

*Journal of Organometallic Chemistry*, 434 (1992) 181–199  
 Elsevier Sequoia S.A., Lausanne  
 JOM 22522

## Coordinated 2-halo-1,3,2-dioxaphosphorinane ligands

### III. *cis*-Mo(CO)<sub>4</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> (E = O, S, NH; R = alkyl, aryl or ER = Cl, Br) complexes: syntheses, spectroscopic studies and the molecular structures of the *cis*-Mo(CO)<sub>4</sub>{<sup>1</sup>PrEP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> (E = O, NH) complexes

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(Received September 10, 1991)

#### Abstract

A study of the reactions of *cis*-Mo(CO)<sub>4</sub>(XP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O))<sub>2</sub> (X = Cl, Br) complexes with a variety of nucleophiles of the type HER (E = NH, O, S; R = H, alkyl, aryl) is reported. The <sup>13</sup>C, <sup>31</sup>P and <sup>95</sup>Mo NMR and IR data for the *cis*-Mo(CO)<sub>4</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> complexes are presented and compared to those previously reported for some Mo(CO)<sub>5</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)} and *cis*-Mo(CO)<sub>4</sub>(Ph<sub>2</sub>PER)<sub>2</sub> complexes. This comparison demonstrates that the effects of variations in the RE substituents in these complexes are similar to those previously observed for the Mo(CO)<sub>5</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)} complexes. The X-ray crystal structures of *cis*-Mo(CO)<sub>4</sub>-<sup>1</sup>PrOP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O))<sub>2</sub> (triclinic space group *P* $\bar{1}$ ; *a* = 8.818(3), *b* = 8.899(1), *c* = 18.847(2) Å;  $\alpha$  = 93.35(1),  $\beta$  = 89.46(2),  $\gamma$  = 115.31(1)°; *V* = 1334.6(4) Å<sup>3</sup>; *Z* = 2) and *cis*-Mo(CO)<sub>4</sub>-<sup>1</sup>PrNHP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O))<sub>2</sub> (monoclinic space group *C2/c*; *a* = 18.30(1), *b* = 10.72(2), *c* = 16.87(1) Å;  $\beta$  = 119.82(5)°, *V* = 2871(4) Å<sup>3</sup>; *Z* = 4) have also been determined. In these complexes, the O<sup>1</sup>Pr group is in an axial position, but the NH<sup>1</sup>Pr group is in an equatorial position.

#### Introduction

The reactions of coordinated P-donor ligands of the type R<sub>2</sub>PX (R<sub>2</sub> = Ph<sub>2</sub>, Me<sub>2</sub>, OalkyleneO; X = halogen) with N-, O- and S-nucleophiles can be used to

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prepare complexes containing P-donor ligands with a variety of unusual substituents [1–14]. They can also be used to prepare complexes with unusual chelating ligands [15–20] and bimetallic complexes [21–31]. These reactions are often the only route to these complexes owing to the instabilities of the free ligands.

The factors affecting the rates of halide substitution in  $\text{Mo}(\text{CO})_{6-n}(\text{R}_2\text{PX})_n$  ( $\text{X} = \text{Cl}, \text{Br}$ ) complexes by O-, S- and N-nucleophiles are poorly understood, and this limits the usefulness of these reactions. In order to better understand these factors, we have studied the reactions of a variety of  $\text{Mo}(\text{CO})_{6-n}(\text{R}_2\text{PX})_n$  ( $\text{R}_2 = \text{Ph}_2, \text{OCH}_2\text{CMe}_2\text{O}$ ;  $\text{X} = \text{Cl}, \text{Br}$ ) complexes with N-, O- and S-nucleophiles [1,5,7,13,14]. In this paper, we present the results of our studies of the reactivities of *cis*- $\text{Mo}(\text{CO})_4\{\text{XP}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\}_2$  complexes and compare these results with those obtained from earlier studies of related complexes [1,13,14]. The products of these reactions have been characterized by multinuclear NMR and IR spectroscopy, and the effects of variations in the phosphorus substituents on the chemical shifts of the carbonyl  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{95}\text{Mo}$  NMR resonances and on the carbonyl IR stretching force constants are compared to those reported for related complexes [13–17,32–36]. X-Ray crystal structures of two of the complexes, *cis*- $\text{Mo}(\text{CO})_4\{\text{PrEP}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\}_2$  ( $\text{E} = \text{NH}, \text{O}$ ), have also been determined, and the results of these studies are presented.

## Experimental

Phosphorus trichloride, phosphorus tribromide, all solid alcohols and amines and all thiols were opened under nitrogen and used as received. Liquid alcohols and amines were dried over molecular sieves, and tetrahydrofuran (THF) and diethyl ether were distilled from calcium hydride under nitrogen before use. 2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane (2-Cl-dmp) [37], 2-bromo-5,5-dimethyl-1,3,2-dioxaphosphorinane (2-Br-dmp) [13] and  $\text{Mo}(\text{CO})_4(\text{norbondiene})$  ( $\text{Mo}(\text{CO})_4(\text{nbnd})$ ) [38] were prepared by literature methods. The ligands and solutions of the complexes were handled under a nitrogen atmosphere.

### *cis*- $(\text{CO})_4\text{Mo}\{\text{ClP}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\}_2$ (I)

Solid  $\text{Mo}(\text{CO})_4(\text{nbnd})$  (4.56 g, 15.2 mmol) was added to a solution of 5.11 g (30.3 mmol) of 2-Cl-dmp in 30 ml of hexanes. The mixture was stirred for 10 min and then the solution was filtered to yield 6.38 g (94.4%) of pure I as an off-white solid (MS: 546, 462, 435, 133, 69 *m/z*).

### *cis*- $(\text{CO})_4\text{Mo}\{\text{BrP}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\}_2$ (II)

The above procedure was repeated with 33.0 g (156 mmol) of 2-Br-dmp and 23.76 g (79.2 mmol) of  $\text{Mo}(\text{CO})_4(\text{nbnd})$  to yield 44.4 g (88.5%) of pure II as an off-white solid (MS: 634, 550, 522, 133, 69 *m/z*).

### *cis*- $(\text{CO})_4\text{Mo}\{\text{nPrOP}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\}_2$ (III)

A solution of 0.74 g (9.0 mmol) of sodium n-propoxide and 1.27 g (2.00 mmol) of II in 10 ml of n-propanol was stirred at ambient temperature for 44 h and then evaporated to dryness. The residue was treated with 40 ml of a 1:1 diethyl ether/hexanes mixture and 50 ml of water. The organic layer was separated, washed with 50 ml of water, dried over anhydrous  $\text{MgSO}_4$  and filtered. The filtrate

was evaporated to dryness to yield 1.10 g (92.7%) of pure **III** as a white solid (MS: 594, 566, 536, 506, 476, 133, 69 *m/z*).

*cis*-(CO)<sub>4</sub>Mo{<sup>n</sup>PrOP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> (**IV**)

The above procedure was repeated with 0.74 g (9.0 mmol) of sodium i-propoxide and 1.27 g (2.00 mmol) of **II** in 10 ml of i-propanol to yield 0.93 g (78%) of pure **IV** as a white solid (MS: 594, 566, 538, 510, 508, 133, 69 *m/z*).

*cis*-(CO)<sub>4</sub>Mo{<sup>n</sup>PrSP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> (**V**)

A solution of 0.79 g (9.6 mmol) of lithium n-propanethiolate and 1.64 g (3.00 mmol) of **I** in 20 ml of THF was stirred at ambient temperature for 66 h and then evaporated to dryness. The residue was treated with 50 ml of dichloromethane and 50 ml of a 5% aqueous Na<sub>2</sub>CO<sub>3</sub> solution. The organic layer was separated, dried over anhydrous MgSO<sub>4</sub> and then filtered. The filtrate was evaporated to dryness, and the residue was recrystallized from n-hexane to yield 1.40 g (74.8%) of pure **V** as a white crystalline solid (MS: 626, 598, 542, 471, 133, 69 *m/z*).

*cis*-(CO)<sub>4</sub>Mo{<sup>n</sup>PrNHP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> (**VI**)

A solution of 1.27 g (2.00 mmol) of **II** in 10 ml of n-propylamine was refluxed for 4 h and then evaporated to dryness. The residue was treated with 20 ml of diethyl ether, and the solution was filtered through a 1 × 2 cm alumina column. The alumina was washed with a 20 ml portion of diethyl ether, and the filtrate and wash were evaporated to dryness to yield 1.16 g (97.8%) of pure **VI** as a colorless oil which solidified upon cooling at -5°C (MS: 592, 564, 536, 508, 480, 478, 421, 133, 69 *m/z*).

