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Metallacrown ethers with *trans*-tetracarbonylmolybdenum(0) centers. X-ray crystal structures of *trans*-Mo(CO)₄{Ph₂P(CH₂CH₂O)_nCH₂CH₂PPh₂-P,P'} (n = 3, 5) and *trans*-Mo(CO)₄{Ph₂P(CH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂)₂PPh₂-P,P'}

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Abstract

Photolysis of the *cis*-Mo(CO)₄{Ph₂P(CH₂CH₂O)_nCH₂CH₂PPh₂-*P*,*P'*}, (**1**, n = 3; **2**, n = 4; **3**, n = 5) metallacrown ethers in tetrahydrofuran under nitrogen gives moderate yields of the corresponding *trans*-Mo(CO)₄{Ph₂P(CH₂CH₂O)_nCH₂CH₂PPh₂-*P*,*P'*} (**4**, n = 3; **5**, n = 4; **6**, n = 5) metallacrown ethers. The *trans*-metallacrown ethers are also obtained when catalytic amounts of HgCl₂ are added to chloroform solutions of the *cis*-metallacrown ethers. The **1** \neq **4** and **2** \neq **5** equilibria are established within 3 min at ambient temperature and approximately equal amounts of the *cis*- and *trans*-metallacrown ethers are present in the equilibrium mixtures. The **3** \neq **6** equilibrium is more complicated because HgCl₂ complexation by **3** also occurs in these solutions. Addition of excess HgCl₂ to the equilibrium mixture of **3** and **6** results in the formation of the X-ray crystal structures of the *trans*-metallacrown ethers **4**-**6** and *trans*-Mo(CO)₄{Ph₂P(CH₂CH₂O)₅CH₂CH₂PPh₂-*P*,*P'*,*O*,*O'*,*O'''*,*O''''*,*O''''*}HgCl₂. Comparison of the X-ray crystal structures of the *trans*-metallacrown ethers **4**-**6** and *trans*-Mo(CO)₄{Ph₂P(CH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂O)₂PPh₂-*P*,*P'*} (**7**) indicates that both ring size and flexibility affect the conformations of the metallacrown ether rings. The larger oxygen–oxygen distances in the *trans*-metallacrown ethers, compared with those in the corresponding *cis*-metallacrown ethers **1**, **3** and *cis*-Mo(CO)₄{Ph₂P(CH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂O)₂)-1-C₆H₄-2-(O

Keywords: Crystal structures; Molybdenum complexes; Carbonyl complexes; Crown ethers complexes

1. Introduction

Cis-trans isomerizations of the cis-tetracarbonylmolybdenum(0) complexes of α, ω -bis(phosphorusdonor)polyether ligands (cis-metallacrown ethers) occur when these complexes are either exposed to UV light [1,2] or treated with catalytic amounts of HgCl₂ [2,3]. All of the HgCl₂-catalyzed reactions that have been studied to date are complete within 3 min at ambient temperature even though the $HgCl_2$ is in a separate phase (solid or aqueous) from that containing the *cis*-metallacrown ether (chloroform-*d*).

The *trans*-metallacrown ethers are unusual in that the chelating bis(phosphorus-donor) ligands bridge the *trans* positions of the octahedral metal centers. Only three complexes of this type [4,5] were known prior to our initial report [1] and these complexes either contained a bis(phosphine) ligand either with a rigid backbone that prevented *cis* coordination [4] or were prepared by ring closure after monodentate phosphine ligands were *trans*-coordinated to the metal center [5]. Unlike the *cis*-metallacrown ethers [6], the *trans*-metal-

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lacrown ethers do not appear to coordinate metal cations. Consistent with this observation, the carbonyl ligands in the *trans*-metallacrown ethers are not activated towards attack by organolithium reagents [3,7].

To gain more insight into the manner in which the unusual coordination mode of the α,ω -bis(phosphorus-donor)polyether ligands in *trans*-metallacrown ethers affects the properties of these complexes, we have stud-

Table 1					
³¹ P and	phenyl	$^{13}\mathrm{C}$	NMR	data ^a	a

No.	P (³¹ P) (ppm)	(³¹ P) (ppm) <i>ipso</i>		ortho	ortho		meta	
		$\delta(^{13}\text{C}) \text{ (ppm)}$	J(PC) (Hz)	$\delta(^{13}\text{C}) \text{ (ppm)}$	J(PC) (Hz)	$\delta(^{13}\text{C}) \text{ (ppm)}$	J(PC) (Hz)	_
1 ^b	20.36s	137.48aq	57 °	132.14aq	9 d	128.30		129.30s
2 ^b	20.11s	136.94aq	56 °	132.13aq	9 ^d	128.35aq	8 e	129.32s
3 ^b	20.44s	136.17aq	62 °	132.12aq	8 d	128.33bs		129.46s
4	35.24s	139.90t	16 ^f	131.77t	6 ^g	128.23t	5 ^h	128.30s
5 ⁱ	32.32s	139.48t	17 ^f	131.70t	6 ^g	128.28bs		129.16s
6	32.53s	139.05t	16 ^f	131.56t	6 ^g	128.18		129.08s

^a b = broad, s = singlet, t = triplet, aq = apparent quintet.

^b Data from Ref. [8].

^c $|^{1}J(PC) + {}^{3}J(PC)|$.

^d $|^2 J(PC) + {}^4 J(PC)|$.

- $e |{}^{3}J(PC) + {}^{5}J(PC)|.$
- ^f $|^{1}J(PC)|$.
- $|^{g}|^{2}J(\mathrm{PC})|.$
- ^h $|^{3}J(PC)|$.
- ⁱ Data from Ref. [1].

