

Structural characterization of tripodal phosphine complexes of transition metals. Examples of chair and twisted-boat conformations in six-membered chelate rings

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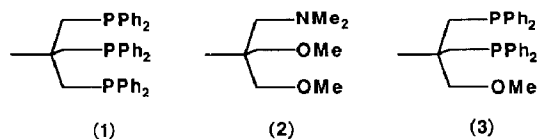
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Abstract

Complexation of a “hybrid” tripodal ligand 2,2-bis(diphenylphosphinomethyl)-1-methoxypropane (P_2O) with group VI carbonyls, nickel(II) and palladium(II) compounds has been studied. Thus P_2O reacts with $M(CO)_6$, $NiCl_2$ and $PdCl_2$ to give $(P_2O)M(CO)_4$ ($M = Cr, Mo, W$), $(P_2O)NiCl_2$ and $(P_2O)PdCl_2$, respectively. All the complexes have been characterized by spectroscopy and elemental analysis, and the crystal structures of the complexes of $(P_2O)Mo(CO)_4$ (**4b**), $(P_2O)W(CO)_4$ (**4c**) and $(P_2O)NiCl_2$ (**6**) have been determined by X-ray diffraction. In all cases, the tripodal ligand behaves solely as a bidentate with two phosphorus donors coordinating to the metal centers. In the examination of the conformations of the six-membered chelate rings, it was found that both **4b** and **4c** were in the twisted-boat form; whereas **6** was in the chair form. The possible reasons for this conformational difference are discussed.

Introduction

Tripodal ligands have received much attention [1–8], but such systems have been limited to the same donor atoms, such as all-phosphorus donors in triphos **1**, and a few nitrogen and oxygen containing “mixed” ligands (**2**) have been used for complexation with titanium metal [8]. Owing to the tripod-like geometry of these ligands, they can ligate three dimensionally such as in *fac*-(triphos)Cr(CO)₃ [3]. This characteristic feature would make tripod-like ligands containing different ligating sites useful for coordination studies. We recently developed the synthesis of a new tripodal ligand **3**, which has both “hard” and “soft” donor sites [6]. Here, we present our results on the coordinating behavior of **3** toward transition metals.



Results and discussion

Group VI complexes

The thermal reaction of **3** with $\text{Cr}(\text{CO})_6$ in boiling xylene was found to give $(\text{3})\text{Cr}(\text{CO})_4$ in 53% yield (eq. 1). Similarly, when $\text{Mo}(\text{CO})_6$ or $\text{W}(\text{CO})_6$ are heated with **3** in toluene the corresponding $(\text{3})\text{M}(\text{CO})_4$ complexes (eq. 1) are obtained. All the reactions were monitored as a function of time by IR spectroscopy, which showed that 8–10 h were required for all of the metal carbonyl to react with **3**. Prolonged heating or photochemical activation of **4b** degrades the tetracarbonyl species with no indication of formation of the tricarbonyl species, $(\text{3})\text{M}(\text{CO})_3$. Another route to the tricarbonyl species involves the reaction of $\text{M}(\text{CH}_3\text{CN})_3(\text{CO})_3$ or (cycloheptatriene) $\text{M}(\text{CO})_3$ with **3** to give **4**. Clearly a “hard” donor atom cannot be forced to coordinate to a group VI metal center, not even through a tripodal linkage. In Table 1 are listed the spectroscopic and analytical data for **4a–4c**. The methylene units attached to the phosphorus group are divided into two groups: those with hydrogen atoms *cis* to the methoxymethyl group in the chelate ring, and those in which they are *trans*. Consequently, the ^1H NMR spectra of **4a–4c** showed an absorption pattern of ABX for these protons because of the geminal coupling ($J(\text{H}-\text{C}-\text{H})$) and the splitting by phosphorus ($J(\text{P}-\text{C}-\text{H})$). The ^{31}P NMR coordi-