*cis*-(CO)<sub>4</sub>Mo{<sup>i</sup>PrNHP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> (**VII**)

The above procedure was repeated with 1.27 g (2.00 mmol) of **II** and 10 ml of i-propylamine to yield 1.15 g (93.4%) of pure **VII** as a colorless oil that solidified upon cooling to -5°C (MS: 592, 564, 536, 508, 480, 478, 421, 133, 69 *m/z*).

*cis*-(CO)<sub>4</sub>Mo{Me-*p*-C<sub>6</sub>H<sub>4</sub>OP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> (**VIII**)

A solution of 0.78 g (6.0 mmol) of sodium *p*-methylphenoxide and 1.27 g (2.00 mmol) of **II** in 20 ml of THF was stirred at ambient temperature for 6 days and then evaporated to dryness. The residue was treated with 40 ml of a 2:1 diethyl ether/hexanes mixture and 50 ml of a 5% aqueous Na<sub>2</sub>CO<sub>3</sub> solution. The organic layer was separated, washed with 50 ml of water, dried over MgSO<sub>4</sub> and filtered. The filtrate was reduced in volume to yield 1.23 g (89.3%) of pure **IX** as an off-white solid upon cooling (MS: 606, 578, 478, 394, 366, 338, 240, 133, 91, 69 *m/z*).

*cis*-(CO)<sub>4</sub>Mo{Me-*p*-C<sub>6</sub>H<sub>4</sub>SP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> (**IX**)

The above procedure was repeated using 0.88 g (6.0 mmol) of sodium *p*-methylthiophenoxide and 1.27 g (2.00 mmol) of **II** to yield 1.26 g (87.5%) of pure **X** as an off-white crystalline solid (MS: 494, 466, 410, 382, 256, 133, 91, 69 *m/z*).

[Et<sub>3</sub>NH][*cis*-(CO)<sub>4</sub>Mo{[(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)PO]<sub>2</sub>H}]<sub>2</sub> (**X**)

A solution of 3.00 g (4.73 mmol) of **II**, 3.0 ml of water and 3.0 ml of triethylamine in 30 ml of acetone was stirred at ambient temperature for 18 h and

Table 1

CO  $^{13}\text{C}$  and  $^{17}\text{O}$ ,  $^{31}\text{P}$  and  $^{95}\text{Mo}$  data for the *cis*- $\text{Mo}(\text{CO})_4\{\text{REP}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})_2\}$  complexes <sup>a</sup>

RE	<i>trans</i> CO		<i>cis</i> CO			P		Mo		
	$\delta^{13}\text{C}$ (ppm)	$ ^2J(\text{PC}) + ^2J(\text{P}'\text{C}) $ (Hz)	$\delta^{13}\text{C}$ (ppm)	$ ^2J(\text{PC}) $ (ppm)	$\delta^{17}\text{O}$ (Hz)	$\delta^{31}\text{P}$ (ppm)	$\delta^{95}\text{Mo}$ (ppm)	$ ^1J(\text{MoP}) $ (Hz)	$\Delta\nu_{1/2}$ (Hz)	
Cl (I)	209.37	39.6	367.9	204.42	14.3	357.5	161.72	-1639.7	246	45
Br (II)	209.98	41.8	370.1	205.08	13.9	358.5	159.13	-1567.2	247	49
O <sup>n</sup> Pr (III)	211.94	27.1	360.5	207.51	14.3	358.1sh	154.99	-1824.4	223	24
O <sup>i</sup> Pr (IV)	212.13	27.8	360.1	207.68	14.3	357.7	154.38	-1809.5	222	28
S <sup>n</sup> Pr (V)	212.39	31.5	364.9	207.09	13.2	358.1	184.97	-1651.8	220	73
NH <sup>n</sup> Pr (VI)	213.76	21.2	362.5	208.72	13.2	358.9	159.47	-1815.1	195	28
NH <sup>i</sup> Pr (VII)	213.89	21.2	362.5	208.88	13.2	358.9	158.28	-1812.0	195	24
OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -Me (VIII)	210.60	30.8	360.9	205.98	14.3	358.5sh	151.22	-1804.9	234	21
SC <sub>6</sub> H <sub>4</sub> - <i>p</i> -Me (IX)	211.38	34.4	364.5	205.76	13.2	358.1	178.95	-1639.5	229	99
O <sub>2</sub> H <sup>-</sup> Et <sub>3</sub> NH <sup>+</sup> (X)	216.62	21.2	361.3	209.01	14.3	353.3	134.63	-1840.3	201	21
OSiMe <sub>3</sub> (XI)	212.81	29.3	360.1	207.90	15.0	355.7	149.37	-1773.9	227	30

<sup>a</sup> sh, shoulder.

then evaporated to dryness. The residue was washed with four 25-ml aliquots of water, and the insoluble portion was recrystallized from a dichloromethane/hexanes mixture to yield 2.24 g (77.8%) of pure **XI** as a white crystalline solid.

#### *cis*-(CO)<sub>4</sub>Mo{Me<sub>3</sub>SiOP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> (**XI**)

A solution of 1.22 g (2.00 mmol) of **X**, 0.51 ml (4.00 mmol) of chlorotrimethylsilane and 0.28 ml (2.00 mmol) of triethylamine in 20 ml of THF was stirred at ambient temperature for 1 h and then evaporated to dryness. The residue was treated with 20 ml of diethyl ether, and the resulting mixture was filtered. The filtrate was evaporated to dryness, and the residue was washed with methanol to yield 0.74 g (60%) of pure **XII** as an off-white solid (MS: 654, 598, 570, 542, 540, 133, 73, 69 *m/z*).

#### Characterization of the complexes

All of the complexes were characterized by  $^{13}\text{C}$ ,  $^{17}\text{O}$ ,  $^{31}\text{P}$  and  $^{95}\text{Mo}$  NMR spectroscopy, and their NMR spectral data are summarized in Tables 1 and 2. The NMR spectra of 0.50 *M* *d*<sub>1</sub>-chloroform solutions of the complexes in nitrogen-filled 10 mm NMR tubes were run on a JEOL FX90Q multinuclear NMR spectrometer (references:  $^{13}\text{C}_{\text{mt}}$  TMS;  $^{17}\text{O}_{\text{ext}}$  H<sub>2</sub>O;  $^{31}\text{P}_{\text{ext}}$  85% H<sub>3</sub>PO<sub>4</sub>;  $^{95}\text{Mo}_{\text{ext}}$  2.0 *M* Na<sub>2</sub>MoO<sub>4</sub>). A complex was considered to be pure if a single resonance appeared in its  $^{31}\text{P}$  NMR spectrum and if all its  $^{13}\text{C}$  NMR resonances could be assigned.

All neutral complexes were characterized by IR spectroscopy (2100–1800  $\text{cm}^{-1}$ ). The spectra were run on a Perkin–Elmer 283B infrared spectrometer with dilute *n*-hexanes solutions of the complexes and pure *n*-hexanes in matched 0.20 mm NaCl cells. Three medium to strong absorptions and, in some cases, a poorly resolved shoulder, were observed. The highest energy absorption was always assigned to the A<sub>1</sub><sup>(1)</sup> band. The assignment of the lower energy absorptions to the A<sub>1</sub><sup>(2)</sup>, B<sub>1</sub> and B<sub>2</sub> bands was carried out as follows. Approximate infrared stretching force constants (Cotton–Kraihanzel approximation [39]) were calculated from all

Table 2

Aliphatic  $^{13}\text{C}$  NMR data for the *cis*- $\text{Mo}(\text{CO})_4(\text{REP}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}))_2$  complexes <sup>a</sup>