Table 2

Aliphatic and carbonyl ¹³C NMR data ^a

No.	C1		C2		C3, C4, C5, C6 (δ(¹³ C)) (ppm)	CO cis		CO trans	
	$\delta(^{13}\text{C}) \text{ (ppm)}$	J(PC) (Hz)	$\delta(^{13}\text{C}) \text{ (ppm)}$	J(PC) (Hz)		$\delta(^{13}\text{C}) \text{ (ppm)}$	J(PC) (Hz)	$\delta(^{13}\text{C}) \text{ (ppm)}$	J(PC) (Hz)
1 ^b	31.83aq	14 °	67.71bs		70.66s, 71.54s	214.96aq	14 ^d	209.79t	9 °
2 ^b	31.31aq	15 °	66.95bs		70.16s, 70.25s, 70.65s	215.08aq	16 ^d	209.69t	8 °
3 ^b	31.34aq	20 °	66.94bs		69.96s, 70.34s, 70.47s, 70.47s	215.05aq	14 ^d	209.55t	9 °
4	34.22aq	11 °	66.91aq	6 ^d	70.02s, 72.82s			210.35w	
5 ^f	34.37aq	11 °	66.96aq	12 ^d	70.24s, 71.03s, 71.07s			210.59t	8 °
6	NO ^g		67.60bs		70.34s, 70.43s, 70.57s, 70.62s			NO	

 a b = broad, s = singlet, t = triplet, aq = apparent quintet, w = weak.

^b Data from Ref. [8].

 $d|^2 J(PC)|.$

 $|^{2}J(PC) + {}^{2}J(P'C)|.$

^f Data from Ref. [5].

^g NO = not observed.

^c $|^{1}J(\text{PC}) + {}^{3}J(\text{PC})|.$

Table 3

Data collection and structure solution and refinement parameters for 4, 6 and 7 a

	4	6	7
Formula	C ₃₆ H ₃₆ Mo ₁ O ₇ P ₂	$C_{40}H_{44}Mo_1O_9P_2$	$C_{42}H_{40}MoO_8P_2$
MW	738.57	826.68	830.19
Space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a (Å)	10.032(2)	12.112(1)	8.834(1)
b (Å)	11.792(2)	13.350(2)	13.947(2)
<i>c</i> (Å)	16.776(2)	14.215(2)	17.440(3)
α (°)	103.13(1)	63.50(1)	71.79(1)
β (°)	99.11(1)	74.16(1)	76.13(1)
γ (°)	109.02(1)	83.39(1)	80.50(1)
$V(\text{\AA}^3)$	1765.8	1978.8	1972.0
Ζ	2	2	2
$d_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.389	1.387	1.399
Crystal dimensions (mm ³)	$1.0 \times 0.5 \times 0.2$	$0.6 \times 0.6 \times 0.2$	$0.3 \times 0.3 \text{V} 0.2$
$h_{\rm max}, h_{\rm min}$	13, -12	0, -15	0, 9
$k_{\text{max}}, k_{\text{min}}$	1, -15	17, -17	-14, 14
l_{\max}, l_{\min}	21, -21	17, -18	-18, 18
λ (Å)	0.71073	0.71073	0.71073
Temperature (°C)	23	23	23
Absorption coefficient (cm^{-1})	4.9	4.5	4.6
θ limits (°)	1.0-27.5	1.0-27.5	1.0-22.5
Decay (%)	-1.3	-5.1	none
Decay corr.	linear	linear	not applicable
Abs. corr.	ψ scan	ψ scan	ψ scan
$T_{\rm max}, T_{\rm min}$ (%)	99.91, 96.02	99.77, 82.46	93.08, 84.14
Reflections measured	9266	9077	5536
Scan type	ω –2 $ heta$	ω –2 θ	ω
Reflections $[I > 2\sigma(I)]$	6760	4110	3206
No. of variables	416	470	478
Function min.	$w(F_{0} - F_{c})^{2}$	$w(F_{o} - F_{c})^{2}$	$w(F_{o} - F_{c})^{2}$
Weighting scheme	non-Poisson	non-Poisson	$w^{-1} = \sigma^2 + 0.0039F^2$
Inst. uncert. fact.	0.03	0.05	not applicable
Extinction corr.	Zachariesen	Zachariesen	not applicable
Extinction coeff.	9.0169×10^{-7}	1.0160×10^{-7}	
R (%) ^a	4.1	7.9	5.47
$R_{\rm w}$ (%) ^b	5.0	8.4	5.99
GOF °	1.581	1.385	0.91
Max., min. residual elect. den. (e $Å^{-3}$)	0.651, -0.116	0.998, -0.274	1.270.68
Max. shift/error	0.00	0.00	0.00

 $\label{eq:rescaled_$

ied the isomerizations of cis-Mo(CO)₄{Ph₂P- $(CH_2CH_2O)_n CH_2CH_2PPh_2-P,P'\}$ (*n* = 3 (1); 4 (2); 5 (3)) metallacrown ethers to the corresponding trans- $Mo(CO)_4 \{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2-P,P'\}$ (n = 3)(4); 4 (5); 5 (6)) metallacrown ethers using both UV light and HgCl₂. X-ray crystal structures of 4, 6 and the previously reported trans-Mo(CO)₄{Ph₂P(CH₂CH₂O)₂- $1-C_6H_4-2-(OCH_2CH_2)_2PPh_2-P,P'$ (7) have also been determined and are compared to that of 5, which was previously reported [1].

2. Experimental section

All NMR spectra were recorded at 21°C on a Bruker ARX 300 MHz NMR spectrometer with a quad (¹H, ^{13}C , ^{19}F , ^{31}P) 5 mm probe. The $^{31}P{^{1}H}$ NMR spectra were referenced to external 85% H₃PO₄ and the $^{13}C{^{1}H}$ spectra were referenced to internal TMS. The ³¹P and ¹³C data for the complexes are given in Tables 1 and 2 with positive chemical shifts downfield from those of the references. Quantitative ³¹P(¹H} NMR spectra were run using a 30° inverse-gated pulse sequence with a 20 s pulse delay. Infrared spectra of dilute dichloromethane solutions of the carbonyl complexes in a 0.2 mm KBr solution cell were run on either a Perkin–Elmer Paragon 1000 FTIR or a Nicolet IR44 FTIR spectrometer. The background for these measurements was pure dichloromethane in the same cell. Elemental analyses of the compounds were performed by Atlantic Microlab, Inc., Norcross, GA.

All the solvents and HgCl₂ were of reagent grade and were used as received. The water was deionized. Tetrahydrofuran (THF) was dried over MgSO₄ before use. Chloroform-d₁ was opened and handled under a dry nitrogen atmosphere at all times. The *cis*-Mo(CO)₄{Ph₂P(CH₂CH₂O)_nCH₂CH₂PPh₂-*P*,*P'*} (*n* = 3 (1), 4 (2), 5 (3)) metallacrown ethers [8,9] and *trans*-Mo(CO)₄{Ph₂P(CH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂)₂-PPh₂-*P*,*P'*} (7) metallacrown ether [2b] were prepared using the literature procedures.

