

Syntheses and NMR spectroscopic characterizations of the bimetallic complexes: $(\text{CO})_5\text{Mo}(\mu\text{-R}_2\text{PXPR}'_2)\text{Mo}(\text{CO})_5$ ($\text{R}_2, \text{R}'_2 = \text{Ph}_2, \text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}$; $\text{X} = \text{O}, \text{NHCH}_2\text{CH}_2\text{NH}$); the structure of $(\text{CO})_5\text{Mo}(\mu\text{-Ph}_2\text{POP}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}))\text{Mo}(\text{CO})_5$

Gary M. Gray *

Chemistry Department, The University of Alabama at Birmingham, Birmingham, AL 35294 (U.S.A.)

and William Watt

Physical and Analytical Chemistry, The Upjohn Co., Kalamazoo, MI 49007 (U.S.A.)

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Abstract

Bimetallic complexes of the types $(\text{CO})_5\text{Mo}(\mu\text{-R}_2\text{PXPR}'_2)\text{Mo}(\text{CO})_5$ ($\text{R}_2, \text{R}'_2 = \text{Ph}_2, \text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}$; $\text{X} = \text{O}, \text{NHCH}_2\text{CH}_2\text{NH}$) have been synthesized by the reactions of $\text{Mo}(\text{CO})_5(\text{R}'_2\text{PX})$ ($\text{X} = \text{Cl}, \text{Br}$) with either $[\text{Et}_3\text{NH}][\text{Mo}(\text{CO})_5(\text{R}_2\text{PO})]$ or $\text{Mo}(\text{CO})_5(\text{R}_2\text{PNHCH}_2\text{CH}_2\text{NH}_2)$. These reactions provide a precise control over the coordination environment of the metals because the bridging, bidentate ligand is formed after the P-donor groups have been coordinated to the metal centers. The ^{13}C and ^{31}P NMR spectra of the complexes are discussed. The ^{13}C NMR spectra of the complexes containing the $\text{R}_2\text{POP}(\text{R}'_2)$ ligands varies significantly with the nature of the R_2 and R'_2 groups. The resonances that are coupled to P are apparent quintets (A portion of an AXX' spin system) for the symmetrical complexes and doublets (A portion of an AXY spin system with no A–Y coupling) for the unsymmetrical complexes. The X-ray crystal structure of $(\text{CO})_5\text{Mo}(\mu\text{-Ph}_2\text{POP}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}))\text{Mo}(\text{CO})_5$ has been determined. The complex crystallizes in the monoclinic space group $P2_1/c$ (a 8.792(2), b 33.946(5), c 10.762(1) Å; β 104.02(1)°; V 3116.3(6) Å³; $Z = 4$). The structural data suggest that the Ph_2P group is a better electron donor (poorer electron acceptor) than is the $\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})$ group and are consistent with NMR spectroscopic results. The $\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})$ ring is in a chair conformation, which is slightly flattened at the P, with $\text{Mo}(\text{CO})_5$ group in the equatorial position.

Introduction

There has been significant interest in recent years in the syntheses and characterizations of polynuclear complexes containing bridging bis(P-donor) ligands. Two approaches have been taken in order to avoid problems with chelation of the bis(P-donor) ligands. The first involves the use of ligands that contain P-donor sites oriented in such a way that chelation is not favorable. Ligands of this type are those in which the P-donor sites are separated either by a single atom bridge as in bis(phosphino)methanes [1], diphosphoxanes [2], diphosphites [3], bis(phosphino)amines [4], and diazaphosphatidines [5] or by a sterically constraining group as in 1,2-bis(phosphino)ethenes [6], bis(phosphino)ethynes [7], 1,2-bis(phosphino)cyclopropanes [8], 2,5-bis(phosphino)furans [9] and bicyclic phosphinephosphites [10].

Polynuclear complexes with bridging bis(P-donor) ligands have also been prepared by reactions between monodentate P-donor ligands of mononuclear complexes. The reactions of coordinated vinylphosphines with secondary phosphines have been used to prepare a variety of polynuclear complexes with bridging bis(phosphino)ethane ligands [11]. The reactions of coordinated chlorophosphines with either water or coordinated $\text{PR}_{3-n}(\text{OH})_n$ ($n = 1, 2$) ligands yield diphosphoxane-bridged complexes [2]. Coordinated chlorophosphines also react with K_2SN_2 to form dinuclear complexes bridged by a $\text{R}_2\text{P}-\text{N}=\text{S}=\text{N}-\text{PR}_2$ ligand [12].

The reactions of coordinated P-donor ligands provide precise control over the coordination environment of the metals through the prior coordination of the monodentate P-donor ligands to the various metal centers. Thus, these reactions may be used to prepare polynuclear complexes containing different metal centers and/or different P-donor groups. In this paper, we report the preparation of a variety of dinuclear Mo carbonyl complexes via the reactions of coordinated P-donor ligands. The multinuclear NMR spectroscopic characterization of the complexes is presented, and the X-ray crystal structure of one of the complexes containing a unique phosphinitephosphorinane bridging ligand, $(\text{CO})_5\text{Mo}(\mu\text{-Ph}_2\text{POP}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}))\text{Mo}(\text{CO})_5$ (II) is discussed.

Experimental

All syntheses and purifications were run under an inert atmosphere (Ar or N_2). Both tetrahydrofuran (THF) and diethyl ether were distilled from CaH_2 before use. Other solvents were used as received. Chlorodiphenylphosphine and ethylenediamine (Aldrich) were used from freshly opened bottles that were kept under an inert atmosphere during transfer of the reagent. Triethylamine was distilled from CaH_2 . Literature methods were used for the preparation of $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PCI})$ [13], $\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{Br})$ and $[\text{Et}_3\text{NH}][\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{O})]$ [14], $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{NH}_2)$ and $\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{-NHCH}_2\text{CH}_2\text{NH}_2)$ [15] and $(\text{CO})_5\text{Mo}(\mu\text{-Ph}_2\text{POPPh}_2)\text{Mo}(\text{CO})_5$, I [2].