RE	CH <sub>2</sub>		C		CH <sub>3</sub>	Group	Other			
	$\delta^{13}\text{C}$ (ppm)	$ ^2J(\text{PC})+^4J(\text{P}'\text{C}) $ (Hz)	$\delta^{13}\text{C}$ (ppm)	$ ^3J(\text{PC})+^5J(\text{P}'\text{C}) $ (Hz)			$\delta^{13}\text{C}$ (ppm)	$ ^nJ(\text{PC})+^{n+2}J(\text{P}'\text{C}) $ (Hz)	<i>n</i>	
Cl (I)	73.31aq	8.8	32.12aq	5.9	22.18s 21.72s 21.46s 20.91s					
Br (II)	75.53aq	6.6	32.52aq	5.9	23.53s 21.75s					
O <sup>n</sup> Pr (III)	72.09aq	5.1	32.42aq	6.6	22.12s	CH <sub>3</sub>	10.44s			
O <sup>1</sup> Pr (IV)	72.15aq	5.9	32.32aq	6.6	23.83s 22.21s	CH <sub>3</sub> CH	22.21s 69.06aq	6.6	3	
S <sup>n</sup> Pr (V)	73.32aq	8.1	32.71aq	5.9	22.53s 22.08s	CH <sub>3</sub> CH <sub>3</sub> CH <sub>2</sub>	13.66s 24.29s			2
NH <sup>n</sup> Pr (VI)	73.84s		32.32aq	7.3	23.15s 21.62s	CH <sub>3</sub> CH <sub>3</sub> CH <sub>2</sub>	11.32s 25.13aq	4.4	3	
NH <sup>1</sup> Pr (VII)	73.97s		32.32aq	7.3	23.22s 21.56s	CH <sub>3</sub> CH	26.08s 42.56aq	5.9	2	
OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -Me (VIII)	72.54aq	5.9	32.35aq	5.9	22.30s 20.71s	CH <sub>3</sub>	22.04s			
SC <sub>6</sub> H <sub>4</sub> - <i>p</i> -Me (IX)	73.81aq	7.3	32.61aq	5.9	22.04s 21.14s	CH <sub>3</sub>	21.72s			
O <sub>2</sub> H <sup>-</sup> Et <sub>3</sub> NH <sup>+</sup> (X)	71.60s		32.55aq	5.9	22.82s 21.92s	CH <sub>3</sub> CH <sub>2</sub>	8.49s 45.68s			
OSiMe <sub>3</sub> (XI)	71.44aq	5.9	32.32aq	5.9	22.34s 22.18s	CH <sub>3</sub>	1.07s			

<sup>a</sup> s, singlet; aq, apparent quintet (A portion of an AXX' spin system).

possible assignments of these bands. The approximate stretching force constants were then used to calculate the frequency of the band assumed to be due to the poorly resolved shoulder. The assignments that gave the best match between the calculated and observed frequencies for this band and for which  $k_1 < k_2$  are given in Table 3. When no poorly resolved shoulder was observed, the band assignments were made so as to be consistent with those made for the other complexes.

Mass spectra of all of the complexes, except for X, which is ionic, were obtained on a Hewlett Packard 5993/95 GS/MS using the solids inlet probe. Parent ions were observed for all of the complexes except VIII and IX.

#### Collection and reduction of X-ray data

Crystals of IV and VII were grown from dichloromethane/heptanes. A clear block of IV of dimensions  $0.29 \times 0.26 \times 0.16 \text{ mm}^3$ , and a clear prism of VII of dimensions  $0.16 \times 0.26 \times 0.81 \text{ mm}^3$  were used for intensity measurements. Diffraction data were collected on a Syntex P2<sub>1</sub> for IV and on a Nicolet P3<sub>F</sub> for VII. Cu-K<sub>α</sub> radiation with a graphite monochromator for IV and a Ni filter for VII was

Table 3

Carbonyl IR stretching frequencies, force constants and calculated frequency for the B<sub>2</sub> band

RE	A <sub>1</sub> <sup>(1)</sup>	A <sub>1</sub> <sup>(2)</sup>	B <sub>1</sub>	B <sub>2</sub>	k <sub>1</sub>	k <sub>2</sub>	k <sub>1</sub>	B <sub>2</sub> (calc.)
Cl (I)	2058	1982	1961 <sup>a</sup>	1971sh	15.98	16.11	0.29	1971
Br (II)	2056	1980sh	1954	<sup>a</sup>	15.99	16.01	0.30	1971
O <sup>n</sup> Pr (III)	2043	1961	1936	1948sh	15.67	15.76	0.32	1950
O <sup>i</sup> Pr (IV)	2042	1961	1933	1950sh	15.70	15.72	0.32	1952
S <sup>n</sup> Pr (V)	2043	1962	1940	<sup>a</sup>	15.66	15.81	0.31	1950
NH <sup>n</sup> Pr (VI)	2030	1942	1919	1930sh	15.35	15.53	0.33	1929
NH <sup>i</sup> Pr (VII)	2029	1941	1918	1928sh	15.34	15.51	0.33	1928
OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -Me (VIII)	2048	1964	1945	<sup>a</sup>	15.67	15.90	0.31	1950
SC <sub>6</sub> H <sub>4</sub> - <i>p</i> -Me (IX)	2045	1963	1944	<sup>a</sup>	15.66	15.87	0.31	1950
OSiMe <sub>3</sub> (XI)	2042	1957	1932	1943sh	15.60	15.72	0.32	1945

<sup>a</sup> Not observed.

used for intensity measurements. Unit cell parameters were determined accurately by least squares fits of Cu-K<sub>α1</sub> 2θ values (λ(Cu-K<sub>α1</sub>) = 1.5402 Å) for 25 high 2θ reflections [40]. Intensity data were measured with a step-scan technique. Ten reflections were periodically monitored and showed no loss of intensity during the data collection. Standard deviations in the intensities were approximated by the equation:

$$s^2(\mathbf{I}) = s^2(\mathbf{I})_{\text{counting statistics}} + (D\mathbf{I})^2$$

where the coefficient ( $D = 0.009$  for **IV**,  $0.020$  for **VII**) of  $\mathbf{I}$  was calculated from the variations in intensities of the monitored reflections. Lorentz and polarization corrections appropriate for a monochromator with 50% perfect character were applied. An absorption correction for intensities of the data from **IV** was applied (min transmission was 0.267 and max transmission was 0.507) [41]. No absorption correction for the data from **VII** was applied.

#### Solution and refinement of the structure

All of the calculations were carried out using the CRYM system of computer programs [42]. Partial trial solutions for **IV** (23 atoms) and **VII** (6 atoms) were obtained by Direct Methods, using GENTAN [43] and MULTAN [44], respectively. Subsequently Fourier syntheses clearly revealed the other non-hydrogen atoms of the complexes. Hydrogen atoms were observed in difference maps very close to positions generated using planar or tetrahedral geometry, and generated positions were used for each structure. The structures were refined by least squares with the coordinates and anisotropic thermal parameters for non-hydrogen atoms included in the refinement. Isotropic thermal parameters for hydrogen atoms were set 0.5 units higher than the isotropic equivalents of the thermal parameters of the attached heavier atoms. The function minimized in the refinement was  $\sum w(F_o^2 - F_c^2)^2$ , where weights  $w$  were  $1/\sigma^2(F_o^2)$ . Atomic form factors were from Doyle and Turner [45], except for hydrogens which were from Stewart *et al.* [46]. In the final refinement cycles, all shifts were less than  $0.23\sigma$  for **IV** and  $0.05\sigma$  for **VII**. A final difference map showed no peaks greater than  $0.7 \text{ e } \text{Å}^{-3}$  for **IV** and  $0.2 \text{ e } \text{Å}^{-3}$  for **VII**. Relevant crystal and experimental data for the complexes are given in Table 4. The positional and isotropic thermal parameters of all non-hydrogen atoms in **IV**