2.1. UV photoisomerizations

Dry THF (150 ml) was poured into an Ace concentric photochemical reactor and purged for 10 min with dry nitrogen. The solid *cis*-metallacrown ether was then added to the THF. This solution was irradiated with a 350 W mercury vapor lamp for 20 min. Water was

Table 4 Selected bond distances (Å) and angles (°) for **4**

Mo-P1	2.472(2)	O1–C3	1.409(9)
Mo-P2	2.472(2)	O2–C4	1.43(1)
Mo-C33	2.031(9)	O2–C5	1.42(1)
Mo-C34	2.025(5)	O3–C6	1.413(7)
Mo-C35	2.019(6)	O3–C7	1.41(1)
Mo-C36	2.014(8)	O4–C33	1.13(1)
P1C1	1.839(7)	O5–C34	1.143(7)
P1-C21	1.837(7)	O6-C35	1.150(8)
P1-C27	1.837(6)	O7–C36	1.15(1)
P2-C8	1.845(8)	C1-C2	1.493(9)
P2-C9	1.844(8)	C3–C4	1.50(1)
P2-C15	1.830(5)	C5-C6	1.50(1)
O1–C2	1.42(1)	C7–C8	1.525(9)
P1-Mo-P2	177.01(7)	C2O1C3	113.0(7)
P1-Mo-C33	88.6(3)	C4-O2-C5	111.6(7)
P1-Mo-C34	89.5(2)	C6-O3-C7	112.5(6)
P1-Mo-C35	91.3(2)	P1C1C2	112.1(6)
P1-Mo-C36	91.3(3)	O1C2C1	109.0(7)
P2-Mo-C33	88.5(3)	O1-C3-C4	114.1(6)
P2-Mo-C34	89.8(2)	O2-C4-C3	110.6(7)
P2-Mo-C35	89.5(2)	O2-C5-C6	110.5(8)
P2-Mo-C36	91.6(3)	O3-C6-C5	110.8(7)
Mo-P1-C1	116.5(3)	O3-C7-C8	109.4(7)
Mo-P1-C21	119.0(3)	P2-C8-C7	114.1(6)
Mo-P1-C27	114.6(2)	Mo-C33-O4	175.2(5)
Mo-P2-C8	118.5(3)	Mo-C34-O5	179.3(7)
Mo-P2-C9	120.9(3)	Mo-C35-O6	178.2(7)
Mo-P2-C15	110.9(2)	Mo-C36-O7	176.4(6)

Table 5 Selected bond distances (Å) and angles (°) for $\mathbf{6}$

Mo-P1	2.487(2)	O3–C6	1.39(1)
Mo-P2	2.471(2)	O3–C7	1.36(2)
Mo-C37	2.019(9)	O4–C8	1.43(1)
Mo-C38	2.01(1)	O4–C9	1.41(1)
Mo-C39	2.03(1)	O5-C10	1.41(1)
Mo-C40	2.02(1)	O5-C11	1.44(1)
P1-C1	1.82(1)	O6-C40	1.14(2)
P1-C13	1.82(1)	O7–C37	1.14(1)
P1-C19	1.839(7)	O8–C38	1.15(1)
P2-C12	1.84(1)	O9–C39	1.14(1)
P2-C25	1.83(1)	C1–C2	1.52(1)
P2-C31	1.829(8)	C3–C4	1.46(2)
O1–C2	1.40(1)	C5-C6	1.51(2)
O1–C3	1.40(1)	C7–C8	1.46(1)
O2–C4	1.38(1)	C9-C10	1.51(2)
O2–C5	1.41(1)	C11-C12	1.50(1)
P1-Mo-P2	173.77(9)	C8O4C9	113.5(9)
P1-Mo-C37	94.7(3)	C10-O5-C11	113.6(7)
P1-Mo-C38	88.0(3)	P1C1C2	113.8(6)
P1-Mo-C39	87.9(3)	O1C2C1	108.9(7)
P1-Mo-C40	91.6(3)	O1-C3-C4	117.3(9)
P2-Mo-C37	91.2(3)	O2-C4-C3	113(1)
P2-Mo-C38	89.9(3)	O2-C5-C6	108.6(9)
P2-Mo-C39	86.2(3)	O3-C6-C5	109(1)
P2-Mo-C40	90.6(3)	O3–C7–C8	117(1)
Mo-P1-C1	118.8(3)	O4–C8–C7	111(1)
Mo-P1-C13	113.0(3)	O4C9C10	108.1(9)
Mo-P1-C19	119.3(3)	O5-C10-C9	113(1)
Mo-P2-C12	117.5(4)	O5-C11-C12	108.9(7)
Mo-P2-C25	115.1(3)	P2-C12-C11	112.9(6)
Mo-P2-C31	119.6(3)	Mo-C37-O7	178(1)
C2O1C3	115.8(7)	Mo-C38-O8	177.4(8)
C4-O2-C5	113.7(8)	Mo-C39-O9	179(1)
C6-O3-C7	117.(1)	Mo-C40-O6	177.9(9)

circulated through a jacket located between the lamp and solution chambers to cool the solution. The irradiation time was chosen to maximize the production of the trans-metallacrown ether and minimize photochemical decomposition. After the irradiation was completed, the solution was evaporated to dryness. The residue was dissolved in methylene chloride and filtered through silica gel. The filtrate was concentrated on a rotary evaporator to 5-10 ml and streaked on to a silica gel prep TLC plate. A 2:5 ethyl acetate:hexanes solvent system was used to develop the plate. The bands containing the cis- and trans-metallacrown ethers were scraped off and the complexes were eluted from the silica gel with methanol. The methanol solutions were evaporated to dryness on a rotary evaporator and the solid products were dried for 2 h under high vacuum (0.5 mm Hg).