(CO)₅Mo(μ-Ph₂POP(OCH₂CMe₂CH₂O))Mo(CO)₅ (II)

A solution of $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PCI})$ (0.73 g, 1.6 mmol) and $[\text{Et}_2\text{NH}][\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{O})]$ (0.78 g, 1.6 mmol) in 20 ml of THF was stirred at ambient temperature for 4 h and then evaporated to dryness. The residue was recrystallized from a diethyl ethyl/hexanes mixture to yield II, m.p. 119.0–120.5 °C (0.96 g, 66%). Anal. Found: C, 40.13; H, 2.47. $\text{C}_{27}\text{H}_{20}\text{Mo}_2\text{O}_{13}\text{P}_2$ calc: C, 40.00; H, 2.47%.

$(CO)_5Mo(\mu-P(OCH_2CMe_2CH_2O)OP(OCH_2CMe_2CH_2O))Mo(CO)_5$ (III)

Method 1. A solution of $Mo(CO)_5(P(OCH_2CMe_2CH_2O)Br)$ (1.22 g, 2.71 mmol) and $[Et_3NH][Mo(CO)_5(P(OCH_2CMe_2CH_2O)O)]$ (1.32 g, 2.71 mmol) in THF was stirred at ambient temperature for 42 h and then evaporated to dryness. The residue was washed with diethyl ether to remove any remaining starting material. The insoluble portion was recrystallized from a dichloromethane/hexanes mixture to yield III, m.p. 193–197 °C with decomposition (0.39 g, 19%). Anal. Found: C, 31.38; H, 2.69. $C_{20}H_{20}Mo_2O_{15}P_2$ calc: C, 31.66; H, 2.64%.

Method 2. A solution of $Mo(CO)_5(P(OCH_2CMe_2CH_2O)Br)$ (2.00 g, 4.45 mmol), deionized water (3.0 ml) and triethylamine (3.0 ml) in 20 ml of THF was stirred at ambient temperature for 18 h and then evaporated to dryness. The residue was treated with 40 ml of water and 40 ml of ethyl ether, and the insoluble III collected by filtration (0.56 g, 26%). The organic phase of the filtrate was separated, dried with $MgSO_4$ and then evaporated to dryness. The residue was recrystallized from a diethyl ether/hexanes mixture to yield $[Et_3NH][Mo(CO)_5(P(OCH_2CMe_2CH_2O)O)]$ (0.91 g, 42%).

$(CO)_5Mo(\mu-Ph_2NHCH_2CH_2NHPh_2)Mo(CO)_5$ (IV)

A solution of $Mo(CO)_5(Ph_2PNHCH_2CH_2NH_2)$ (0.960 g, 2.00 mmol), $Mo(CO)_5(Ph_2PCl)$ (0.913 g, 2.00 mmol) and triethylamine (0.56 ml, 4.0 mmol) in 25 ml of diethyl ether was stirred at ambient temperature for 80 h. The reaction mixture was then filtered to remove the triethylammonium chloride precipitate, and the filtrate was evaporated to dryness. The residue was recrystallized from a diethyl ether/hexanes mixture to yield IV (1.11 g, 61.7%). A second recrystallization from a dichloromethane/hexanes mixture yielded pure product, m.p. 155.5–158.5 °C with decomposition. Anal. Found: C, 47.78; H, 2.93. $C_{36}H_{26}Mo_2N_2O_{10}P_2$ calc: C, 47.79; H, 2.88%.

$(CO)_5Mo(\mu-Ph_2PNHCH_2CH_2NHP(OCH_2CMe_2CH_2O))Mo(CO)_5$ (V)

A solution of $Mo(CO)_5(P(OCH_2CMe_2CH_2O)NHCH_2CH_2NH_2)$ (0.856 g, 2.00 mmol), $Mo(CO)_5(Ph_2PCl)$ (0.913 g, 2.00 mmol) and triethylamine (0.56 ml, 4.0 mmol) in 25 ml of THF was stirred at ambient temperature for 20 h. The reaction mixture was then filtered to remove the triethylammonium chloride precipitate, and the filtrate was evaporated to dryness. The residue was recrystallized from a diethyl ether/hexanes mixture to yield V (0.86 g, 51%). Recrystallization from a dichloromethane/hexanes mixture yielded pure product, m.p. 118.5–121.5 °C. Anal. Found: C, 40.98; H, 3.09. $C_{29}H_{26}Mo_2N_2O_{12}P_2$ calc: C, 40.85; H, 3.05%.

Characterization of the complexes

Multinuclear NMR spectra of 0.2 M chloroform- d_1 solutions of the complexes were run on either JEOL FX90Q or Nicolet 300 MHz Fourier transform NMR spectrometers, and the NMR data are given in Tables 1 and 2. Elemental analyses were run either by Galbraith Laboratories, Knoxville, TN or by Atlantic Microlabs, Atlanta, GA.

Collection and reduction of X-ray data

A clear prismatic crystal of II, $0.08 \times 0.16 \times 0.31$ mm, was used for data collection. Diffraction data was collected on a Syntex P1 diffractometer using

Table 1

Multinuclear NMR data (δ (ppm), J (Hz)) for the $(\text{CO})_5\text{Mo}(\mu\text{-R}_2\text{PXP}'_2)\text{Mo}(\text{CO})_5$ complexes

Complex	<i>trans</i> CO		<i>cis</i> CO		NCH ₂			P	
	$\delta(^{13}\text{C})$	J	$\delta(^{13}\text{C})$	J	$\delta(^{13}\text{C})$	$ ^2J(\text{PC}) $	$ ^3J(\text{PC}) $	$\delta(^{31}\text{P})$	$ ^2J(\text{PP}) $
I	209.59 ^a	30 ^b	204.78 ^a	10 ^b	–	–	–	151.60	–
II	209.12 ^c	30 ^d	204.77 ^c	10 ^d	–	–	–	147.83 ^c	59
	208.05 ^c	46 ^d	203.89 ^c	14 ^d	–	–	–	136.86 ^c	–
III	207.61 ^a	47 ^b	203.70 ^a	14 ^b	–	–	–	134.80	–
IV	210.09 ^c	25 ^d	205.43 ^c	10 ^d	44.54	7	7	64.58	–
V	210.26 ^c	24 ^d	205.47 ^c	10 ^d	44.50	8	3	62.88	–
	208.30 ^c	35 ^d	204.84 ^c	13 ^d	41.27	7	5	142.67	–

