ligands in the *trans*-metallacrown ethers.



(9)

We have also found that the reactions of the Ph$_2$P(CH$_2$CH$_2$O)$_n$CH$_2$CH$_2$PPh$_2$ (n = 4, 5) ligands with *fac*-RuCl$_2$(CO)$_3$(THF) yield the *cis,cis,trans*-RuCl$_2$(CO)$_2${Ph$_2$P(CH$_2$-CH$_2$O)$_n$CH$_2$CH$_2$PPh$_2$-P,P′} trans-metallacrown ethers as the major products (Eq. (10)).[14] The X-ray crystal structure of *cis,cis,trans*-$RuCl_2(CO)_2\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}$, **5**, has been determined and is shown in Fig. 5. This structure is unusual in that it contains two different rotomers of the $RuCl_2(CO)_2$ group relative to the metallacrown ether ring. In the major rotomer, the metallacrown ether ring bisects the angle between one carbonyl and one chloride, but, in the minor rotamer, the metallacrown ether ring bisects the angle between the two chlorides. The fact that the third rotamer, in which the metallacrown ether ring would bisect the angle between two carbonyls, is not observed suggests that this rotomer has a significantly different conformation than do the others. This proposal is supported by the fact that the torsion angles for the metallacrown ether ring in **5** are quite different from those for the identical metallacrown ether ring in **4** that does bisect an angle between two carbonyls. This difference in conformation is also reflected in the P–M–P bond angle which is less distorted in **5** (177.70(8) Å) than in **4** (175.69(4) Å).



(10)

The solution conformations of the *trans*-metallacrown ethers with octahedral metal centers is also of interest, particularly in view of the fact that rotomers are observed in the X-ray crystal structure of **5**. For both **4** and **5**, a single, sharp 1:2:1 triplet is observed for the carbonyls in the ^{13}C NMR spectra, indicating that all the carbonyl environments are averaged in solution at ambient temperature. Thus, these molecules can be thought of as molecular gyroscopes. As the temperature is lowered, no changes in the carbonyl resonances are observed until the temperature reaches −40°C and then they begin to broaden. At −80°C, a single resonance is still observed for each complex with that for **4** being broader than that for **5**. This demonstrates that the barrier to rotation about the phosphorus–metal–phosphorus axis is quite low in both **4** and **5**. with the barrier in **5**

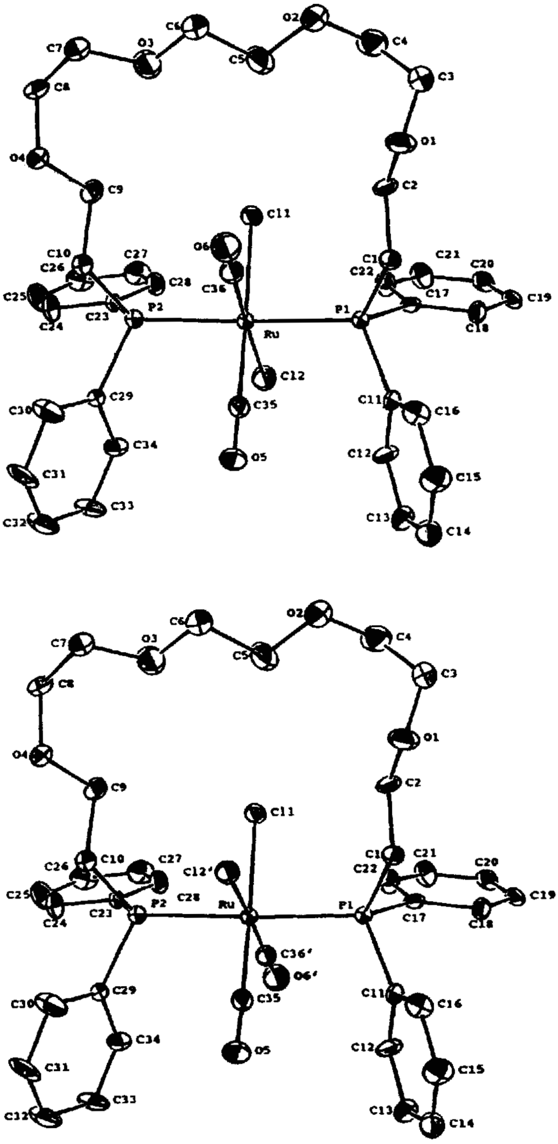


FIGURE 5 X-ray crystal structure of the two rotomers of *cis,cis,trans*-RuCl$_2$(CO)$_2${Ph$_2$P(CH$_2$CH$_2$O)$_4$CH$_2$CH$_2$PPh$_2$-P,P'}, 5.

slightly lower than that in **4**. The slightly lower barrier in **5** may be a result of the fact that the carbonyl environments in **5** can be averaged without moving the metallacrown ether ring over the larger carbonyl ligands, but this is not possible in **4**. The low rotation barriers in these complexes are the first direct experimental evidence to support the current view that there is no significant dπ-dπ bonding between transition metals and phosphine ligands.[19]

The reactions of the $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ (n = 4, 5) ligands with *fac*-$RuCl_2(CO)_3(THF)$ yield minor products that appear to be oligomers with bridging $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ ligands (Eq. (10))[14] based on the similarities of their ^{31}P and ^{13}C NMR coordination chemical shifts to those of *cis,cis,trans*-$RuCl_2(CO)_2\{Ph_2P(CH_2CH_2O)_2Me\}_2$. An X-ray crystal structure of one of these oligomers, [*cis,cis,trans*-$RuCl_2(CO)_2\{\mu$-$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-P,P′}]$_2$, has been obtained and is shown in Fig. 6. The fact that these oligomeric complexes are obtained during the preparation of *trans*-metallacrown ethers but not during the preparation of the *cis*-metallacrown ethers is not surprising. In order for the $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ ligand to trans