2.2. trans-Mo(CO)₄{Ph₂P(CH₂CH₂O)₃CH₂CH₂PPh₂-P,P'} (4)

Using the above procedure 0.122 g (0.165 mmol) of 1 yielded 0.030 g (24%) of 4 and 0.020 g (16%) of 1 was

recovered. Anal. Found: C, 52.20; H, 4.99. Calc. for $C_{36}H_{36}MoO_7P_2$ (4). 1.5 CH_2Cl_2 : C, 52.01; H, 4.54%. IR (CH₂Cl₂) (4) (cm⁻¹): ν (s, CO) 1895.

2.3. trans-Mo(CO)₄{Ph₂P(CH₂CH₂O)₄CH₂CH₂-PPh₂-P,P'} (**5**)

Using the above procedure 0.129 g (0.165 mmol) of **2** yielded 0.030 g (23%) of **5** and 0.060 g (47%) of **2** was recovered. *Anal.* Found: C, 57.82; H, 5.33. Calc. for $C_{38}H_{40}MoO_8P_2$ (**5**): C, 58.32; H, 5.15%. IR (CH₂Cl₂) (**5**) (cm⁻¹): v(s, CO) 1896.

2.4. trans-Mo(CO)₄{Ph₂P(CH₂CH₂O)₅CH₂CH₂-PPh₂-P,P'} (6)

Using the above procedure 0.136 g (0.165 mmol) of **3** yielded 0.040 g (29%) of **6** and 0.050 g (37%) of **3** was recovered. *Anal.* Found: C, 58.22; H, 5.37. Calc. for $C_{40}H_{44}MoO_9P_2$ (**6**): C, 58.12; H, 5.36%. IR (CH₂Cl₂) (**6**) (cm⁻¹): v(s, CO) 1895.

2.5. ³¹P NMR studies of isomerizations catalyzed by $HgCl_2$

A chloroform-d₁ solution of the *cis*-metallacrown

Table 6								
Selected	bond	distances	(Å)	and	angles	(°)	for	7

Mo-P1	2.468(2)	O2–C5	1.424(14)
Mo-P2	2.483(2)	O3-C10	1.345(19)
Mo-C39	2.039(8)	O3-C11	1.411(24)
Mo-C40	2.024(9)	O4-C12	1.433(11)
Mo-C41	2.022(8)	O4-C13	1.396(10)
Mo-C42	2.013(8)	O5-C39	1.131(10)
P1-C1	1.859(7)	O6-C40	1.144(10)
P1-C15	1.840(7)	O7–C41	1.133(10)
P1-C21	1.828 (9)	O8–C42	1.155(10)
P2-C14	1.858(7)	C1C2	1.514(10)
P2-C27	1.852(9)	C3–C4	1.563(15)
P2-C33	1.834(7)	C5-C10	1.366(22)
O1–C2	1.412(11)	C11-C12	1.385(21)
O1–C3	1.422(9)	C13-C14	1.504(10)
O2–C4	1.307(11)		
P1-Mo-P2	172.0(1)	C402C5	107.8(8)
P1-Mo-C39	91.7(3)	C10-O3-C11	113.4(11)
P1-Mo-C40	89.6(2)	C12-O4-C13	110.2(7)
P1-Mo-C41	93.3(3)	P1C1C2	115.9(5)
P1-Mo-C42	82.8(3)	O1C2C1	110.2(7)
P2-Mo-C39	95.9(3)	O1-C3-C4	113.1(9)
P2-Mo-C40	83.2(2)	O2C4C4	108.9(8)
P2-Mo-C41	90.3(3)	O2-C5-C10	120.0(11)
P2-Mo-C42	94.7(3)	O3-C10-C5	115.7(11)
Mo-P1-C1	118.6(3)	O3-C11-C12	107.5(13)
Mo-P1-C15	113.1(3)	O4-C12-C11	113.3(11)
Mo-P1-C21	119.6(2)	O4-C13-C14	109.3(6)
Mo-P2-C14	113.9(3)	Mo-C39-O5	178.0(7)
Mo-P2-C27	121.6(2)	Mo-C40-O6	174.3(6)
Mo-P2-C33	112.0(3)	Mo-C41-O7	177.8(7)
C2O1C3	111.4(7)	Mo-C42-O8	174.4(7)

ether of known concentration was prepared in an NMR tube. The headspace of the tube was then flushed with nitrogen and the tube was carefully sealed with a septum cap. Both the ${}^{13}C{}^{1}H$ and ${}^{31}P{}^{1}H$ NMR spectra of this solution were recorded. Then, an aliquot of a 45 mg ml⁻¹ aqueous solution of HgCl₂ was injected under the surface of the chloroform-d₁ solution and dispersed by vigorous shaking. A ³¹P{¹H} NMR spectrum was run as quickly as possible and then ³¹P{¹H} NMR spectra were taken at regular intervals until no change was observed in the ratio of the integrals of the resonances due to the cis- and trans-metallacrown ethers. At this point a quantitative ${}^{31}P{}^{1}H{}$ NMR spectrum was run and the resonances due to the cis- and trans-metallacrown ethers were integrated to determine accurately the concentrations of both complexes.

A 0.60 ml solution of **1** was made for the NMR study with 0.093 g (0.13 mmol) of **1** dissolved in chloroformd₁. A volume of 10.0 μ l of the 45 mg ml⁻¹ aqueous HgCl₂ (0.0018 mmol) was added to this solution.

A 0.66 ml solution of **2** was made for the NMR study with 0.020 g (0.024 mmol) of **2** dissolved in chloroformd₁. A volume of 1.5 μ l of the 45 mg ml⁻¹ aqueous HgCl₂ (0.00024 mmol) was added to this solution.

A 0.66 ml solution of **3** was made for the NMR study with 0.089 g (0.11 mmol) of **3** dissolved in chloroformd₁. A volume of 37.3 μ l of 45 mg ml⁻¹ aqueous HgCl₂ (0.0062 mmol) was added to this solution.

2.6. Collection of the X-ray diffraction data and solution of the crystal structures **4**, **6** and **7**

Crystals of each compound were grown at room temperature by the diffusion of methanol into a dichloromethane solution of the complex. All the crystals were mounted and aligned on an Enraf–Nonius CAD4 diffractometer with κ -geometry. All the data were collected at 23°C with Mo K_{α} radiation ($\lambda =$ 0.71073 Å), and corrected for Lorentz and polarization effects as well as for absorption. Cell constants were determined by the least-squares refinement of 25 reflections with sin θ/λ between 0.30 and 0.36. Details of the data collections are given in Table 3.