^a Apparent quintet. ^b $J = |^2J(\text{PC}) + ^4J(\text{P}'\text{C})|$. ^c Doublet. ^d $J = |^2J(\text{PC})|$.

graphite-monochromated $\text{Cu-K}\alpha$ radiation. Unit cell dimensions were determined accurately by a least squares fit of $\text{Cu-K}\alpha_1 2\theta$ values ($\lambda(K\alpha_1) = 1.5402 \text{ \AA}$) for 25 high 2θ reflections [16]. The intensity data were measured using a step-scan technique with a scan rate of $2^\circ/\text{min}$, a scan width of 3.4° and a $2\theta_{\text{max}}$ of 136° . 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:

$$\sigma^2(I) = \sigma^2(I)_{\text{counting statistics}} + (0.011I)^2$$

where the coefficient of I was calculated from variations in the intensities of the monitored reflections. Of 5085 total unique reflections measured, 4499 had intensities $> 3\sigma$. Lorentz and polarization corrections appropriate for a monochromator with 50% perfect character were applied to the intensity data. An absorption correction for intensities was also applied [17]; min. transmission was 0.311 and max. transmission was 0.512.

Solution and refinement of the structure

All the calculations were carried out using the CRYM system of computer programs [18]. A partial trial solution, 11 atoms, was obtained by a combination of Patterson analysis and direct methods using MULTAN80 [19]. Subsequent Fourier syntheses revealed the non-hydrogen atoms of the complex. Hydrogen atoms were clearly located in difference-Fourier very close to positions generated using planar or tetrahedral geometry therefore the generated positions were used. The structure was refined using least squares methods with the coordinates of all the atoms and the anisotropic thermal parameters of the non-hydrogen atoms included in the refinement. The isotropic thermal parameters of the hydrogens were fixed at a value 0.5 units higher than the isotropic thermal parameters of the attached heavy atoms. The function minimized in the refinement was $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Atomic form factors were from Doyle and Turner [20], except for those of hydrogen, which were from Stewart, Davidson and Simpson [21]. In the final refinement cycle, all shifts were less than 0.63σ . The final R factor was 0.031, and the standard deviation of fit was 2.31. A final difference map showed no peaks greater than 0.8 e\AA^{-3} . Relevant crystal and experimental data for the complex are given in Table 3. The positional and isotropic thermal parameters of all non-hydro-

(Continued on p. 155)

Table 2
 ^{13}C NMR data (δ (ppm), J (Hz)) for the Ph_2P and $\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})$ groups in the $(\text{CO})_5\text{Mo}(\mu\text{-R}_2\text{PXP}'_2)\text{Mo}(\text{CO})_5$ complexes

Complex	phenyl		ortho		meta		para		phosphorinane		
	$\delta(^{13}\text{C})$	J	$\delta(^{13}\text{C})$	J	$\delta(^{13}\text{C})$	J	$\delta(^{13}\text{C})$	J	CH_2	C	CH_3
									$\delta(^{13}\text{C})$	$\delta(^{13}\text{C})$	$\delta(^{13}\text{C})$
I	139.07 ^a	33 ^b	131.06 ^a	15 ^c	128.37 ^a	10 ^d	131.00 ^e	—	—	—	—
II	139.57 ^f	36 ^g	130.84 ^f	15 ^h	128.71 ^f	10 ⁱ	131.43 ^e	73.79 ^f	8 ^h	32.08 ^f	22.14 ^e
III	—	—	—	—	—	—	—	73.75 ^a	7 ^c	32.44 ^a	21.59 ^e
IV	136.32 ^f	40 ^g	131.13 ^f	13 ^h	128.58 ^f	9 ⁱ	130.27 ^e	—	—	—	21.96 ^e
V	136.36 ^f	39 ^g	131.22 ^f	13 ^h	128.54 ^f	9 ⁱ	130.18 ^e	74.13 ^e	—	32.43 ^f	22.98 ^e

^a Apparent quintet. ^b $J = |1^1J(\text{PC}) + 3^1J(\text{P}'\text{C})|$. ^c $J = |2^1J(\text{PC}) + 4^1J(\text{P}'\text{C})|$. ^d $J = |3^1J(\text{PC}) + 5^1J(\text{PC})|$. ^e Singlet. ^f Doublet. ^g $J = |1^1J(\text{PC})|$. ^h $J = |2^1J(\text{PC})|$. ⁱ $J = |3^1J(\text{PC})|$.

Table 3

Crystal data and data collection procedures for complex II

Formula	$C_{27}H_{20}O_{13}P_2Mo_2$
Molecular weight (daltons)	806.28
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	8.792(2)
b (Å)	33.946(5)
c (Å)	10.762(1)
β (°)	104.02(1)
V (Å ³)	3116.3(6)
Z	4
ρ (calc) (g/cm ³)	1.718
Crystal dimensions (mm)	0.082 × 0.16 × 0.31
Absorption coefficient (ϵ) (cm ⁻¹)	78.00
Radiation (Å)	Cu- K_{α} , 1.5418
Temperature (°C)	-150(2)
2θ limits (°)	$2.0 \leq 2\theta \leq 137$
Scan type	$\theta/2\theta$
Scan speed (°/min)	2.0
Scan range (°)	$3.4 + \dots \tan \theta$
Number of unique data	5085
Number of data with $I \geq 0$	4468
Number of variables	1357
R (%)	3.1
R_w (%)	5.7
Error in observation of unit weight	2.31 electrons