Table 1
Spectroscopic and analytical data for **4a–4c**

Complex	^1H NMR	^{31}P NMR ^a	IR (Toluene)	Analysis (%)			
				Calcd		Found	
				C:	H:	C:	H:
4a	7.62–7.52 (m, 4H)	41.09 (66.2)	2006 (m)	$\text{C}_{34}\text{H}_{32}\text{O}_5\text{P}_2\text{Cr}$ 64.35; 5.08 63.15; 5.15			
	7.52–7.45 (m, 4 H)		1999 (m)				
	7.45–7.30 (m, 12 H)		1917 (m)				
	2.94 (s, 3 H), 2.76 (s, 2 H)		1882 (s)				
	2.52 (dd, J 15, 6 Hz, 2 H)						
	2.30 (dd, J 15, 9 Hz, 2 H)						
0.75 (s, 3 H)							
4b	7.68–7.53 (m, 4 H)	19.59 (40.7)	2017 (m)	$\text{C}_{34}\text{H}_{32}\text{O}_5\text{P}_2\text{Mo}$ 60.18; 4.75 60.09; 4.76			
	7.53–7.42 (m, 4 H)		1919 (m)				
	7.42–7.30 (m, 12 H)		1892(s)				
	2.99 (s, 3 H), 2.83 (s, 2 H)						
	2.53 (dd, J 15, 6 Hz, 2 H)						
	2.42 (dd, J 15, 9 Hz, 2 H)						
0.75 (s, 3 H)							
4c	7.62–7.50 (m, 4 H)	0.01 (25.1)	2014 (m)	$\text{C}_{34}\text{H}_{32}\text{O}_5\text{P}_2\text{W}$ 53.28; 4.21 53.24; 4.29			
	7.50–7.42 (m, 4 H)		1913 (m)				
	7.42–7.39 (m, 12 H)		1882 (s)				
	2.98 (s, 3 H), 2.82 (s, 2 H)						
	2.63 (dd, J 15, 6 Hz, 2 H)						
	2.50 (dd, J 15, 9 Hz, 2 H)						
0.76 (s, 3 H)							

^a The coordination chemical shifts (Δ_δ) are given in the parentheses. $\Delta_\delta = \delta(\text{complex}) - \delta(\text{free ligand})$ in ppm.

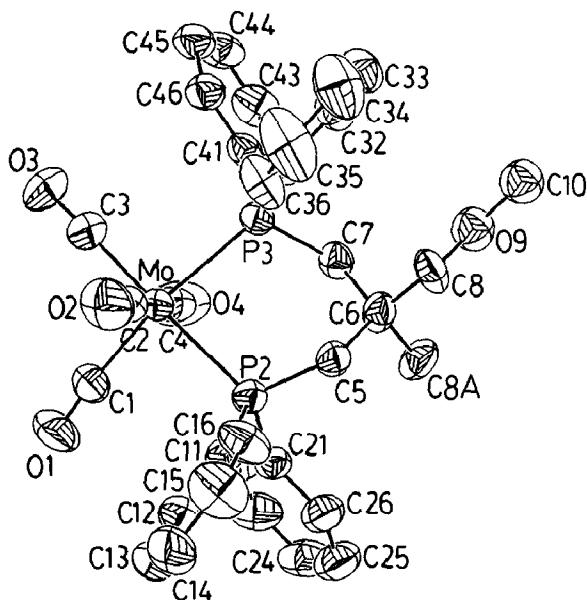
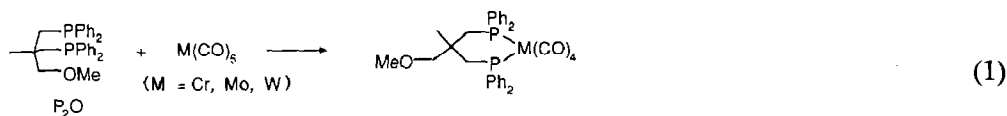
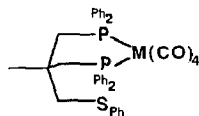


Fig. 1. The ORTEP plot of complex of **4b**.

nation chemical shifts (Table 1) which are found to fall in the order $\text{Cr} > \text{Mo} > \text{W}$, are similar to those for $(\text{dpppe})\text{M}(\text{CO})_4$ [dppp = 1,3-bis(diphenylphosphino)propane] [9] and $(\text{P}_2\text{S})\text{M}(\text{CO})_4$ (**5**) [7].