Table 4

Crystal data and data collection procedures for **IV** and **VII**

Formula	$C_{20}H_{34}MoO_{10}P_2$	$C_{20}H_{36}MoN_2O_8P_2$
Molecular weight (Da)	592.37	590.40
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
$a$ (Å)	8.818(3)	18.30(1)
$b$ (Å)	8.899(1)	10.72(2)
$c$ (Å)	18.847(2)	16.87(1)
$\alpha$ (°)	93.35(1)	
$\beta$ (°)	89.46(1)	119.82(5)
$\gamma$ (°)	115.36(1)	
$V$ (Å <sup>3</sup> )	1134.6(4)	2871(4)
$Z$	2	4
$\rho$ (g/cm <sup>3</sup> )	1.47	1.34
Crystal dimensions (mm)	0.29 × 0.26 × 0.16	0.16 × 0.26 × 0.81
$\mu$ (Cu- $K_\alpha$ ) (cm <sup>-1</sup> )	53.4	48.1
Radiation (Å)	Cu- $K_\alpha$ (1.5418)	Cu- $K_\alpha$ (1.5418)
Temperature (K)	123	291
$2\theta$ limits (°)	$2.0 \leq 2\theta \leq 136$	$2.0 \leq 2\theta \leq 136$
Scan type	$\omega-2\theta$	$\omega-2\theta$
Scan speed (°/min)	2	2
Scan width (°)	3.4	3.4
Number of unique data	4413	1000
Number of data with $I > 3\sigma$	4324	930
$R$ (%)	4.1	4.1
$R_w$ (%)	10.0	9.7
Standard deviation of fit	6.41	3.80

and **VII** are given in Table 5, and bond lengths and angles in **IV** and **VII** are given in Tables 6 and 7. Pertinent torsion angles for **IV** and **VII** are given in Table 8. Tables of anisotropic thermal parameters, close intermolecular contacts, positional parameters for hydrogen atoms and structure factors are available from the authors. ORTEP drawings of the molecules with the atom numbering schemes are shown in Figs. 1 and 2. Ball and stick drawings of the 1,3,2-dioxaphosphorinane rings and substituents in each structure are shown in Figs. 3 and 4.

## Results and discussion

### Syntheses

We have reported that the rates of halide substitution by N-, O- and S-nucleophiles in  $Mo(CO)_5(XP(OCH_2CMe_2CH_2O))$  (X = Cl (**XII**), Br (**XIII**)) are much lower than in  $Mo(CO)_5(Ph_2PCI)$  (**XIV**) and that bromides are more rapidly displaced than chlorides [13]. We have now extended this study to include *cis*- $Mo(CO)_4(XP(OCH_2CMe_2CH_2O))_2$  (X = Cl (**I**), Br (**II**)), prepared as shown in eq. 1.

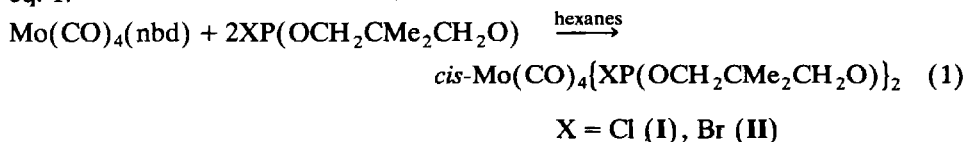


Table 5

Fractional coordinates with estimated standard deviations ( $\times 10^4$ ) and  $B_{\text{eq}}$  ( $\text{\AA}^2$ ) for IV and VII <sup>a</sup>

	IV			VII					
	x	y	z	$B_{\text{eq}}$		x	y	z	$B_{\text{eq}}$
Mo	8638(1)	4267(1)	2444(1)	0.79(1)	Mo	5000	277(1)	7500	4.11(2)
O(1)	6661(6)	4146(5)	3010(2)	1.9(2)	O(1)	3812(5)	268(6)	6416(7)	5.2(2)
O(2)	5534(4)	4104(4)	3342(2)	2.8(1)	O(1)	3167(4)	286(6)	5781(5)	8.1(2)
O(2)	7262(5)	2206(4)	1815(2)	1.5(1)	O(2)	5305(6)	1609(6)	6888(7)	6.0(2)
O(2)	6516(4)	1073(3)	1437(1)	2.4(1)	O(2)	5499(7)	2392(5)	6552(7)	9.4(3)
O(3)	8163(5)	5677(5)	1763(2)	1.7(1)	P(1)	5287(1)	-1393(1)	6696(1)	3.99(5)
O(3)	7875(4)	6492(4)	1386(2)	2.4(1)	N(5)	4557(4)	-2460(5)	6269(5)	5.7(2)
O(4)	10183(5)	6376(5)	3032(2)	1.7(1)	O(6)	4485(6)	-3473(7)	5674(6)	6.8(3)
O(4)	11036(4)	7550(3)	3354(2)	2.6(1)	O(7)	3659(8)	-3501(9)	4853(7)	10.9(4)
P(1)	11035(1)	4549(1)	1703(1)	0.87(3)	O(8)	4700(11)	-4692(7)	6164(11)	9.8(4)
O(A1)	12621(3)	6300(3)	1835(1)	1.22(9)	O(3)	5368(3)	-1054(4)	5815(3)	4.6(2)
O(A2)	13962(5)	6785(4)	1317(2)	1.4(1)	O(4)	6161(3)	-2198(3)	7267(4)	5.4(1)
O(A3)	13300(5)	6762(4)	567(2)	1.2(1)	O(A1)	6915(6)	-1627(6)	7411(6)	5.4(2)
O(MA1)	12563(6)	8029(5)	530(2)	1.8(2)	O(A2)	6910(6)	-1340(6)	6506(7)	4.9(2)
O(MA2)	14764(6)	7171(5)	59(2)	2.1(2)	O(A3)	6133(6)	-492(6)	5960(6)	5.7(2)
O(A4)	11959(5)	5012(4)	371(2)	1.2(1)	O(MA1)	6854(8)	-2489(9)	6006(8)	7.1(3)
O(A5)	10579(3)	4521(3)	876(1)	1.07(9)	O(MA2)	7685(7)	-624(9)	6709(9)	7.2(3)
O(5)	11965(3)	3349(3)	1703(1)	1.26(9)					
O(6)	11066(5)	1537(4)	1697(2)	1.5(1)					
O(7)	10468(6)	805(5)	949(2)	2.0(2)					
O(8)	12283(6)	950(5)	2004(2)	2.2(2)					
P(2)	9204(1)	2714(1)	3353(1)	0.96(3)					
O(B1)	9200(3)	3531(3)	4139(1)	1.10(9)					
O(B2)	9808(5)	2948(4)	4734(2)	1.3(1)					
O(B3)	11578(5)	3119(4)	4613(2)	1.3(1)					
O(MB1)	12816(5)	4952(4)	4552(2)	1.7(1)					
O(MB2)	12106(5)	2412(5)	5234(2)	1.8(1)					
O(B4)	11580(5)	2103(4)	3932(2)	1.3(1)					
O(B5)	11000(3)	2678(3)	3327(1)	1.22(9)					
O(9)	8062(3)	764(3)	3428(1)	1.29(9)					
O(10)	6234(5)	-10(5)	3333(2)	1.6(1)					
O(11)	5767(6)	-1790(5)	3081(2)	2.4(2)					
O(12)	5410(6)	158(5)	4022(2)	2.4(2)					

<sup>a</sup>  $B_{\text{eq}} = 4/3 (a^2 B_{11} + b^2 B_{22} + c^2 B_{33} + ab \cos \gamma B_{12} + ac \cos \beta B_{13} + bc \cos \alpha B_{23})$ .