All the three compounds crystallized in the triclinic crystal system with the possible space groups being the centrosymmetric space group $P\overline{1}$ (No. 2) or the non-centrosymmetric space group P1 (No. 1). In all cases, the intensity statistics clearly favored the centrosymmetric space group. This was later confirmed by the successful solution and refinement of each of the crystal structures. All the structures were solved with Patterson methods. All the hydrogen atoms were placed at calculated positions with the appropriate staggered geometry.



Fig. 1. ORTEP drawing of the molecular structure of *trans*-Mo(CO)₄{ $Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2-P,P'$ } (4). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

In all cases, refinement converged with no parameter varying by more than 0.01σ . The final difference-Fourier maps possessed no unexplained anomalous peaks. Selected bond distances and angles for structures **4**, **6** and **7** are presented in Tables 4–6, respectively.

2.7. trans-Mo(CO)₄{Ph₂P(CH₂CH₂O)₃CH₂CH₂PPh₂-P,P'} (**4**)

A colorless blocky crystal (dimensions = $1.0 \times 0.5 \times 0.2 \text{ mm}^3$) was glued to the tip of a glass fiber with epoxy cement. Data (9266) were collected by means of an $\omega - 2\theta$ scan out to $\sin \theta / \lambda = 0.65$. This data set contained 6760 unique reflections with $I > 3\sigma(I)$. No appreciable decay was noted during the data collection. Structure solution and refinement were accomplished using the MOIEN program package. The structure converged with R = 4.1% and $R_w = 5.0\%$. The final difference-Fourier map showed residual electron density in the range $-0.116 \text{ e} \text{ Å}^{-3} - 0.651 \text{ e} \text{ Å}^{-3}$. The final labeling of the atoms is presented in Fig. 1.

2.8. trans-Mo(CO)₄{Ph₂P(CH₂CH₂O)₃CH₂CH₂PPh₂-P,P'} (6)

A yellow blocky crystal (dimensions = $0.6 \times 0.6 \times 0.2$ mm³) was glued to the tip of a glass fiber with epoxy

cement. The crystal was then mounted and aligned upon the diffractometer. Data (9077) were collected by means of an ω -2 θ scan out to sin $\theta/\lambda = 0.65$. This data set contained 4110 unique reflections with $I > 3\sigma(I)$. Analysis of the three standard reflections revealed a 5.1% decay during the data collection. This was corrected by a linear decay correction. Structure solution and refinement were accomplished using the MOIEN program package. The structure converged with R =7.9% and $R_w = 8.4\%$. The final difference-Fourier map showed residual electron density in the range -0.274e Å⁻³-0.998 e Å⁻³. The final labeling of the atoms is presented in Fig. 2.

2.9. trans- $Mo(CO)_4 \{Ph_2P(CH_2CH_2O)_2 - 1 - C_6H_4 - 2 - (OCH_2CH_2)_2PPh_2 - P,P'\}$ (7)

A colorless blocky crystal (dimensions = $0.3 \times 0.3 \times 0.2 \text{ mm}^3$) was placed in a thin-walled glass capillary under aerobic conditions. The crystal was then mounted and aligned upon the diffractometer. Data (5536) were collected by means of an ω scan out to sin $\theta/\lambda = 0.54$. This data set contained 3206 unique reflections with $I > 3\sigma(I)$. No appreciable decay was noted during the data collection. Structure solution and refinement were accomplished using the SHELXTL-PC program package. The structure converged with R = 5.5% and $R_w = 6.0\%$. The final difference-Fourier map showed no anomalous features after refinement, with the residual electron density in the range -0.68 e Å⁻³ to 1.27 e Å⁻³. The final labeling of the atoms is presented in Fig. 3.

3. Results and discussion

3.1. UV photoisomerizations

In a recent communication [1] we reported the isomerization of the *cis*-metallacrown ether **2** into the *trans*-metallacrown ether **5** upon exposure to UV radiation for 12 min, as shown in (Eq. (1)).



We have now carried out photolyses of 1-3 under identical conditions to determine if the size of the metallacrown ether ring influences the reaction. Irradiation of 0.0011 M solutions of the cis-metallacrown ethers 1-3 with UV light for 20 min resulted in complex reaction mixtures in which the primary components were the cis- and trans-metallacrown ethers. The cis:trans ratio in each of the crude reaction mixtures is nearly the same, based on the integration of the ³¹P NMR resonances (1:4 = 60:40, 2:5 = 57:43,3:6 = 56:44). This suggests that the ring size does not have a significant effect upon the extent of the isomerization. The isolated yields of trans- and cis-metallacrown ethers from thin layer chromatography were not consistent with the ³¹P NMR data (a 24% yield for 4, a 23% yield for 5 and a 29% yield for 6 with a 16% reclamation of 1, a 47% reclamation of 2 and a 37% reclamation of 3) because the two isomers were not totally resolved by chromatography. It is interesting to note, however, that the total metallacrown ether recovery for the n = 3 metallacrown ethers (40%) was significantly lower than for the n = 4 (70%) and n = 5(66%) metallacrown ethers. This suggests that, although the smaller ring does not appear to affect the *cis:trans* ratio, it does allow more side reactions to occur.



Fig. 2. ORTEP drawing of the molecular structure of *trans*-Mo(CO)₄{ $Ph_2P(CH_2CH_2O)_5CH_2CH_2PPh_2-P,P'$ } (6). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.



Fig. 3. ORTEP drawing of the molecular structure of trans-Mo(CO)₄{Ph₂P(CH₂CH₂O)₂-1-C₆H₄-2-(OCH₂CH₂)₂PPh₂-*P*,*P'*} (7). Thermal ellipsoids are drawn at the 25% probability level and hydrogen atoms are omitted for clarity.

i

3.2. HgCl₂-catalyzed isomerizations

We have also recently reported that HgCl₂ serves as a catalyst for the isomerization of 2–5, but forms a 1:1 adduct with 3 [2a]. To rationalize these seemingly contradictory results and to determine if HgCl₂ catalysis is a better route to the *trans*-metallacrown ethers than UV photolysis, we have studied the reactions of the three *cis*-metallacrown ethers 1–3 with HgCl₂ under identical conditions. These studies were carried out in mixtures of chloroform-*d* and water to test the phase transfer abilities of the *cis*-metallacrown ethers and the reactions were followed by ³¹P{¹H} NMR spectroscopy.