(**4a**: M = Cr;
4b: M = Mo;
4c: M = W)



(5)

Crystals suitable for the X-ray study of **4b** and **4c** were obtained from dichloromethane and methanol. Complexes **4b** and **4c** are isomorphous, i.e. they have the same atomic residues at crystallographic sites. Both molecules contain tripodal ligand **3** coordinated to the $\text{M}(\text{CO})_4$ moiety through two phosphorus atoms to form a *cis* octahedral geometry. Figures 1 and 2 show different views of **4b**. The atomic coordinates and thermal parameters for **4b** and **4c** are given in Table 2 and Table 3, respectively. Selected bond distances and bond angles are listed in Table 4. All bond distances are within expected ranges, such as 2.50–2.52 Å typical for metal-phosphorus bond lengths. In the structure of **4b**, the four metal carbonyl distances fall into two different groups whose average values are 1.983 and 1.998 Å. The two

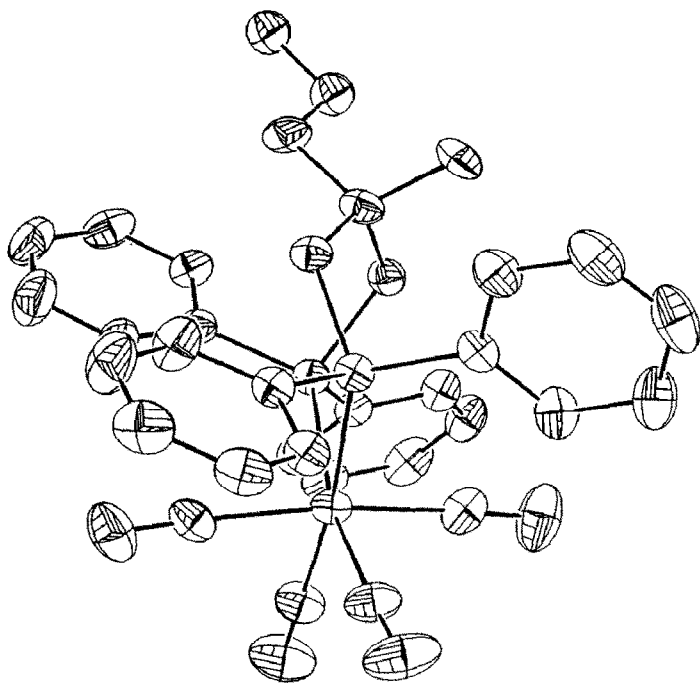


Fig. 2. Another view of the crystal structure of **4b**.

metal–carbon bonds *trans* to phosphorus atoms are slightly shorter, as expected, than those mutually *trans* to carbonyl groups; but the inverse is observed in **4c**, 1.984 vs. 1.970 Å.

NiCl₂ and PdCl₂ complexes

A solution of **3** in acetone was treated with NiCl₂·DME [DME = 1,2-dimethoxyethane] (also in acetone) at room temperature, complex **6** was immediately formed as was indicated by the change in color to orange. However, when this solution was heated under reflux for 2 h, the complex could be isolated as an orange solid. The conductivity (1.7 Ω⁻¹ cm² mol⁻¹) and the electronic absorptions (466, 312, 283, 276 and 239 nm) are almost identical with those reported for the complex (triphos)NiCl₂ [5].