Table 6

## Bond lengths and angles with estimated standard deviations for IV

Atoms			
<i>Bond lengths (Å)</i>			
Mo–C(1)	2.003(4)	C(A3)–C(A4)	1.526(4)
Mo–C(2)	2.028(3)	C(A4)–O(A5)	1.467(4)
Mo–C(3)	2.013(3)	O(5)–C(6)	1.461(3)
Mo–C(4)	2.051(3)	C(6)–C(7)	1.518(5)
Mo–P(1)	2.452(1)	C(6)–C(8)	1.511(5)
Mo–P(2)	2.444(1)	P(2)–O(B1)	1.612(2)
C(1)–O(1)	1.157(5)	P(2)–O(B5)	1.598(3)
C(2)–O(2)	1.147(4)	P(2)–O(9)	1.605(2)
C(3)–O(3)	1.146(4)	O(B1)–C(B2)	1.460(4)
C(4)–O(4)	1.135(4)	C(B2)–C(B3)	1.519(5)
P(1)–O(A1)	1.595(2)	C(B3)–C(MB1)	1.537(4)
P(1)–O(A5)	1.609(2)	C(B3)–C(MB2)	1.527(4)
P(1)–O(5)	1.601(2)	C(B3)–C(B4)	1.527(4)
O(A1)–C(A2)	1.459(4)	C(B4)–O(B5)	1.457(4)
C(A2)–C(A3)	1.529(5)	O(9)–C(10)	1.465(5)
C(A3)–C(MA1)	1.528(3)	C(10)–C(11)	1.503(3)
C(A3)–C(MA2)	1.528(6)	C(10)–C(12)	1.514(6)
<i>Angles (°)</i>			
C(1)–Mo–C(2)	93.7(1)	C(A2)–C(A3)–C(MA2)	107.7(3)
C(1)–Mo–C(3)	88.9(1)	C(MA1)–C(A3)–C(A4)	110.1(3)
C(1)–Mo–C(4)	90.6(1)	C(MA2)–C(A3)–C(A4)	109.2(2)
C(1)–Mo–P(1)	176.2(1)	C(A3)–C(A4)–O(A5)	111.1(2)
C(1)–Mo–P(2)	88.0(1)	P(1)–O(A5)–C(A4)	117.7(2)
C(2)–Mo–C(3)	89.7(1)	P(1)–O(5)–C(6)	123.0(2)
C(2)–Mo–C(4)	175.7(2)	O(5)–C(6)–C(7)	110.5(2)
C(2)–Mo–P(1)	86.8(1)	O(5)–C(6)–C(8)	105.7(3)
C(2)–Mo–P(2)	94.2(1)	C(7)–C(6)–C(8)	113.0(2)
C(3)–Mo–C(4)	89.9(1)	Mo–P(2)–O(B1)	111.2(1)
C(3)–Mo–P(1)	87.3(1)	Mo–P(2)–O(B5)	116.1(1)
C(3)–Mo–P(2)	175.2(1)	Mo–P(2)–O(9)	122.1(1)
C(4)–Mo–P(1)	88.9(1)	P(2)–O(B1)–C(B2)	118.4(1)
C(4)–Mo–P(2)	86.4(1)	O(B1)–P(2)–O(B5)	102.7(1)
P(1)–Mo–P(2)	95.8(1)	O(B1)–P(2)–O(9)	103.6(1)
Mo–C(1)–O(1)	178.9(3)	O(B5)–P(2)–O(9)	98.7(1)
Mo–C(2)–O(2)	177.3(3)	O(B1)–C(B2)–C(B3)	111.5(3)
Mo–C(3)–O(3)	178.5(3)	C(B2)–C(B3)–C(B4)	108.6(3)
Mo–C(4)–O(4)	179.6(3)	C(MB1)–C(B3)–C(MB2)	109.6(3)
Mo–P(1)–O(A1)	113.4(1)	C(B2)–C(B3)–C(MB1)	111.0(2)
Mo–P(1)–O(A5)	110.5(1)	C(B2)–C(B3)–C(MB2)	108.9(3)
Mo–P(1)–O(5)	124.9(1)	C(MB1)–C(B3)–C(B4)	110.0(3)
O(A1)–P(1)–O(A5)	103.2(1)	C(MB2)–C(B3)–C(B4)	108.6(2)
O(A1)–P(1)–O(5)	99.2(1)	C(B3)–C(B4)–O(B5)	110.7(2)
O(A5)–P(1)–O(5)	103.2(1)	P(2)–O(B5)–C(B4)	119.4(2)
P(1)–O(A1)–C(A2)	118.5(2)	P(2)–O(9)–C(10)	123.2(1)
O(A1)–C(A2)–C(A3)	111.6(3)	O(9)–C(10)–C(11)	105.8(3)
C(A2)–C(A3)–C(A4)	108.4(2)	O(9)–C(10)–C(12)	110.0(3)
C(MA1)–C(A3)–C(MA2)	110.4(2)	C(11)–C(10)–C(12)	113.2(3)
C(A2)–C(A3)–C(MA1)	110.9(2)		

Table 7

Bond lengths and angles with estimated standard deviations for **VII**

Atoms			
<i>Bond lengths (Å)</i>			
Mo–C(1)	2.029(8)	C(6)–C(7)	1.457(13)
Mo–C(2)	1.997(7)	C(6)–C(8)	1.491(13)
Mo–P(1)	2.455(1)	O(3)–C(A3)	1.428(6)
C(1)–O(1)	1.134(11)	O(4)–C(A1)	1.416(6)
C(2)–O(2)	1.162(10)	C(A1)–C(A2)	1.553(12)
P(1)–N(5)	1.629(5)	C(A2)–C(A3)	1.547(10)
P(1)–O(3)	1.608(5)	C(A2)–C(MA1)	1.467(13)
P(1)–O(4)	1.642(4)	C(A2)–C(MA2)	1.493(9)
N(5)–C(6)	1.440(10)		
<i>Angles (°)</i>			
C(1)–Mo–C(2)	89.3(3)	N(5)–C(6)–C(8)	111.5(8)
C(1)–Mo–P(1)	85.7(2)	C(7)–C(6)–C(8)	111.8(8)
C(2)–Mo–P(1)	92.5(2)	P(1)–O(3)–C(A3)	118.0(5)
Mo–C(1)–O(1)	176.1(6)	P(1)–O(4)–C(A1)	117.1(4)
Mo–C(2)–O(2)	178.3(8)	O(4)–C(A1)–C(A2)	112.9(6)
Mo–P(1)–N(5)	113.8(2)	C(A1)–C(A2)–C(A3)	104.8(5)
Mo–P(1)–O(3)	119.3(2)	C(A1)–C(A2)–C(MA1)	111.3(7)
Mo–P(1)–O(4)	118.2(2)	C(A1)–C(A2)–C(MA2)	109.6(8)
N(5)–P(1)–O(3)	100.5(3)	C(A3)–C(A2)–C(MA1)	111.7(8)
N(5)–P(1)–O(4)	103.6(2)	C(A3)–C(A2)–C(MA2)	108.8(6)
O(3)–P(1)–O(4)	98.7(2)	C(MA1)–C(A2)–C(MA2)	110.5(6)
P(1)–N(5)–C(6)	127.5(4)	O(3)–C(A3)–C(A2)	112.8(5)
N(5)–C(6)–C(7)	111.7(6)		

The rates of halide substitutions in **I** and **II** are lower than those in **XII** and **XIII**. Complex **I** reacts with NaO<sup>n</sup>Pr in n-propanol at ambient temperature to give a mixture of products after 8 days of reaction. In contrast, **XII** reacts with LiO<sup>n</sup>Pr in THF to give a quantitative yield of the alkoxy-substituted product after 66 h at ambient temperature. Complex **II** does react cleanly with either NaO<sup>n</sup>Pr in

Table 8

Torsion angles with estimated standard deviations for the 1,3,2-phosphorinane rings in **IV** and **VII**

Atoms	Angle (°)	Atoms	Angle (°)
<b>IV</b>			
O(A5)–P(1)–O(A1)–C(A2)	–45.8(2)	O(B5)–P(2)–O(B1)–C(B2)	–44.2(2)
P(1)–O(A1)–C(A2)–C(A3)	55.9(2)	P(2)–O(B1)–C(B2)–C(B3)	55.9(3)
O(A1)–C(A2)–C(A3)–C(A4)	–58.2(3)	O(B1)–C(B2)–C(B3)–C(B4)	–59.1(2)
C(A2)–C(A3)–C(A4)–O(A5)	58.9(3)	C(B2)–C(B3)–C(B4)–O(B5)	58.8(3)
C(A3)–C(A4)–O(A5)–P(1)	–57.2(3)	C(B3)–C(B4)–O(B5)–P(2)	–56.3(3)
C(A4)–O(A5)–P(1)–O(A1)	46.3(1)	C(B4)–O(B5)–P(2)–O(B1)	45.1(2)
<b>VII</b>			
O(4)–P(1)–O(3)–C(A3)	–55.2(4)	C(A3)–C(A2)–C(A1)–O(4)	57.6(7)
P(1)–O(3)–C(A3)–C(A2)	61.8(7)	C(A2)–C(A1)–O(4)–P(1)	–62.0(6)
O(3)–C(A3)–C(A2)–C(A1)	–56.8(8)	C(A1)–O(4)–P(1)–O(3)	52.3(5)