For 1 the *cis-trans* equilibrium is established in less than 3 min, which is the time needed to add the aqueous HgCl₂ solution to the chloroform-*d* solution of 1, shake the two layers vigorously and record qualitative ³¹P{¹H} NMR spectra. No change in this ratio is observed if the mixture is allowed to stand for several hours. The reaction is obviously catalytic, based on the fact that a 100:1 mole ratio of 1 to HgCl₂ was used. Equimolar amounts of 1 and 4 were present in the equilibrium mixture and the equilibrium constant for the reaction at 21°C, calculated using Eq. (2), was 1.0.

$$K_{\rm eq} = [trans]/[cis] \tag{2}$$

The HgCl₂-catalyzed isomerization of 2-5 was nearly identical to that of 1-4. With a 100:1 mole ratio of 2 to HgCl₂ the equilibrium was established within 3 min and gave equimolar amounts of 2 and 5. The equilibrium constant for the reaction at 21°C, calculated using Eq. (2), was 1.0. The results for the HgCl₂-catalyzed isomerizations of 1-4 and 2-5 are consistent with those of the UV photoisomerizations in which nearly equimolar amounts of the *cis*- and *trans*-metallacrown ethers are observed in the crude reaction products after 20 min of photolysis.

The HgCl₂-catalyzed isomerization of 3-6 was quite different from those of 1-4 and 2-5. No isomerization was observed with a 100:1 mole ratio of 3 to HgCl₂.

Table 7 Effect of $HgCl_2$ on the equilibrium between $3 \cdot HgCl_2$ and 6

HgCl ₂ :metallacrown ether	mol% $3 \cdot \text{HgCl}_2$	mol% 6
1:1	77.5	22.5
2:1	86.3	13.7
3:1	92.3	7.7
4:1	96.4	3.6



Fig. 4. *Cis-trans* equilibrium constants for various metallacrown ethers.

Table 8 Bond angles (°) around the Mo in the *trans*-metallacrown ethers

	4	5	6	7
P1-Mo-P2	177.01	175.69	173.77	172.0
Avg. P–Mo–C towards ring ($\angle PMoC_{svn}$)	89.56	90.32	92.02	87.6
Avg. P–Mo–C away from ring ($\angle PMoC_{anti}$)	90.55	89.65	88.00	92.8
Difference between ideal and observed ^a	+2.99	-4.31	-6.23	+8.0

 $^{a}(+)$ indicates that the P1–Mo–P2 angle is directed towards the same side of the molybdenum as the metallacrown ether ring; (-) indicates that the P1–Mo–P2 angle that is <180° is directed towards the opposite side of the molybdenum from the metallacrown ether ring.

When the mole ratio of **3** to $HgCl_2$ was changed to 20:1, the isomerization occurred slowly and, after 7 h, the **3:6** ratio was 64:36. With a 10:1 mole ratio of **3** to $HgCl_2$ the rate of the isomerization increased and, after 2 h, the **3:6** ratio was 56:44. No attempts were made to calculate the equilibrium constants for this isomerization because the $HgCl_2$ not only serves as a catalyst but also binds to **3** to form a bimetallic complex **3**·HgCl₂. This suggests that coordination of the $HgCl_2$ by **3** inhibits its ability to catalyze the isomerization of **3**–6, perhaps by saturating all of the coordination sites on the Hg^{2+} cation.

Because $HgCl_2$ does not bind strongly to the *trans*metallacrown ether **6** but does bind strongly to the *cis*-metallacrown ether **3**, it seemed likely that the addition of excess of $HgCl_2$ to the reaction mixture should

3.3. Cis-trans isomerizations in $Mo(CO)_4$ -containing metallacrown ethers

As shown in Fig. 4, changing the steric constraints in $Mo(CO)_4$ -containing metallacrown ether rings has a significant effect on the *cis-trans* equilibrium constants. As might be expected, steric bulk next to the phosphorus-donor group (10 and 11) shifts the equilibrium towards the *trans* isomer. Surprisingly, replacing the central ethylene in 2 with a 1,2-phenylene group in 8 has an equally strong effect in the opposite direction in spite of the fact that the steric requirements of the 1,2-phenylene group are transmitted to the *cis*-Mo(CO)₄ center through the flexible oxyethylene groups. This suggests that there are a limited number of

trans-Mo(CO)₄{Ph₂P(CH₂CH₂O)₅CH₂CH₂PPh₂-P,P'}, 6



trans-Mo(CO)₄{Ph₂P(CH₂CH₂O)₄CH₂CH₂PPh₂-P,P'}, 5



trans-Mo(CO)₄{Ph₂P(CH₂CH₂O)₃CH₂CH₂PPh₂-P,P'}, 4



Fig. 5. Ball and stick drawings of the *trans*-metallacrown ethers with oxyethylene bridges **4**–**6**, in equivalent orientations.