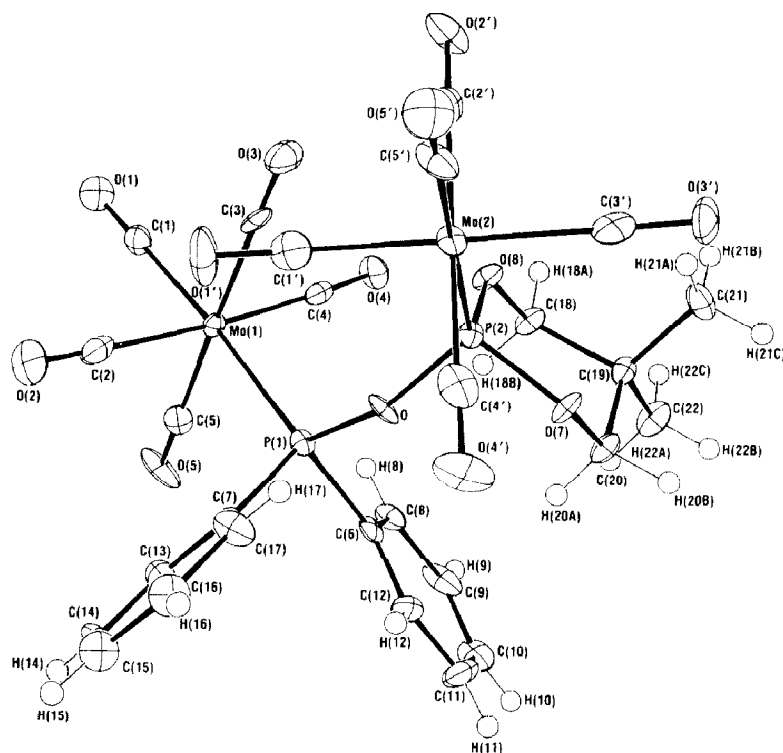


Fig. 1. ORTEP drawing [31] of the molecular structure of $(CO)_5Mo(\mu-Ph_2POP(OCH_2CMe_2CH_2O))Mo(CO)_5$, II. The thermal ellipsoids are drawn at the 50% probability level.

Table 4

Fractional coordinates ($\times 10^4$) and B_{eq} (\AA^2) with e.s.d.s for II ^{a,b}

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Mo(1)	6191(1)	1724(1)	5830(1)	1.08(1)
C(1)	7525(4)	2002(1)	4814(3)	1.8(1)
O(1)	8272(3)	2161(1)	4237(2)	2.8(1)
C(2)	5811(4)	2268(1)	6575(3)	1.9(1)
O(2)	5641(3)	2569(1)	6979(2)	2.9(1)
C(3)	8131(4)	1634(1)	7297(3)	1.6(1)
O(3)	9227(3)	1573(1)	8083(2)	2.4(1)
C(4)	6718(4)	1203(1)	5111(3)	1.5(1)
O(4)	7078(3)	915(1)	4702(2)	1.8(1)
C(5)	4310(4)	1790(1)	4280(3)	1.8(1)
O(5)	3297(3)	1821(1)	3395(2)	2.8(1)
P(1)	4464(1)	1432(1)	7104(1)	1.00(3)
C(6)	2921(4)	1085(1)	6387(3)	1.2(1)
C(7)	3331(4)	1793(1)	7751(3)	1.3(1)
C(8)	2878(4)	901(1)	5219(3)	1.5(1)
C(9)	1700(4)	627(1)	4731(3)	2.0(1)
C(10)	584(4)	539(1)	5389(4)	2.3(2)
C(11)	624(4)	721(1)	6553(3)	2.3(2)
C(12)	1785(4)	992(1)	7044(3)	1.7(1)
C(13)	2240(4)	2020(1)	6878(3)	1.8(1)
C(14)	1356(4)	2301(1)	7308(3)	2.2(1)
C(15)	1522(4)	2356(1)	8612(4)	2.5(2)
C(16)	2589(4)	2133(1)	9479(3)	2.6(2)
C(17)	3497(4)	1853(1)	9053(3)	1.9(1)
O	5260(3)	1197(1)	8440(2)	1.4(1)
P(2)	6575(1)	898(1)	9222(1)	1.02(3)
O(7)	5527(3)	542(1)	9521(2)	1.3(1)
O(8)	7394(3)	722(1)	8168(2)	1.2(1)
C(18)	6571(4)	441(1)	7198(3)	1.4(1)
C(19)	5868(4)	100(1)	7797(3)	1.2(1)
C(20)	4731(4)	273(1)	8512(3)	1.3(1)
C(21)	7148(4)	-143(1)	8685(3)	1.9(1)
C(22)	4920(4)	-156(1)	6714(3)	1.8(1)
Mo(2)	8214(1)	1158(1)	11209(1)	1.14(1)
C(1')	7921(4)	1726(1)	10531(3)	2.2(1)
O(1')	7763(4)	2039(1)	10169(3)	4.0(1)
C(2')	10232(4)	1103(1)	10575(3)	2.0(1)
O(2')	11353(3)	1065(1)	10235(3)	3.2(1)
C(3')	8526(4)	594(1)	11871(3)	1.8(1)
O(3')	8714(3)	279(1)	12242(2)	2.6(1)
C(4')	6160(4)	1199(1)	11779(3)	1.9(1)
O(4')	5003(3)	1214(1)	12072(2)	2.9(1)
C(5')	9457(4)	1368(1)	12929(3)	2.0(1)
O(5')	10140(3)	1486(1)	13894(2)	3.0(1)

^a Atoms numbered as shown in Fig. 1. ^b $B_{\text{eq}} = 4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab \cos(\gamma B_{12}) + ac \cos(\beta B_{13}) + bc \cos(\alpha B_{23})]$.

gen atoms are given in Table 4, and pertinent bond lengths and bond angles are given in Table 5. Tables of anisotropic thermal parameters, torsion angles, close intermolecular contacts, heavy atom-hydrogen bond lengths and structure factors

Table 5

Important bond distances (Å) and angles (°) with e.s.d.s for II as labeled in Figure 1