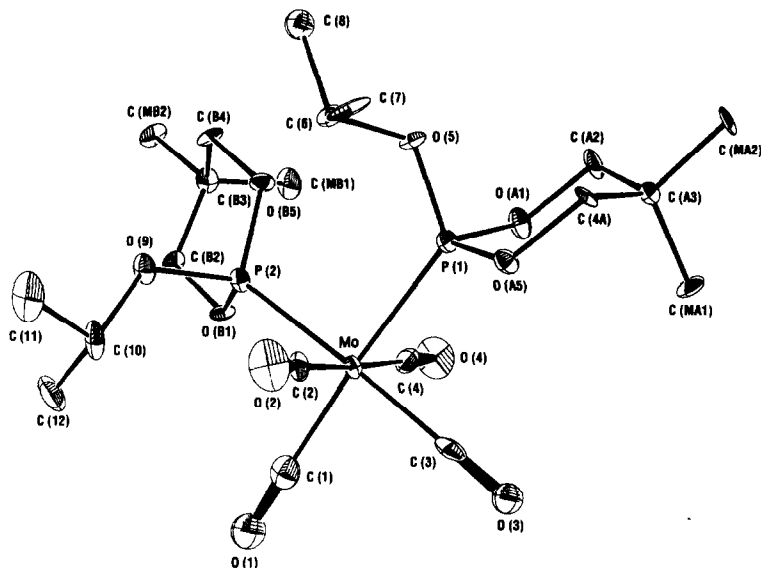
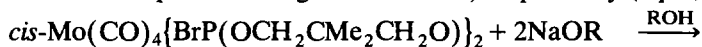
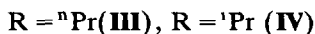


Fig. 1. ORTEP drawing of *cis*-Mo(CO)<sub>4</sub>(<sup>1</sup>PrOP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O))<sub>2</sub> (IV) [67]. The hydrogens are omitted for clarity, and the thermal ellipsoids are drawn at the 50% probability level.

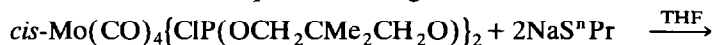
*n*-propanol (complete after 44 h) or NaO<sup>1</sup>Pr in *i*-propanol (complete after 114 h) at ambient temperature to give **III** and **IV**, respectively (eq. 2).



**II**



The reaction of **I** with LiS<sup>*n*</sup>Pr in THF at ambient temperature (eq. 3) was also much slower than the reaction of **XII** with LiS<sup>*n*</sup>Pr under nearly identical conditions (80 h versus 18 h). In further contrast to **XII**, **I** did not react cleanly with LiS<sup>*n*</sup>Pr in THF at ambient temperature but gave a number of unidentified products.

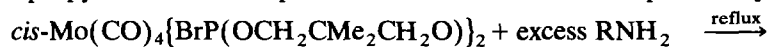


**I**

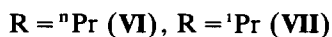


**V**

Complex **II** reacted with refluxing aliphatic amines to yield the corresponding *cis*-Mo(CO)<sub>4</sub>{RNHP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> (R = <sup>*n*</sup>Pr (**VI**), <sup>*1*</sup>Pr (**VII**)) complexes in high yields as shown in eq. 4. These are the same conditions used to substitute the chloride in **XII** with *n*-propylamine. In contrast, the reaction of **XIII** with neat *i*-propylamine was complete after 66 h at ambient temperature [13].



**II**



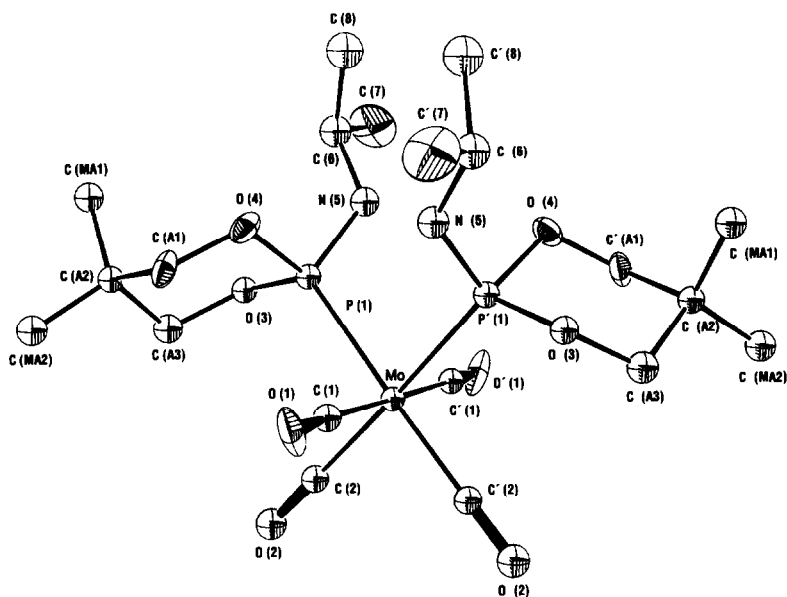


Fig. 2. ORTEP drawing of *cis*-Mo(CO)<sub>4</sub>(<sup>1</sup>PrNHP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O))<sub>2</sub> (VII) [67]. The hydrogens are omitted for clarity, and the thermal ellipsoids are drawn at the 50% probability level.

The reactions of **II** with the sodium salts of *p*-methylphenol or *p*-methylthiophenol in THF at ambient temperature (eq. 5) were complete after 6 days and 18 h, respectively. The reaction of NaOC<sub>6</sub>H<sub>4</sub>-*p*-Me with **II** was much slower than

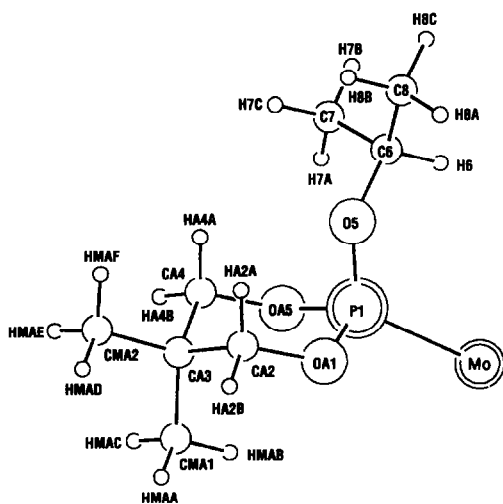


Fig. 3. Ball and stick drawing of *cis*-Mo(CO)<sub>4</sub>(<sup>1</sup>PrOP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O))<sub>2</sub> showing the ring conformation.

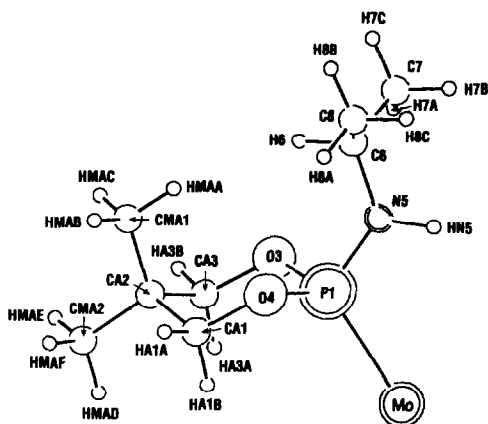
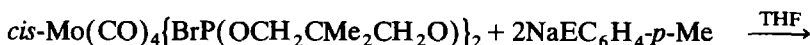
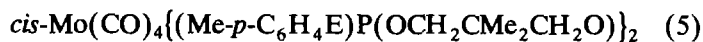


Fig. 4. Ball and stick drawing of *cis*-Mo(CO)<sub>4</sub>(<sup>i</sup>PrNHP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O))<sub>2</sub> showing the ring conformation.

that with **XII** (6 days versus 66 h).

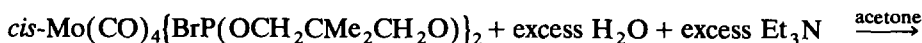


**II**



E = O (**VIII**), E = S (**IX**)

The reaction of **II** with Et<sub>3</sub>N and water in acetone at ambient temperature (eq. 6) occurred at approximately the same rate as did the hydrolysis of **XIII** under the same conditions. It is not appropriate to compare the rates of these reactions, however, because quite different products are obtained.

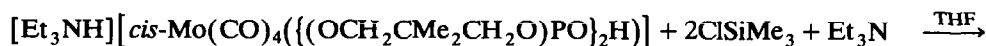


**II**



**X**

The reaction of **X** with ClSiMe<sub>3</sub> (eq. 7) is complete in 1 h at ambient temperature. This reaction is quite similar to that of [Et<sub>3</sub>NH][Mo(CO)<sub>5</sub>{(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)PO}] with ClSiMe<sub>3</sub>.