Table 9						
Selected	torsion	angles	(°)	for	4–7	

4		5		6		7	
Mo-P1-C1-C2	60.2	Mo-P1-C1-C2	65.5	Mo-P1-C1-C2	65.8	Mo-P1-C1-C2	-66.6
P1-C1-C2-O1	178.1	P1C1C2O1	-173.4	P1-C1-C2-O1	172.0	P1-C1-C2-O1	95.4
C1C2O1C3	165.7	C1-C2-O1-C3	-166.4	C1-C2-O1-C3	179.8	C1C2O1C3	-179.6
C2O1C3C4	-80.6	C2-O1-C3-C4	-61.5	C2-O1-C3-C4	-76.2	C2-O1-C3-C4	179.1
O1-C3-C4-O2	77.0	O1-C3-C4-O2	-50.5	O1-C3-C4-O2	73.7	O1-C3-C4-O2	82.9
C3-C4-O2-C5	177.1	C3-C4-O2-C5	157.9	C3-C4-O2-C5	-158.8	C3-C4-O2-C5	164.1
		C4-O2-C5-C6	-177.8	C4-O2-C5-C6	-174.2	C4-O2-C5-C10	84.4
		O2-C5-C6-O3	142.4	O2-C5-C6-O3	74.7	O2-C5-C10-O3	-16.2
				C5-C6-O3-C7	-174.1		
				C6-O3-C7-C8	-67.9		
				O3-C7-C8-O4	82.9		
		C5-C6-O3-C7	168.9	C7-C8-O4-C9	-156.7	C5-C10-O3-C11	-174.7
C4O2C5C6	-172.2	C6-O3-C7-C8	173.9	C8-O4-C9-C10	-172.7	C10-O3-C11-C12	170.9
O2-C5-C6-O3	-82.0	O3-C7-C8-O4	-79.6	O4-C9-C10-O5	-65.9	O3-C11-C12-O4	-70.3
C5-C6-O3-C7	-172.6	C7-C8-O4-C9	82.8	C9-C10-O5-C11	91.5	C11-C12-O4-C13	-145.4
C6-O3-C7-C8	178.1	C8-O4-C9-C10	178.4	C10-O5-C11-C12	130.4	C12-O4-C13-C14	178.4
O3-C7-C8-P2	85.6	O4-C9-C10-P2	-173.5	O5-C11-C12-P2	-173.7	O4-C13-C14-P2	-178.5
C7–C8–P2–Mo	-66.4	C9-C10-P2-Mo	-65.3	C11-C12-P2-Mo	-69.9	C13-C14-P2-Mo	-60.0

Table 10 Distances (Å) between the ether oxygens in the *trans*-metallacrown ethers

Bonds between oxygens	4		5		6		7	
3	01–02 02–03	3.047 3.040	01-02 02-03 03-04	2.864 3.372 3.057	01-02 02-03 03-04 04-05	3.035 2.898 3.087 2.882	01-02 02-03 03-04	3.050 2.683 2.826
6	01–03	5.527	01–03 02–04	5.633 6.083	01–03 02–04 03–05	5.861 5.374 5.167	01–03 02–04	4.476 4.491
9			01–04	7.619	O1–O4 O2–O5	7.976 6.368	01–04	5.332
12					O1–O5	8.314		

conformations for the metallacrown ether rings, most likely due to the steric bulk of the phosphorus-donor groups.

3.4. Solid state conformations

The molecular structures of **4**, **6** and *trans*- $Mo(CO)_4\{Ph_2P(CH_2CH_2O)_2 - 1 - C_6H_4 - 2 - (OCH_2CH_2)_2 - PPh_2 - P, P'\}$ (7) have been determined, and are compared to that of **5**, which was previously reported [1]. The coordination environment about the molybdenum in each of the complexes is a distorted octahedron with the phosphines occupying *trans* coordination sites.

One of the most interesting aspects of these structures is the insight that they provide into ring strain in the *trans*-metallacrown ethers. The magnitude of the ring strain is easily measured by the difference between

the ideal (180°) and observed P1-Mo-P2 bond angles. The direction of the ring strain, either towards or away from the metallacrown ether ring, is more difficult to determine. Perhaps the best means of estimating this is to compare the average of the P-Mo-C angles for the two carbonyls that point towards the metallacrown ether ring $(\angle PMoC_{syn})$ with the average of the P-Mo-C angles for the two carbonyls that point away from the metallacrown ether ring ($\angle PMoC_{anti}$). If $\angle PMoC_{syn}$ is smaller than $\angle PMoC_{anti}$, the P1-Mo-P2 angle is distorted towards the metallacrown ether ring, suggesting that the ligand is too small to span the *trans* positions. If $\angle PMoC_{svn}$ is larger than $\angle PMoC_{anti}$, the P1-Mo-P2 angle is distorted away from the metallacrown ether ring, suggesting that the ligand easily spans the trans positions and pushes the phosphines away from the metallacrown ether ring. From the data summarized in Table 8 the least distortion is observed

in 4 and is towards the metallacrown ether ring. The distortion in 5 is slightly larger than in 4 but is away from the metallacrown ether ring. The distortion in $\mathbf{6}$ is in the same direction as in 5 but is significantly greater while the distortion in 7 is even larger than in 6 but is directed towards the metallacrown ether ring as is that in 4. These data indicate that the ligands with only oxyethylene groups can readily span the trans positions of the octahedral metal center (in 4-6), and that the difficulty in packing these ligands on one side of the trans-Mo(CO)₄ group increases as the number of oxyethylene groups increases (4 < 5 < 6). In contrast, the metallacrown ether ring in 7, which contains a sterically constraining 1,2-phenylene group, has difficulty bridging the trans positions of the octahedral metal center. These inferences about the ring strain in the trans-metallacrown ethers are consistent with the values of K_{ct} that were discussed above. The K_{ct} values for $1 \rightleftharpoons 4$ and $2 \rightleftharpoons 5$ are identical, as expected from the lack of significant ring strain in either trans-metallacrown ether. In contrast, the $K_{\rm ct}$ value for $\mathbf{8} \rightleftharpoons \mathbf{7}$ is much smaller than for $1 \rightleftharpoons 4$ and $2 \rightleftharpoons 5$, consistent with the greater ring strain in 7.

The conformations of the metallacrown ether rings in the *trans*-metallacrown ethers are also of interest. As shown in Fig. 5, the conformations near the metal center for the *trans*-metallacrown ethers with oxyethylene bridges (**4**–**6**) are nearly identical. This is apparently due to the steric constraints imposed by the carbonyl ligands and the diphenylphosphino groups on the molybdenum. Thus the torsion angles about both P–C bonds and about the C–C and C–O bonds of one Ph₂PCH₂CH₂O group in **4**–**6** are nearly identical. In contrast, the steric constraints imposed by the 1,2-phenylene group in **7** result in a significantly different ring conformation as shown by the different torsion angles in Table 9.

The major conformational differences between the metallacrown ether rings in 4-6 occur after the first oxygens (O1 and O3 in 4, O1 and O4 in 5, and O1 and O5 in 6). The angle between the least-squares plane through the ether oxygens and the least-squares plane through Mo, P1, P2 and the centroids of the carbonyl carbons group on each side of the metallacrown ether ring (C33/C34 and C35/C36 for 4, C35/C37 and C36/C38 for 5 [1] and C37/C38 and C39/C40 for 6) is quite dependent on the size of the *trans*-metallacrown ether ring. This angle is significantly larger for 4 (68°) and 5 (72°) than for 6 (39.2°), suggesting that the large metallacrown ether ring in 6 folds to minimize the crystal packing forces.