Mo(1)–P(1)	2.484(1)	Mo(2)–P(2)	2.435(1)
Mo(1)–C(1)	2.023(3)	Mo(2)–C(1')	2.056(3)
Mo(1)–C(2)	2.073(3)	Mo(2)–C(2')	2.058(3)
Mo(1)–C(3)	2.046(3)	Mo(2)–C(3')	2.038(3)
Mo(1)–C(4)	2.028(3)	Mo(2)–C(4')	2.048(3)
Mo(1)–C(5)	2.056(3)	Mo(2)–C(5')	2.036(3)
C(1)–O(1)	1.142(4)	C(1')–O(1')	1.130(4)
C(2)–O(2)	1.135(4)	C(2')–O(2')	1.139(4)
C(3)–O(3)	1.137(4)	C(3')–O(3')	1.138(4)
C(4)–O(4)	1.148(4)	C(4')–O(4')	1.137(4)
C(5)–O(5)	1.141(4)	C(5')–O(5')	1.140(4)
P(1)–O	1.645(2)	P(2)–O	1.614(2)
P(1)–C(6)	1.822(3)	P(2)–O(7)	1.600(2)
P(1)–C(7)	1.820(3)	P(2)–O(8)	1.600(2)
		O(7)–C(20)	1.460(3)
		O(8)–C(18)	1.468(3)
		C(18)–C(19)	1.527(4)
		C(19)–C(20)	1.519(4)
		C(19)–C(21)	1.529(4)
		C(19)–C(22)	1.529(4)
P(1)–Mo(1)–C(1)	175.5(1)	P(2)–Mo(2)–C(1')	91.8(1)
P(1)–Mo(1)–C(2)	88.0(1)	P(2)–Mo(2)–C(2')	92.8(1)
P(1)–Mo(1)–C(3)	91.3(1)	P(2)–Mo(2)–C(3')	88.1(1)
P(1)–Mo(1)–C(4)	95.2(1)	P(2)–Mo(2)–C(4')	84.9(1)
P(1)–Mo(1)–C(5)	90.7(1)	P(2)–Mo(2)–C(5')	176.0(1)
C(1)–Mo(1)–C(2)	87.8(1)	C(1')–Mo(2)–C(2')	92.8(1)
C(1)–Mo(1)–C(3)	90.1(1)	C(1')–Mo(2)–C(3')	179.3(1)
C(1)–Mo(1)–C(4)	89.2(1)	C(1')–Mo(2)–C(4')	90.0(1)
C(1)–Mo(1)–C(5)	88.1(1)	C(1')–Mo(2)–C(5')	89.3(1)
C(2)–Mo(1)–C(3)	90.9(1)	C(2')–Mo(2)–C(3')	88.7(1)
C(2)–Mo(1)–C(4)	176.0(1)	C(2')–Mo(2)–C(4')	177.7(1)
C(2)–Mo(1)–C(5)	92.5(1)	C(2')–Mo(2)–C(5')	91.0(1)
C(3)–Mo(1)–C(4)	86.6(1)	C(3')–Mo(2)–C(4')	90.7(1)
C(3)–Mo(1)–C(5)	176.1(1)	C(3')–Mo(2)–C(5')	90.8(1)
C(4)–Mo(1)–C(5)	90.0(1)	C(4')–Mo(2)–C(5')	91.3(1)
Mo(1)–P(1)–O	119.2(1)	Mo(2)–P(2)–O	115.2(1)
Mo(1)–P(1)–C(6)	121.1(1)	Mo(2)–P(2)–O(7)	110.2(1)
Mo(1)–P(1)–C(7)	114.1(1)	Mo(2)–P(2)–O(8)	119.1(1)
C(6)–P(1)–C(7)	100.2(1)	O(7)–P(2)–O(8)	103.8(1)
C(6)–P(1)–O	99.9(1)	O(7)–P(2)–O	101.9(1)
C(7)–P(1)–O	98.5(1)	O(8)–P(2)–O	104.7(1)
P(1)–O–P(2)	149.3(1)	P(2)–O(7)–C(20)	121.3(2)
		P(2)–O(8)–C(18)	121.2(2)
		O(7)–C(20)–C(19)	111.2(2)
		O(8)–C(18)–C(19)	111.8(2)
		C(18)–C(19)–C(20)	107.8(2)
		C(18)–C(19)–C(21)	111.1(2)
		C(18)–C(19)–C(22)	108.1(2)
		C(20)–C(19)–C(21)	111.5(2)
		C(20)–C(19)–C(22)	107.5(2)

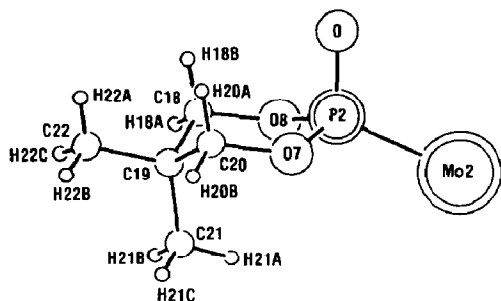


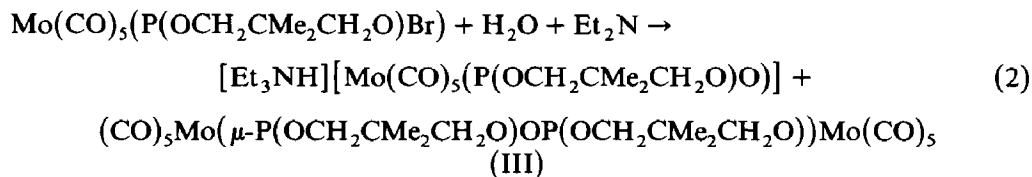
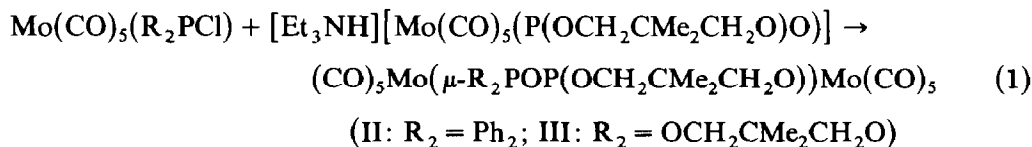
Fig. 2. A ball and stick model of the 5,5-dimethyl-1,3,2-dioxaphosphorinane ring in $(\text{CO})_5\text{Mo}(\mu\text{-Ph}_2\text{POP}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}))\text{Mo}(\text{CO})_5$, II.

are available from the authors. An ORTEP drawing of the molecule is shown in Fig. 1, and a ball and stick drawing of the phosphorinane ring is shown in Fig. 2.