The complex (P₂O)NiCl₂·CH₂Cl₂ can be isolated as a crystalline solid; its structure is depicted in Figs. 3 and 4. The atomic coordinates and thermal parameters are listed in Table 5. Some important bond distances and angles of the complex **6** and those of **4b** and **4c** are listed in Table 4 for comparison. The Ni(II) center is tetra-coordinated with two chloride ligands and two phosphorus donors in a square-planar geometry, with the Ni atom slightly (0.031(1) Å) out of the plane. The oxygen donor of the tripodal ligand **3** remains uncoordinated, which is similar to that in the complex (triphos)NiCl₂ that has one dangling phosphorus donor [10]. A symmetry plane passes through the complex at the Ni atom, the C5 carbon and the oxygen atom. The Ni–P bond distances are 2.164(2) Å, and the Ni–Cl are 2.207(2) Å. The angles of both Cl–Ni–Cl and P–Ni–P are slightly distorted from 90°.

Table 2

The atomic coordinates and thermal parameters for **4b**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso}
Mo	0.72723(4)	0.35416(2)	0.25734(2)	3.63(2)
P2	0.86855(11)	0.25030(7)	0.23008(7)	3.60(5)
P3	0.73187(11)	0.28676(7)	0.39267(7)	3.53(6)
C1	0.7576(5)	0.4078(3)	0.1575(3)	5.4(3)
O1	0.7817(4)	0.43747(21)	0.10157(23)	8.8(3)
C2	0.5954(4)	0.2956(3)	0.1842(3)	4.7(3)
O2	0.5189(3)	0.26523(23)	0.14020(20)	7.38(23)
C3	0.6023(4)	0.4277(3)	0.2768(3)	5.4(3)
O3	0.5296(4)	0.47049(22)	0.28669(23)	8.24(25)
C4	0.8473(5)	0.4231(3)	0.3238(3)	5.2(3)
O4	0.9138(4)	0.46626(22)	0.36050(24)	8.35(25)
C5	0.8736(4)	0.16613(24)	0.2969(3)	3.88(22)
C6	0.9226(4)	0.1722(3)	0.3914(3)	4.18(22)
C7	0.8812(4)	0.24495(25)	0.43072(24)	3.94(23)
C11	0.8201(4)	0.20571(25)	0.1287(3)	3.87(21)
C12	0.8478(4)	0.2419(3)	0.0591(3)	4.48(24)
C13	0.8091(5)	0.2123(3)	-0.0189(3)	5.3(3)
C14	0.7415(5)	0.1483(3)	-0.0306(3)	6.3(3)
C15	0.7122(5)	0.1120(3)	0.0362(3)	7.2(3)
C16	0.7509(5)	0.1405(3)	0.1163(3)	5.8(3)
C21	1.0242(4)	0.2731(3)	0.2264(2)	3.9(2)
C22	1.0641(4)	0.3474(3)	0.2360(3)	5.0(3)
C23	1.1825(5)	0.3663(3)	0.2332(3)	6.5(3)
C24	1.2616(5)	0.3100(4)	0.2216(3)	7.1(4)
C25	1.2217(5)	0.2372(3)	0.2098(3)	6.6(3)
C26	1.1049(4)	0.2181(3)	0.2129(3)	5.4(3)
C31	0.6270(4)	0.2112(3)	0.4067(3)	3.9(2)
C32	0.6221(4)	0.1831(3)	0.4853(3)	4.6(3)
C33	0.5485(5)	0.1229(3)	0.4947(3)	6.1(3)
C34	0.4785(6)	0.0897(3)	0.4282(4)	8.1(4)
C35	0.4828(6)	0.1171(3)	0.3504(3)	9.1(4)
C36	0.5556(5)	0.1771(3)	0.3409(3)	5.9(3)
C41	0.7153(4)	0.3529(2)	0.4763(2)	3.7(2)
C42	0.8130(4)	0.3844(3)	0.5288(3)	4.7(3)
C43	0.7949(5)	0.4362(3)	0.5896(3)	5.7(3)
C44	0.6807(5)	0.4548(3)	0.5979(3)	6.2(3)
C45	0.5841(5)	0.4233(3)	0.5459(3)	5.3(3)
C46	0.6015(4)	0.3734(3)	0.4852(3)	4.5(2)
C8	0.8728(5)	0.0993(3)	0.4270(3)	4.8(3)
C8A	1.0620(4)	0.1741(3)	0.4098(3)	5.2(3)
O9	0.9177(4)	0.1043(3)	0.5148(3)	5.5(1)
C10	0.8694(6)	0.0423(4)	0.5580(4)	5.6(2)
O9A	1.0898(10)	0.1036(6)	0.3727(7)	6.0(3)
C10A	1.1980(21)	0.0781(13)	0.3912(14)	10.3(7)