The distances between the ether oxygens in *trans*metallacrown ethers should affect their abilities to bind the alkali metal cations. These distances are summarized in Table 10 for the four *trans*-metallacrown ethers. Distances between the oxygens separated by a single ethylene group are similar with one exception (O2–O3 for 5) because all the ethylene groups, except the one bridging the O2 and O3 oxygens in 5, are gauche. The distances between the other oxygens are more variable, but are significantly smaller in 7 with the sterically constraining 1,2-phenylene group than in the trans-metallacrown ethers with oxyethylene bridges. It is also interesting that the sterically constraining 1,2phenylene group in 7 causes the O1–O4 distance (5.332 Å) to be much smaller than the O1–O4 distance in 5 (7.619 Å), and even slightly smaller than the O1–O3 distance in 4 (5.527 Å). This is further support for the suggestion that the introduction of the sterically constraining groups into metallacrown ethers may greatly affect the abilities of these complexes to bind the alkali metal cations [2b,6].

As expected, the distances between the ether oxygens separated by more than one ethylene group are significantly larger in the *trans*-metallacrown ethers than in the *cis*-metallacrown ethers containing the same α,ω -bis(phosphine)polyether ligands. This is most easily observed for the distance between the first and last oxygens in the metallacrown ether ring (O1–O3: 4.481 Å for 1 [8] versus 5.527 Å for 4; O1–O5: 7.445 Å for 3 [10] versus 8.314 Å for 6). The longer O–O distances in the *trans*-metallacrown ethers may explain why these complexes, unlike the *cis*-metallacrown ethers, do not bind the alkali metal cations strongly.

3.5. ³¹P, ¹H, and ¹³C NMR spectroscopic studies

The ³¹P{¹H} NMR chemical shifts for the *trans*metallacrown ethers are downfield of those in the cismetallacrown ethers, indicating that the phosphorus is more deshielded in the trans-metallacrown ethers [1,3]. The ${}^{13}C{}^{1}H$ NMR chemical shifts of the C_{ipso} and C1 carbons in the trans-metallacrown ethers are also downfield of those in the cis-metallacrown ethers, consistent with the ${}^{31}P{}^{1}H$ NMR data. There is some variation in the differences in the chemical shifts for the three pairs of *cis*- and *trans*-metallacrown ethers ($\Delta \delta$: **4**–**1** = 14.88 ppm, **5**–**2** = 12.21 ppm, **6**–**3** = 12.09 ppm). The larger difference between the ${}^{31}P{}^{1}H$ NMR chemical shifts of 4 and 1 is consistent with the smaller metallacrown ether rings in these complexes. The smaller metallacrown ether ring in 4 may also explain why the ${}^{13}C{}^{1}H$ NMR resonance of either the C3 or C4 methylene of 4 is found 1.5 ppm farther downfield than any of the other ¹³C resonances of the ring methylenes in the metallacrown ethers.

4. Summary

Cis-trans isomerization of metallacrown ethers occurs when the *cis*-metallacrown ethers are irradiated with UV light, and is also efficiently catalyzed by HgCl₂. The HgCl₂-catalyzed isomerizations of 1-4 and 2-5 are very rapid. In contrast, the HgCl₂-catalyzed isomerization of 3-6 is significantly slower, probably because 3 strongly coordinates HgCl₂. The equilibrium constants for the *cis*-*trans* isomerization of Mo(CO)₄- containing metallacrown ethers are very sensitive to the nature of the metallacrown ether ring. Sterically bulky groups adjacent to the phosphine favor the *trans*-isomer and sterically constraining groups in the metallacrown ether ring favoring the *cis*-isomer. Sterically constraining groups in the metallacrown ether ring also affect the solid state conformation of the *trans*-metallacrown ether, as indicated by the smaller distances between the ether oxygens separated by more than one ethylene group.

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References

- [1] G.M Gray, C.H. Duffey, Organometallics 13 (1994) 1542.
- [2] (a) G.M Gray, C.H. Duffey, Organometallics 14 (1995) 245. (b)
 C.H. Duffey, C.H. Lake, G.M. Gray, Organometallics 17 (1998), 3550.
- [3] M. Hariharasarma, C.H. Lake, C.L. Watkins, G.M. Gray, J. Organomet. Chem. 580 (1999) 328.
- [4] E. Baumgartner, F.J.S. Reed, L.M. Venanzi, F. Bachechi, P. Mura, L. Zambonelli, Helv. Chim. Acta 66 (1983) 2752.
- [5] R.A. Leising, J.L. Grzybowski, K.J. Takeuchi, Inorg. Chem. 27 (1988) 1020.
- [6] G.M. Gray, F.P. Fish, C.H. Duffey, Inorg. Chim. Acta 246 (1996) 229 (Special edition on Macrocyclic Complexes).
- [7] (a) J. Powell, A. Kuksis, C.J. May, S.C. Nyberg, S.J. Smith, J. Am. Chem. Soc. 103 (1981) 5941. (b) J. Powell, S.C. Nyberg, S.J. Smith, Inorg. Chim. Acta 76 (1983) L75. (c) J. Powell, K.S. Ng, W.W. Ng, S.C. Nyberg, J. Organomet. Chem. 243 (1983) C1. (d) J. Powell, M. Gregg, A. Kuskis, P. Meindl, J. Am. Chem. Soc. 105 (1983) 1064.
 (e) J. Powell, M.R. Gregg, A. Kuksis, C.J. May, S.J. Smith, Organometallics 8 (1989) 2918. (f) J. Powell, A. Kuskis, C.J. May, P.E. Meindl, S.J. Smith, Organometallics 8 (1989) 2933. (g) J. Powell, M.R. Gregg, P.E. Meindl, Organometallics 8 (1989) 2942.
- [8] A. Varshney, G.M. Gray, Inorg. Chem. 30 (1991) 1748.
- [9] A. Varshney, M.L. Webster, G.M. Gray, Inorg. Chem. 31 (1992) 2580.
- [10] G.M. Gray, D.C. Smith Jr., C.H. Duffey, Inorg. Chim. Acta 300– 302 (2000) 581.