Results and discussion

Syntheses

The reactions used to prepare the dinuclear phosphinite-phosphorinane, II, and diphosphorinane, III, complexes are shown in eqs. 1 and 2. The first is similar to that reported for the

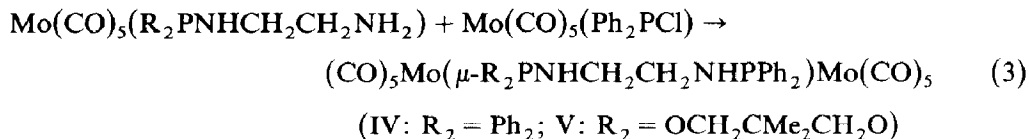


synthesis of $(\text{CO})_5\text{Mo}(\mu\text{-Ph}_2\text{POPPh}_2)\text{Mo}(\text{CO})_5$, I, [2]. This reaction gave a reasonably good yield of II (66%) but a poor yield of III (19%). The low yield of III may be explained as follows. The displacement of bromide from $\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{Br})$ is much slower than is the displacement of chloride from $\text{Mo}(\text{CO})_5\text{-}(\text{Ph}_2\text{PCl})$ [14]. Because phosphorinane complexes slowly decompose in solution, the longer reaction times necessary for the bromide displacement from $\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{Br})$ result in decomposition of the product and in lower yields of III.

The formation of the III in the second reaction was unexpected. The hydrolysis of $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PCl})$ under the same conditions gives a nearly quantitative yield of $[\text{Et}_3\text{NH}][\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PO})]$ [2b]. The formation of the III during the hydrolysis of $\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{Br})$ may be due to the slow rate of nucleophilic displacement of bromide from the complex [14]. This may allow the hydrolysis product, $\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{O})^-$, to compete with water for the unreacted $\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{Br})$.

The reaction used to prepare the dinuclear bis(aminophosphine) and

aminophosphine-aminophosphorinane complexes is shown in eq. 3. The products



are moderately stable materials that can be purified by crystallization. However, upon standing either in solution or in the solid state, they slowly decompose. An attempt was made to prepare the dinuclear bis(aminophosphorinane) complex by using $\text{Mo(CO)}_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{Br})$ in place of $\text{Mo(CO)}_5(\text{Ph}_2\text{PCl})$ in eq. 3. This reaction did not go to completion, as indicated by TLC, and none of the desired product could be isolated from the reaction mixture after the reaction had been allowed to run for long periods of time. The failure of this reaction appears to be due to the same factors that result in the low yields of III.

Spectroscopic characterizations

The dinuclear complexes, I–V, have been characterized by ^{13}C and ^{31}P NMR spectroscopy and the NMR data are summarized in Tables 1 and 2. The chemical shifts of the ^{31}P and carbonyl, phenyl and phosphorinane ^{13}C NMR resonances of the dinuclear complexes are similar to those previously reported for mononuclear complexes of the types, $\text{Mo(CO)}_5(\text{R}_2\text{PXR}')$ ($\text{R}_2 = \text{Ph}_2, \text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}$; $\text{R}' = n\text{-Pr, } i\text{-Pr, } p\text{-tolyl}$) [14a,22]. The ^{13}C NMR resonances of the carbonyl groups shift downfield as the P-substituents are varied in the order $\text{Ph}_2\text{PNHR} > \text{Ph}_2\text{POR} > \text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{NHR} > \text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{OR}$. This order is consistent with the relative electronegativities of the P-substituents and indicates that the Ph_2PNHR is the best electron donor while the $\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{OR}$ group is the poorest electron donor [23].

The ^{13}C NMR resonances observed for the ^{31}P -coupled ^{13}C nuclei in the $(\text{CO})_5\text{Mo}(\mu\text{-PR}_2\text{OPR}')\text{Mo(CO)}_5$ complexes are quite different. Apparent quintets are observed for both the *cis* and *trans* carbonyl ^{13}C resonances of the symmetric complexes ($\text{R}_2 = \text{R}'_2$). When $\text{R}_2 = \text{R}'_2 = \text{Ph}_2$, I, the *ipso*, *ortho* and *meta* phenyl ^{13}C NMR resonances are also apparent quintets while when $\text{R}_2 = \text{R}'_2 = \text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}$, II, both the methylene and quaternary ^{13}C NMR resonances of the phosphorinane are apparent quintets. In contrast, in the asymmetric complex ($\text{R}_2 \neq \text{R}'_2$), III, the *cis* and *trans* carbonyl, the phenyl *ipso*, *ortho* and *meta* and the phosphorinane methylene and quaternary ^{13}C NMR resonances are all doublets. These differences are due to the different spin systems in the complexes. In the symmetric complexes, the resonances of the P-coupled ^{13}C nuclei are the A portions of an AXX' spin system [24]. In the unsymmetrical complex, the resonances of the ^{31}P -coupled ^{13}C nuclei are the A portions of AXY spin systems. A doublet, rather than a doublet of doublets is observed for the ^{13}C resonances of the asymmetric complexes because the ^{13}C nuclei are only coupled to one of the two ^{31}P nuclei. Comparison of the magnitudes of ${}^nJ(\text{PC}) + {}^{n+2}J(\text{P}'\text{C})$ and ${}^nJ(\text{PC})$ for similar resonances in the two types of complexes suggests that one of the P–C coupling constants in the symmetric complexes is also close to zero. This does not affect the type of resonance observed for the ^{31}P -coupled ^{13}C nuclei in these complexes because an apparent quintet will be observed for the A portion of an AXX' spin system as long as significant X–X' and A–X coupling occurs [24].

X-ray crystal structure of (CO)₅Mo(μ-Ph₂POP(OCH₂CMe₂CH₂O))Mo(CO)₅, II

Few complexes containing identical metal centers connected by a bis(P-donor) ligand with different P-donor sites have been structurally characterized. The structures of these complexes are of interest because they allow the effects of the different P-donor centers on the bonding in the metal centers to be compared.