Displacement reactions of **6** by other phosphines were also studied. (P₂O)NiCl₂ undergoes no ligand substitution reactions with triphenylphosphine, even at elevated temperatures. On the other hand, dppe [dppe = 1,2-bis(diphenylphosphino)ethane] reacts instantly with **6** to generate the free tripodal ligand **3**, (dppe)NiCl₂ and (dppe)₂NiCl₂ as identified by ³¹P NMR spectroscopy.

Table 3

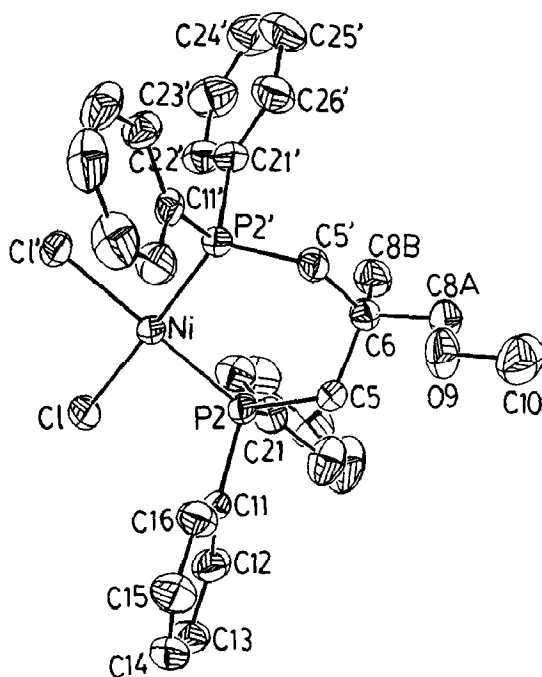
The atomic coordinates and thermal parameters for **4c**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso}
W	0.72733(3)	0.354186(17)	0.257170(18)	3.400(14)
P2	0.86782(17)	0.25007(11)	0.22972(11)	3.38(9)
P3	0.73236(16)	0.28701(11)	0.39226(11)	3.26(9)
C1	0.7596(7)	0.4076(4)	0.1567(5)	5.0(4)
O1	0.7827(6)	0.4372(3)	0.1003(4)	8.2(4)
C2	0.5961(7)	0.2975(5)	0.1849(4)	4.6(5)
O2	0.5188(5)	0.2657(4)	0.1402(3)	6.9(4)
C3	0.6030(7)	0.4281(4)	0.2766(5)	5.0(4)
O3	0.5298(5)	0.4713(3)	0.2876(4)	7.9(4)
C4	0.8465(7)	0.4219(4)	0.3237(5)	4.9(5)
O4	0.9148(5)	0.4656(4)	0.3610(4)	7.9(4)
C5	0.8737(6)	0.1665(4)	0.2962(4)	3.7(3)
C6	0.9226(6)	0.1711(4)	0.3911(4)	3.8(3)
C7	0.8816(6)	0.2444(4)	0.4304(4)	3.7(4)
C11	0.8188(6)	0.2056(4)	0.1283(4)	3.5(3)
C12	0.8479(6)	0.2415(4)	0.0595(5)	4.2(4)
C13	0.8095(8)	0.2123(5)	-0.0197(5)	5.2(5)
C14	0.7409(8)	0.1487(6)	-0.0308(5)	6.0(5)
C15	0.7118(8)	0.1118(5)	0.0361(6)	6.9(6)
C16	0.7487(7)	0.1404(5)	0.1158(4)	5.5(5)
C21	1.0233(6)	0.2732(4)	0.2259(4)	3.6(4)
C22	1.0626(6)	0.3481(5)	0.2345(4)	4.5(4)
C23	1.1817(8)	0.3666(5)	0.2321(5)	6.4(5)
C24	1.2606(8)	0.3107(7)	0.2196(5)	6.9(6)
C25	1.2204(8)	0.2366(6)	0.2097(5)	6.5(5)
C26	1.1032(7)	0.2176(4)	0.2121(5)	4.9(4)
C31	0.6274(6)	0.2111(4)	0.4058(4)	3.6(4)
C32	0.6225(7)	0.1837(4)	0.4843(4)	4.4(4)
C33	0.5505(9)	0.1233(5)	0.4955(5)	5.8(5)
C34	0.4788(9)	0.0892(5)	0.4291(7)	7.9(6)
C35	0.4830(9)	0.1164(6)	0.3502(6)	8.7(6)
C36	0.5572(8)	0.1771(5)	0.3397(5)	5.8(5)
C41	0.7139(6)	0.3529(4)	0.4758(4)	3.4(3)
C42	0.8124(6)	0.3845(4)	0.5291(4)	4.3(4)
C43	0.7919(8)	0.4367(5)	0.5903(5)	5.6(5)
C44	0.6779(9)	0.4543(5)	0.5982(5)	5.8(5)
C45	0.5831(7)	0.4241(4)	0.5459(5)	4.9(5)
C46	0.5996(7)	0.3733(4)	0.4846(4)	4.2(4)
C8	0.8731(7)	0.0983(4)	0.4277(4)	4.3(4)
C8A	1.0628(6)	0.1727(4)	0.4097(4)	4.6(4)
O9	0.9167(6)	0.1028(4)	0.5144(4)	5.54(17)
C10	0.8719(9)	0.0414(6)	0.5597(6)	5.3(3)
O9A	1.0900(17)	0.1026(10)	0.3728(10)	6.0(4)
C10A	1.198(3)	0.0809(19)	0.3873(20)	9.2(10)