**X**



**XI**

The slower reactions of N-, O- and S-nucleophiles with **I** and **II** compared to those with **XII** and **XIII**, and the very different reactions of **II** and **XIII** with NaO<sup>n</sup>Pr and NaO<sup>i</sup>Pr and with LiS<sup>n</sup>Pr and LiS<sup>i</sup>Pr are most easily explained by the

increased steric congestion in the *cis* complexes. This supports the hypothesis that the lower rates of halide substitution reactions in the 2-halo-1,3,2-dioxaphosphorinane complexes compared to chlorodiphenylphosphine complexes are due to steric effects [13].

The rates of halide substitution in *cis*-Mo(CO)<sub>4</sub>{XP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> (X = Cl (I), Br (II)) are also substantially lower than in *cis*-Mo(CO)<sub>4</sub>(Ph<sub>2</sub>PCI)<sub>2</sub> (XV). Displacements of the chloride in XV by N-, O- and S-nucleophiles are completed in 30 min at ambient temperature in the presence of triethylamine [5]. In contrast, as discussed in detail above, the reactions of I and II with the same nucleophiles require several hours or days and more forcing reaction conditions.

### Spectroscopic characterization

The <sup>13</sup>C and <sup>17</sup>O NMR data for the carbonyl ligands in the *cis*-Mo(CO)<sub>4</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> complexes are given in Table 1. Two, equally intense <sup>13</sup>C NMR resonances are observed for the carbonyl ligands of each of the *cis*-Mo(CO)<sub>4</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> complexes. The downfield resonances are assigned to the carbonyls *trans* to the phosphorinane ligands (*trans* carbonyls) and are apparent quintets (A portions of AX<sub>2</sub>' spin systems). The upfield resonances are assigned to the carbonyls *trans* to other carbonyls (*cis* carbonyls) and are triplets (A portions of AX<sub>2</sub> spin systems) [15]. Two equally intense singlets are also observed in the <sup>17</sup>O NMR spectra of these complexes. The downfield resonances are assigned to the *trans* carbonyls on the basis of our earlier studies [32]. The carbonyl <sup>13</sup>C NMR resonances are upfield and the <sup>17</sup>O NMR resonances are downfield of similar resonances for *cis* and *trans* carbonyl ligands in *cis*-Mo(CO)<sub>4</sub>(Ph<sub>2</sub>PER)<sub>2</sub> complexes. This is consistent with earlier results that suggest that the REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O) ligands are better π-acceptors than are the Ph<sub>2</sub>PER ligands [13,14].

Four <sup>13</sup>C NMR resonances are generally observed for the 5,5-dimethyl-1,3,2-dioxaphosphorinane rings in each of the *cis*-Mo(CO)<sub>4</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> complexes as shown in Table 2. One resonance is observed between 71.4 and 75.6 ppm and is due to the 4,6-methylene carbons adjacent to the oxygens. This resonance is either a singlet or an apparent quintet depending on the magnitude of <sup>2</sup>J(PC) + <sup>4</sup>J(P'C). A second resonance is observed between 32.1 and 32.8 ppm and is due to the 5 carbon that is bonded to both methyls. This is always an apparent quintet. The last two resonances are observed between 20.7 and 23.8 ppm and are due to the two inequivalent methyls. These are always singlets. The only exception to this is in the <sup>13</sup>C NMR spectrum of *cis*-Mo(CO)<sub>4</sub>{CIP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> (I) which has four methyl resonances. The four methyl <sup>13</sup>C NMR resonances of I do not appear to be due to inequivalent conformations of the phosphorinane rings because a single resonance is observed for each of the other carbons and for the phosphorus and because only two <sup>1</sup>H NMR resonances are observed for the methyls.

A single <sup>31</sup>P and <sup>95</sup>Mo NMR resonance are observed for each of the *cis*-Mo(CO)<sub>4</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> complexes as shown in Table 1. The <sup>31</sup>P NMR resonances are all singlets and are used as a measure of the purity of the complexes. The <sup>95</sup>Mo resonances are all triplets (A portions of AX<sub>2</sub> spin systems). The magnitudes of <sup>1</sup>J(MoP) range from 195 to 246 Hz. These magnitudes are similar to those observed for Mo(CO)<sub>5</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)} complexes [13]

and 60–80 Hz larger than those observed for *cis*-Mo(CO)<sub>4</sub>(Ph<sub>2</sub>PER)<sub>2</sub> complexes [34]. The magnitude of <sup>1</sup>J(MoP) also appears to depend on the nature of the E group with the largest values for Cl and Br, intermediate values for O and S and the smallest values for N. This trend is consistent with that observed in earlier studies [34]. The <sup>95</sup>Mo resonances are relatively narrow ( $21 \leq \Delta\nu_{1/2} \leq 99$ ), and the half-widths depend upon the natures of both E and R with E = O or N and smaller R groups giving narrower resonances.

### Correlation studies

It is well established that generally poor correlations are observed between the chemical shifts of various NMR resonances and IR stretching force constants in Mo(CO)<sub>6-n</sub>(P-donor ligand)<sub>n</sub> ( $n = 1, 2$ ) complexes as groups on the phosphorus are varied due to the simultaneous variations in both the steric and electronic properties of the P-donor ligands [13,14,32–36,47–54]. However, in some cases good correlations are observed, and these provide insight into the steric and electronic effects in the complexes. For the *cis*-Mo(CO)<sub>4</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> complexes, good correlations (levels of confidence > 99.9%) are observed between the chemical shifts of the *trans* <sup>13</sup>CO NMR resonance and both  $k_1$  ( $r = -0.929$ ) and the chemical shifts of the *cis* <sup>13</sup>CO NMR resonance ( $r = 0.912$ ), between the chemical shifts of the *cis* <sup>13</sup>C NMR resonance and  $k_2$  ( $r = -0.979$ ) and between  $k_1$  and  $k_2$  ( $r = 0.944$ ) as the ER groups are varied. In contrast, the only good correlation that is observed between the chemical shifts of either the *trans* or *cis* C<sup>17</sup>O NMR resonances and any of the other NMR resonances or carbonyl IR stretching force constants as the RE groups are varied is between the chemical shifts of the *trans* C<sup>17</sup>O and <sup>95</sup>Mo NMR resonances ( $r = 0.901$ ). These correlations are even worse than those for the C<sup>17</sup>O NMR resonances in the Mo(CO)<sub>5</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)} complexes. This suggests that the dioxaphosphorinane ligands are more sterically crowded in the *cis* complexes, and this is consistent with the lower reactivity of the halides in these complexes.

A study of the correlations between the chemical shifts of the various NMR resonances of the *cis*-Mo(CO)<sub>4</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> complexes and the chemical shifts of similar resonances in the Mo(CO)<sub>5</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)} and *cis*-Mo(CO)<sub>4</sub>(Ph<sub>2</sub>PER)<sub>2</sub> complexes as the ER groups are varied provides insight in the effects of variations in the phosphorus substituents in these complexes. Good correlations are observed between the chemical shifts of the *cis* <sup>13</sup>CO ( $r = 0.995$ ), *trans* C<sup>17</sup>O ( $r = 0.964$ ), <sup>31</sup>P ( $r = 0.958$ ) and <sup>95</sup>Mo ( $r = 0.966$ ) NMR resonances of the *cis*-Mo(CO)<sub>4</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> and Mo(CO)<sub>5</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)} complexes as the ER groups are varied. The correlation between the chemical shifts of the *trans* <sup>13</sup>CO NMR resonances of the two complexes is not as good ( $r = 0.864$ ) but improves if the data for the E = S complexes are removed ( $r = 0.987$ ). The poor correlations using the data with E = S complexes may be due to the fact that phosphorus–sulfur bonds are considerable longer than are phosphorus–nitrogen and phosphorus–oxygen bonds which may alter both the steric bulk and the electron donor–acceptor properties of the ligands. The correlation between the chemical shifts of the *cis* C<sup>17</sup>O NMR resonances of the two sets of complexes is poor ( $r = 0.332$  for all data) because of the insensitivity of the chemical shifts of the *cis* C<sup>17</sup>O resonances to variations in the ER groups. These good correlations suggest that, with the exception of the E = S ligands, variations

in the ER groups have exactly the same effects upon the steric and electronic properties of the 1,3,2-dioxaphosphorinane ligands in the two complexes.