The molecular structure of II is shown in Fig. 1. The ligand environments about each of the Mo atoms are similar to those in other (CO)₅Mo(P-ligand) complexes and are best described as slightly distorted octahedra [25]. The dihedral angles between the equatorial planes for the donor atoms are 89.3, 89.4 and 89.1° for the Mo(CO)₅(Ph₂PO-) group and 89.1, 89.7 and 88.4° for the Mo(CO)₅(P(OCH₂CMe₂CH₂O)O-) group. The average Mo-C bond length of 2.048(3) Å corresponds to a bond order of approximately 1.5 [26]. The Mo-P bond lengths are similar to those in other complexes [27] and are shorter than those predicted from single bond covalent radii (neutral Mo = 1.61 Å [26], neutral P = 1.10 Å [28]). This suggests that $d_{\pi}-d_{\pi}$ Mo-P bonding occurs in both of the Mo carbonyl centers in II [27a].

The Mo-C bond length for the CO ligand *trans* to the P-ligand in the Mo(CO)₅(Ph₂PO-) group (2.023(3) Å) is significant shorter than that in the Mo(CO)₅(P(OCH₂CMe₂CH₂O)O-) group (2.036(3) Å) while the Mo-P bond length in the Mo(CO)₅(Ph₂PO-) group (2.484(1) Å) is significant longer than that in the Mo(CO)₅P(OCH₂CMe₂CH₂O)O-) group (2.435(1) Å). These results indicate that the Ph₂PO- group is a poorer π -acceptor than is the P(OCH₂CMe₂CH₂O)O- group consistent with the NMR results.

The geometry of the P-O-P bridging group in II closely resembles that observed in other complexes containing two metal centers bridged by a single R₂POP(R)₂ ligand. The P(1)-O-P(2) angle of 149.3(1)° is quite similar to those reported for (CO)₅Mo(μ-Ph₂POPPh₂)Fe(CO)₄ (146.4(2)°) [2d] and (η^5 -C₅H₅)(CO)₂Mn(μ-Ph₂POPPh₂)Mn(CO)₂(η^5 -C₅H₅) (142°) [2e]. The P-O distance for the Ph₂PO- group (P(1)-O = 1.645(2) Å) is identical to that reported for (CO)₅Mo(μ-Ph₂POPPh₂)Fe(CO)₄ (P-O = 1.641(3) Å) while the P-O distance for the P(OCH₂CMe₂CH₂O)O- group (P(2)-O = 1.614(2) Å) is close to that reported for K₄[Pt₂(μ-O₂POPO₂)₄MeI] (1.602(5) Å) [3c].

An interesting aspect of the structure of II is the conformation of the phosphorinane ring, shown in Fig. 2. The ring is somewhat flattened about the P(OC-)₂ group because the P-O-C ring angles (P(2)-O(7)-C(20) = 121.3(2)° and P(2)-O(8)-C(18) = 121.2(2)° are larger than the tetrahedral angle while the O-P-O angle (O(7)-P(2)-O(8) = 103.8(1)°) is smaller. The Mo(CO)₅ group occupies an equatorial position while the OPPh₂Mo(CO)₅ group occupies an axial position. The conformation of the phosphorinane ring in II is similar to that reported for the phosphorinane ring in *cis*-Mo(CO)₄(P(OCHMeCH₂CHMeO)OMe)₂ [29]. Occupation of the equatorial position by the Mo(CO)₅ group in II is consistent with previous ¹H NMR spectroscopic studies of Mo(CO)₅(P(OCH₂CMe₂CH₂O)X) (X = alkyl, aryl, alkoxy, alkylthio, amino) complexes [30]. This, together with the similar ¹H NMR spectra of Mo(CO)₅(P(OCH₂CMe₂CH₂O)Br), [Et₃NH][Mo(CO)₅(P(OCH₂CMe₂CH₂O)O)] and II, suggests that the phosphorinane ring conformation remains invariant during the hydrolysis of Mo(CO)₅(P(OCH₂CMe₂CH₂O)Br) and the formation of II.

Conclusions

The reactions of coordinated P-ligands provide a facile means for the preparation of unusual bimetallic complexes with unsymmetrical, bridging bis(P-donor) ligands. The ^{13}C NMR spectra of the complexes with $\text{R}_2\text{POPR}'_2$ bridging ligands vary dramatically as the P-substituents are varied due to changes in the NMR spin systems in the complexes. The ^{13}C NMR spectra and the X-ray molecular structure of II indicate that the $\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})$ group is a poorer electron donor (better electron acceptor) than is the PPh_2 group. This is as expected based upon the electronegativities of the P substituents. The X-ray crystal structure of II also indicates that the conformation of the $\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})$ ring is similar to that proposed for other $\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{R})$ complexes. The conformation of the ring appears to remain invariant during the 2-step synthesis of II from $\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{Br})$.