The Pd^{II} complex was formed by stirring a mixture of **3** and PdCl₂ in dichloromethane and methanol, and was isolated as a yellow solid. The ³¹P NMR showed a single absorption at 16.93 ppm, which indicates that two phosphorus donors coordinate to the metal center. The ¹H NMR chemical shift of the methylene unit attached to the oxygen atom is similar to that of **4b**, indicating that the oxygen donor remains uncoordinated.

Table 4. Selected bond distances (Å) and bond angles (°) for **4b**, **4c** and **6**.

4b		4c		6	
Mo–P2	2.519(1)	W–P2	2.511(2)	Ni–Cl	2.207(2)
Mo–P3	2.515(1)	W–P3	2.502(2)	Ni–P	2.164(2)
Mo–C1	1.981(5)	W–C1	1.990(8)	P2–C5	1.826(4)
Mo–C2	2.012(5)	W–C2	1.980(8)	C5–C6	1.537(5)
Mo–C3	1.985(5)	W–C3	1.979(8)		
Mo–C4	1.984(5)	W–C4	1.961(8)		
P2–C5	1.833(4)	P2–C5	1.815(7)		
P3–C7	1.842(5)	P3–C7	1.843(7)		
C5–C6	1.555(6)	C5–C6	1.555(9)		
C6–C7	1.541(6)	C6–C7	1.542(9)		
C1–O1	1.137(6)	C1–O1	1.135(9)		
C2–O2	1.150(6)	C2–O2	1.17(1)		
C3–O3	1.148(6)	C3–O3	1.159(9)		
C4–O4	1.154(6)	C4–O4	1.17(1)		
P2–Mo–P3	85.08(4)	P2–W–P3	85.10(6)	Cl–Ni–Cl'	92.24
P2–Mo–C1	88.6(1)	P2–W–C1	88.0(2)	Cl–Ni–P2	86.11(7)
P2–Mo–C2	87.3(1)	P2–W–C2	87.8(2)	Cl–Ni–P2'	177.70(5)
P2–Mo–C3	173.9(2)	P2–W–C3	174.0(2)	P2–Ni–P2'	85.49(7)
P2–Mo–C4	98.2(2)	P2–W–C4	98.2(2)	Ni–P2–C5	120.1(1)
P3–Mo–C1	169.0(2)	P3–W–C1	168.3(2)	P2–C5–C6	118.7(3)
P3–Mo–C2	100.4(1)	P3–W–C2	100.7(2)		
P3–Mo–C3	93.1(1)	P3–W–C3	93.2(2)		
P3–Mo–C4	84.2(1)	P3–W–C4	83.7(2)		
C2–Mo–C4	173.2(2)	C2–W–C4	172.9(3)		
Mo–P2–C5	114.8(1)	W–P2–C5	115.0(2)		
Mo–P3–C7	110.5(1)	W–P3–C7	110.7(2)		
Mo–C1–O1	176.1(5)	W–C1–O1	177.2(7)		
Mo–C2–O2	176.8(4)	W–C2–O2	177.7(6)		
Mo–C3–O3	178.9(4)	W–C3–O3	179.6(6)		
Mo–C4–O4	176.5(4)	W–C4–O4	176.4(7)		