The correlations between the chemical shifts of the various NMR resonances of the *cis*-Mo(CO)<sub>4</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> and *cis*-Mo(CO)<sub>4</sub>(Ph<sub>2</sub>PER)<sub>2</sub> complexes are much worse. The only good correlations that are observed as the ER groups are varied are between the chemical shifts of the *trans* <sup>13</sup>CO ( $r = 0.954$ ) and <sup>95</sup>Mo ( $r = 0.943$ ) NMR resonances of the two sets of complexes. A fair correlation is observed between the *cis* <sup>13</sup>CO NMR resonances of the complexes ( $r = 0.813$ ). The correlation coefficients are similar to those reported for the correlations between the chemical shifts of similar resonances in Mo(CO)<sub>5</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)} and Mo(CO)<sub>5</sub>(Ph<sub>2</sub>PER) (*trans* <sup>13</sup>CO,  $r = 0.967$ ; <sup>95</sup>Mo,  $r = 0.925$ ; *cis* <sup>13</sup>CO,  $r = 0.848$ ). Because these are the resonances that would be least affected by variations in the steric bulk of the ligands, this suggests that variations in the ER groups have different effects on the steric properties of the ligands. This also supports the hypothesis that the effects of the phosphorus substituents on the chemical shifts of the various NMR resonances of their complexes are not additive [13].

#### Crystallographic studies

There is considerable interest in the phosphorus stereochemistry and ring conformation in 1,3,2-dioxaphosphorinanes [29,31,55–65]. Earlier studies have demonstrated that the phosphorus stereochemistry depends upon both the steric and electronic properties of the phosphorus substituents. However, most of these studies have focussed on 3-coordinate 1,3,2-dioxaphosphorinanes and their oxo, thio and seleno derivatives, and few have examined metal complexes of the 3-coordinate 1,3,2-dioxaphosphorinanes. In addition, no crystallographic studies of isoelectronic 2-alkoxy- and 2-alkylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane complexes have been reported. Thus, comparison of the molecular structures of the *cis*-Mo(CO)<sub>4</sub>{<sup>t</sup>PrEP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> (E = O (IV), NH (VII)) complexes should provide new insight into the factors affecting the phosphorus stereochemistry in the 1,3,2-dioxaphosphorinanes.

The space groups of the crystals of IV and VII are quite different. Complex IV crystallizes in a *P* $\bar{1}$  space group with a complete molecule of IV as the asymmetric unit. This means that the phosphorinane rings are symmetry inequivalent. In contrast, VII crystallizes in a *C*2/*c* space group with the molecule occupying a special position on a twofold axis. One half of VII comprises the asymmetric unit in this crystal, and thus the phosphorinane rings are symmetry equivalent.

The very different conformations of IV and VII appear to be due primarily to differences in the stereochemistry at the phosphorus. In IV, the molybdenum carbonyl group is equatorial in both phosphorinane rings (torsion angles: Mo–P(1)–O(A1)–C(A2) = –165.3(2)°, Mo–P(1)–O(A5)–C(A4) = 167.8(1)°, Mo–P(2)–O(B1)–C(B2) = –169.2(2)°, Mo–P(2)–O(B5)–C(B4) = 166.7(1)°) and the *i*-propoxy group is axial (torsion angles: O(5)–P(1)–O(A5)–C(A4) = –56.5(2)°, O(5)–P(1)–O(A1)–C(A2) = 62.2(2)°, O(9)–P(2)–O(B1)–C(B2) = 57.9(3)°, O(9)–P(2)–O(B5)–C(B4) = –61.0(2)°). In contrast, in VII, the molybdenum carbonyl group is axial (torsion angles: Mo–P(1)–O(4)–C(A1) = –77.8(5)°, Mo–P(1)–O(3)–C(A3) = 77.1(4)°) and the *i*-propylamino group is equatorial (torsion angles: N(5)–P(1)–O(4)–C(A1) = 155.4(5)°, N(5)–P(1)–O(3)–C(A3) = –157.9(4)°). The equatorial *i*-



propylamino groups in **VII** apparently allow the phosphorinane ligands to rotate about the molybdenum–phosphorus bonds to achieve a symmetrical arrangement, but this is not possible with axial *i*-propoxy groups. These conformations are consistent with those previously reported for other molybdenum carbonyl complexes of 5,5-dimethyl-1,3,2-dioxaphosphorinane ligands [29,31,57].

The axial site preference for 2-alkoxy groups in 1,3,2-dioxaphosphorinanes is well established and has been explained using electronic arguments [55]. In contrast, the site preference for amino substituents is less clear. Dimethylamino groups tend to occupy equatorial sites but primary amines, even with sterically demanding substituents, show less equatorial site preference. The greater equatorial site presence of the dimethylamino group has been explained as arising from unfavorable steric interactions between the *N*-methyl group and axial 4,6-phosphorinane hydrogens [55] when the amine is in the axial position. These do not occur with primary amines [55]. For example, the phenylamino group in 5,5-dimethyl-2-oxo-2-(phenylamino)-1,3,2-dioxaphosphorinane is in the axial position [66]. Given the steric bulk of the molybdenum carbonyl group, it seems unlikely that the above steric arguments can be used to explain the equatorial site preference of the *i*-propylamino groups in **VII**, especially in view of the fact that the very similar *i*-propoxy groups in **IV** occupy the axial sites in both phosphorinane rings.

The equatorial site preference of the *i*-propylamino groups in **VII** is not due to hydrogen bonding between the two primary amines. The N(5)–N(5)' distance of 3.38 Å is too long and the N(5)–H(N5)–N(5) angle of 95.4° is much too low for a hydrogen bond. In addition, we have observed similar site preferences for oxygen- and nitrogen-substituents in 1,3,2-dioxaphosphorinane-(pentacarbonyl)molybdenum complexes in which hydrogen bonding could not occur [29,31]. This strongly supports our contention that electronic effects are responsible for the site preferences in **IV** and **VII**.

The different phosphorus stereochemistries in **IV** and **VII** also affect the phosphorinane ring conformations in the two complexes. The rings in both complexes are chairs that are somewhat flattened about the P(OC)<sub>2</sub> group because the P–O–C angles are larger than the tetrahedral angle (average of 118.5° for **IV** and 117.6° for **VII**) and the O–P–O angles are smaller than the tetrahedral angle (average of 103.0° in **IV** and 98.7° in **VII**). However, the flattening of the P(OC)<sub>2</sub> groups is more pronounced in **IV** as indicated by the significantly smaller P–O–C–C torsion angles (Table 8).

## Summary

The rates of halide substitution by N-, O- and S-nucleophiles in the *cis*-Mo(CO)<sub>4</sub>{XP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> (X = Cl, Br) complexes are significantly lower than in the Mo(CO)<sub>5</sub>{XP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)} complexes. This appears to be due to the increased steric congestion in the *cis* complexes and supports our hypothesis that the steric effects are the primary reason for the low rates of nucleophilic displacement of halides in 1,3,2-dioxaphosphorinane complexes.

The correlations between chemical shifts of similar NMR resonances of the *cis*-Mo(CO)<sub>4</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> and Mo(CO)<sub>5</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)} (E = NH, O, S; R = alkyl, aryl, silyl or ER = Cl, Br) complexes as the RE groups

are varied are good. In contrast, correlations between chemical shifts of similar NMR resonances of the *cis*-Mo(CO)<sub>4</sub>{REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> and *cis*-Mo(CO)<sub>4</sub>(Ph<sub>2</sub>PER)<sub>2</sub> complexes as the RE groups are varied are poor. These results indicate that the effects of the variations in RE groups on the steric and electronic properties of REP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O) and Ph<sub>2</sub>PER ligands are quite different.

The isoelectronic *cis*-Mo(CO)<sub>4</sub>{<sup>1</sup>PrEP(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)}<sub>2</sub> (E = NH (VII), O (IV)) complexes have different molecular structures. The *i*-propylamino group in VII is equatorial but the *i*-propoxy group in IV is axial. Studies of related systems provide no explanation for this behavior; however, it would seem to be electronic, rather than steric in origin because the *i*-propylamino and *i*-propoxy groups, with the exception of the sterically insignificant amine hydrogen, are the same size.

### Acknowledgements

This work was supported by J.T. Baker Chemical Co. and the Upjohn Co.

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