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References

- 1 R.J. Puddephatt, *Chem. Soc. Rev.*, 12 (1983) 99 and references therein.
- 2 (a) H. Vahrenkamp, *Chem. Ber.*, 105 (1972) 3574. (b) C.S. Kraihanzel and C.M. Bartish, *J. Am. Chem. Soc.*, 94 (1972) 3572. (c) E.H. Wong, F.C. Bradley and E.J. Gabe, *J. Organomet. Chem.*, 244 (1983) 235. (d) E.H. Wong, F.C. Bradley, L. Prasad and E.J. Gabe, *ibid.*, 263 (1984) 167.
- 3 (a) A.L. de Preez, I.L. Marais, R.J. Haines, A. Pidcock and M. Safari, *J. Chem. Soc., Dalton Trans.*, (1981) 1918. (b) C.-M. Che, W.P. Schaefer, H.B. Gray, M.K. Dickson, P.B. Stein and D.M. Roundhill, *J. Am. Chem. Soc.*, 104 (1982) 1962. (c) D.E. Berry, G.W. Bushnell and K.R. Dixon, *Inorg. Chem.*, 22 (1983) 1962. (d) J. Gimeno, V. Riera, M.A. Ruiz, A.M. Manotti Lanfredi and A. Tiripicchio, *J. Organomet. Chem.*, 268 (1984) C13. (e) C.-M. Che, T.C.W. Mak and H.B. Gray, *Inorg. Chem.*, 23 (1984) 4386. (f) D.E. Berry, K.A. Beveridge, G.W. Bushnell, K.R. Dixon and A. Pidcock, *Can. J. Chem.*, 64 (1986) 343.
- 4 (a) J. Ellermann, G. Szucsányi, K. Geibel and E. Wilhelm, *J. Organomet. Chem.*, 263 (1984) 297. (b) G. Liehr, G. Szucsányi and J. Ellermann, *ibid.*, 265 (1984) 95. (c) J. Ellermann, G. Szucsányi and E. Wilhelm, *Chem. Ber.*, 118 (1985) 1588. (d) R. Usò, J. Fornies, R. Navarro and J.I. Cebollada, *J. Organomet. Chem.*, 304 (1986) 381. (e) J. Ellermann and W. Wend, *Zeit. Anorg. Allg. Chem.*, 543 (1986) 169.
- 5 (a) J.C.T.R. Burckett St. Laurent, P.B. Hitchcock and J.F. Nixon, *J. Organomet. Chem.*, 249 (1983) 243. (b) J.C.T.R. Burckett St. Laurent, J. Sinclair and J.F. Nixon, *ibid.*, 269 (1984) 379. (c) O.J. Scherer, R. Anselman and W.S. Sheldrick, *ibid.*, 263 (1984) C26.
- 6 G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, *J. Organomet. Chem.*, 323 (1987) 313.
- 7 (a) H.C. Clark, G. Ferguson, P.N. Kapoor and M. Parvez, *Inorg. Chem.*, 24 (1985) 3924. (b) O. Orama, *J. Organomet. Chem.*, 314 (1986) 273.
- 8 J.M. Brown and A.R. Lucy, *J. Organomet. Chem.*, 314 (1986) 241.
- 9 (a) J.M. Brown and L.R. Canning, *J. Chem. Soc., Chem. Commun.*, 1983, 460. (b) J.M. Brown, L.R. Canning and A.R. Lucy, *ibid.*, 1984, 915.
- 10 P.M. Strickland, E.J. Volco and J.G. Verkade, *J. Am. Chem. Soc.*, 105 (1983) 2494.
- 11 (a) R.L. Keiter, R.D. Borger, M.J. Madigan, S.L. Kaiser and D.L. Rowley, *Inorg. Chim. Acta*, 76 (1983) L5. (b) J.A. Iggo and B.L. Shaw, *J. Chem. Soc., Dalton Trans.*, (1985) 1009.
- 12 (a) T. Chivers, C. Lensink and J.F. Richardson, *Organometallics*, 5 (1986) 819. (b) T. Chivers, C. Lensink and J.F. Richardson, *J. Organomet. Chem.*, 325 (1987) 169.

- 13 C.S. Kraihanzel and C.M. Bartish, *J. Organomet. Chem.*, 43 (1972) 343.
- 14 (a) G.M. Gray, J.E. Whitten and J.W. Box, *Inorg. Chim. Acta*, 116 (1986) 21. (b) G.M. Gray, J.E. Whitten and J.W. Box, *ibid.*, 120 (1986) 25.
- 15 G.M. Gray, N. Takada, A.L. Zell and H. Einspahr, *J. Organomet. Chem.*, 342 (1988) 339.
- 16 D.J. Duchamp, *A.C.S. Symp. Ser.*, 46 (1977) 98.
- 17 W.R. Busing and H.A. Levy, *Acta Cryst.*, 10 (1957) 180.
- 18 D.J. Duchamp, CRYM, A System of Crystallographic Programs, The Upjohn Co., Kalamazoo, MI, 1984.
- 19 P. Main, S.J. Fiske, S.E. Hull, L. Seeinger, G. Germain, J.P. Declercq and M.M. Woolfson, MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, Univ. of York, England, and Univ. of Louvain, Belgium, 1980.
- 20 P.A. Doyle and P.S. Turner, *Acta Cryst.*, A24 (1968) 390.
- 21 R.F. Stewart, E.R. Davidson and W.T. Simpson, *J. Chem. Phys.*, 42 (1965) 3175.
- 22 G.M. Gray, *Inorg. Chim. Acta*, 81 (1984) 157.
- 23 G.M. Bodner and L.J. Todd, *Inorg. Chem.*, 13 (1974) 1335.
- 24 D.A. Redfield, J.H. Nelson and L.W. Cary, *Inorg. Nucl. Chem. Lett.*, 10 (1974) 727.
- 25 F.A. Cotton, D.J. Darensbourg and W.H. Ilsley, *Inorg. Chem.*, 20 (1981) 578.
- 26 F.A. Cotton and R.M. King, *ibid.*, 4 (1965) 314.
- 27 (a) K.K. Cheung, T.F. Lai and S.Y. Lam, *J. Chem. Soc. A*, (1970), 3345. (b) D.M. Bridges, G.D. Holywell, D.W.H. Rankin and J.M. Freeman, *J. Organomet. Chem.*, 32 (1971) 87. (c) J.R. DeLerno, L.M. Trefonas, M.Y. Darensbourg and R.J. Majeste, *Inorg. Chem.*, 15 (1976) 816.
- 28 L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell Univ. Press, New York.
- 29 R.A. Jacobsen, B.A. Karcher, R.A. Montag, S.M. Socol, L.J. Van de Griend and J.G. Verkade, *Phosphorus and Sulfur*, 11 (1981) 27.
- 30 (a) C.M. Bartish and C.S. Kraihanzel, *Inorg. Chem.*, 12 (1973) 391. (b) C.S. Kraihanzel and C.M. Bartish, *Phosphorus*, 4 (1974) 271.
- 31 C.F. Johnson, ORTEP: A Fortran Thermal-Ellipsoid Program for Crystal Structure Illustrations, Report ORNL-3974, revised, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.