Fig. 3. The ORTEP plot of complex of **6**.

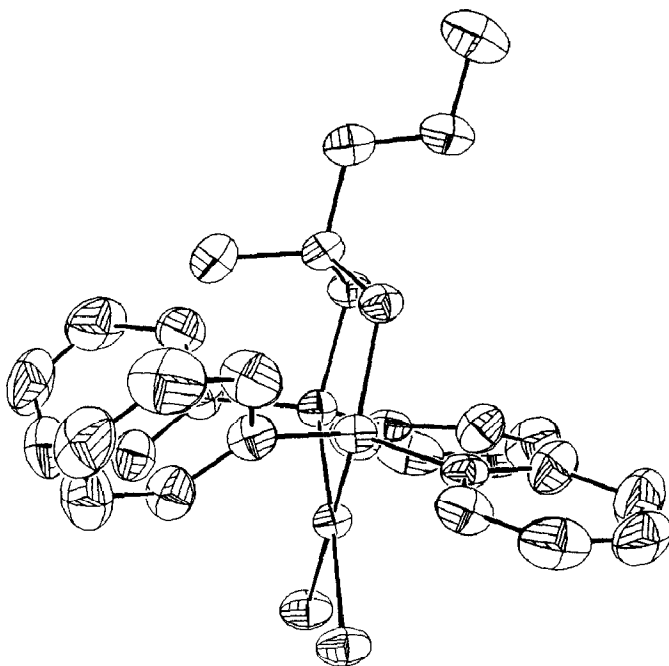


Fig. 4. Another view of the crystal structure of 6.

Table 5

The atomic coordinates and thermal parameters for 6

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso}
Ni	0.68969(10)	1/4	0.27588(8)	2.28(4)
Cl	0.82647(14)	0.33975(6)	0.22496(12)	3.45(6)
P2	0.55522(14)	0.34038(6)	0.31861(11)	2.48(6)
C5	0.4184(5)	0.32030(23)	0.4044(4)	2.69(21)
C6	0.3148(7)	1/4	0.3637(6)	2.7(3)
C8B	0.2193(8)	1/4	0.2117(6)	3.9(4)
C8A	0.1998(8)	1/4	0.4390(7)	3.5(4)
O9	0.2805(5)	1/4	0.5773(4)	4.7(3)
C10	0.1769(10)	1/4	0.6521(8)	6.0(5)
C11	0.6806(5)	0.40877(23)	0.4316(4)	2.79(21)
C12	0.6948(6)	0.4826(3)	0.3960(4)	3.8(3)
C13	0.7964(6)	0.5306(3)	0.4861(5)	5.3(3)
C14	0.8851(6)	0.5069(3)	0.6096(5)	5.6(3)
C15	0.8733(6)	0.4334(3)	0.6468(5)	5.5(3)
C16	0.7721(6)	0.3844(3)	0.5589(5)	4.1(3)
C21	0.4410(5)	0.39156(25)	0.1687(4)	3.16(23)
C22	0.4451(6)	0.3702(3)	0.0460(4)	3.87(25)
C23	0.3577(7)	0.4082(3)	-0.0680(5)	5.3(3)
C24	0.2670(7)	0.4678(3)	-0.0585(5)	6.3(3)
C25	0.2592(7)	0.4892(3)	0.0617(6)	6.4(4)
C26	0.3456(6)	0.4506(3)	0.1756(5)	4.7(3)
C	0.1812(13)	3/4	0.0704(9)	10.5(9)
Cl1	0.3691(4)	3/4	0.1924(3)	11.7(3)
Cl2	0.0418(4)	3/4	0.1356(3)	13.2(3)