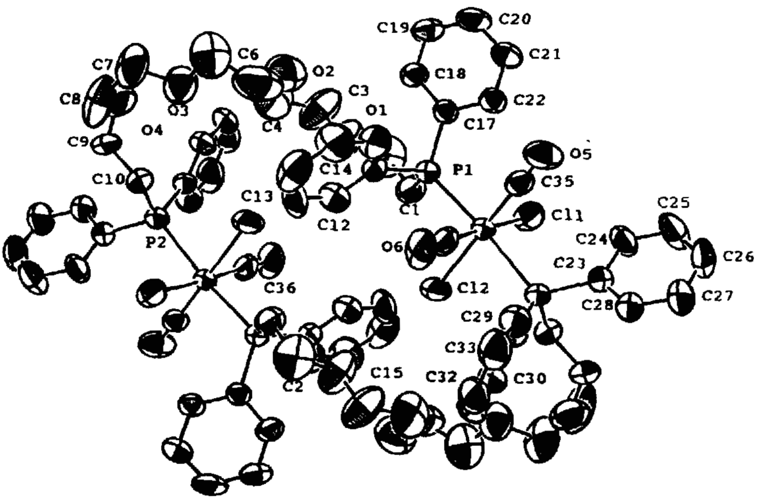


FIGURE 6 X-ray crystal structure of [*cis,cis,trans*-$RuCl_2(CO)_2\{\mu$-$Ph_2P(CH_2CH_2O)_4$-$CH_2CH_2PPh_2$-P,P′}]$_2$.

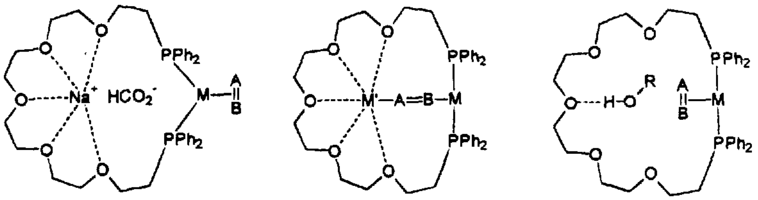
coordinate, it must wrap around the other ligands on an octahedral metal center. This is not necessary when the ligand coordinates in a cis fashion. In addition, it is unlikely that ether oxygen-coordinated intermediates could play a role in trans coordination. These results are similar to those observed with square planar Rh(I), Pd(II) and Pt(II) complexes of long chain bis(phosphine) ligands.[20]

The complex $[cis,cis,trans\text{-RuCl}_2(\text{CO})_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_4\text{-CH}_2\text{CH}_2\text{PPh}_2\text{-}P,P'\}]_2$ is the first example of a dimetallacrown ether. Because the phosphine ligands are trans coordinated to the Ru, the complex appears to contain two separate metallacrown ether sites separated by a carbonyl and a chloride ligand on each ruthenium. The Ru–Ru distance of 9.1961(9) Å indicates that there is no interaction between the two rutheniums. This structure is intriguing because it may be possible to bind metal cations on one or both of the metallacrown ether sites forming either tri- or tetranuclear complexes, and coordination of one metal cation could affect the coordination of the second. Further, it may be possible to replace two of the monodentate ligands, either chloride or carbonyl, on the ruthenium with a bidentate ligand spanning the two metal centers. This could also have interesting effects on the metal cation binding abilities of this complex.

CONCLUSIONS

Metallacrown ethers in which the P-donor groups are either cis- or trans-coordinated to the transition metal complex are readily prepared. The *cis*- and *trans*-metallacrown ethers exhibit quite different crown ether ring conformations. Of particular interest in this regard are *trans*-metallacrown ethers with octahedral metal centers because these complexes behave as molecular gyroscopes. The *cis*-metallacrown ethers selectively bind metal cations and can also bind small molecules capable of hydrogen bonding. The bimetallic complexes appear to contain molecular clefts that could allow a ligand to coordinate to both metals. This type of coordination has been proposed as a mechanism by which carbonyl ligands on the transition metal are activated by metal cation binding.

These results suggest that platinum-group metallacrown ethers could exhibit catalytic activities and selectivities that are quite different from those of platinum-group metal complex catalysts with simple



Phase Transfer **Bimetallic Coordination** **Substrate Preorganization**

FIGURE 7 Potential catalytic mechanisms involving metallacrown ethers.

mono- or bidentate phosphorus-donor ligands. The phase transfer ability of the metallacrown ethers should allow such complexes to serve as catalysts for two-phase reductions employing water-soluble reducing agents. Bimetallic metallacrown ethers, formed by coordination of a hard metal cations to a Pt-group metallacrown ether, could exhibit unusual activities and selectivities for reactions involving substrates that can bind to both metals. Metallacrown ethers could also exhibit unusual catalytic activities and selectivities for reactions in which the substrates could be preorganized by coordination of one to the Pt-group metal center and hydrogen bonding of another to a metallacrown ether oxygen. These possibilities, illustrated in Fig. 7, suggest that the study of the catalytic applications of metallacrown ethers will be an extremely fruitful research area, and preliminary investigations are currently underway in our laboratories.

Acknowledgments

I would like to especially thank the students who did this work: Dr. Ashima Varshney, who received her Ph.D. in 1990, current Ph.D. students Ms. Christina H. Duffey and Dale C. Smith, Jr., and a talented undergraduate student, Ms. Mary L. Webster. I would also like to thank the Petroleum Research Fund of the American Chemical Society and Research Corporation for support of this work and Johnson Mathey for a generous loan of platinum-group metal salts.

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