Table 6

Some important torsional angles ($^{\circ}$) for complexes **4b**, **4c** and **6**

<i>(a) Six-membered chelate ring around M–P2–C5–C6–Cx–Py</i>			
	4b , M = Mo $x = 7, y = 3$	4c , M = W $x = 7, y = 3$	6 , M = Ni $x = 5', y = 2'$
M–P2–C5–C6	–65.4(2)	–65.0(3)	–42.5
P2–C5–C6–Cx	41.5(2)	40.7(3)	67.7
C5–C6–Cx–Py	33.9(2)	34.5(3)	–67.7
C6–Cx–Py–M	–74.6(2)	–74.6(3)	42.5
Cx–Py–M–P2	34.3(1)	34.1(2)	–13.2
Py–M–P2–C5	16.6(1)	16.4(2)	13.2
<i>(b) Between equatorial ligands and phenyl groups</i>			
	4b , M = Mo	4c , M = W	6
C11–P2–M–C1	–58.8(2)	–59.2(3)	Cl–Ni–P2–C11 –51.8(1)
C21–P2–M–C1	59.3(2)	58.9(3)	Cl–Ni–P2–C21 68.0(1)
C31–P3–M–C3	84.2(2)	84.5(3)	
C41–P3–M–C3	–37.8(2)	–36.8(2)	

Conformational analysis

The torsional angles around the six-membered chelate rings for complexes **4b**, **4c** and **6**, are listed in Table 6 for comparison. Species **4b** and **4c** have similar torsional angles around the ring, M–P2–C5–C6–C7–P3, and they share the +g, –g alternation. The four positive and two negative torsional angles in the rings indicate their chelate rings to be in twist-boat conformations. In contrast, the conformation of the chelate ring on **6** adopts a chair form, which is manifested in the characteristic alternating +g, –g torsional angles. However, this chair conformation is distorted near the P2, Ni, P2' end, as shown in Fig. 4.

Theoretical studies have indicated that the chair conformation is the most stable form in a six-membered chelate ring associated with its octahedral complex [11]; indeed, there are many examples which confirm this. Typically, the structure of $(OC)_4WPPH_2CH(CH_2CH_2PPh_2)CH_2PPh_2$ (**7**) shows its chelate ring to be in the chair form with CH_2PPh_2 substituent occupying an equatorial position [12]. If **4b** and **4c** were forced into a chair conformation, like in **7**, three major interactions would arise (Fig. 5): (1) the 1,3-diaxial interaction between methyl and phenyl groups; (2) the “eclipsed” interactions between equatorial ligands and phenyl groups; and (3) the interactions between the apical ligands and hydrogen atoms. Thus, the six-membered chelate rings in **4b** and **4c** adopt a twisted-boat form, which excludes some of those interactions. The dihedral angles between equatorial ligands and phenyl groups (listed in Table 6) in **4b** and **4c** are the result of minimizing the “eclipsed” interactions. The unusually large C31–P3–M–C3 angle makes the C2–M–P3–C31 (M = Mo, $-3.7(2)^{\circ}$; M = W, $-2.9(2)^{\circ}$) angle smaller, and distorts the P3–M–C2 angle from 90° [M = Mo, $100.4(1)^{\circ}$; M = W, $100.7(2)^{\circ}$].

Interestingly, the six-membered chelate ring in species **6** prefers the stable chair form. Without the apical ligands in **6**, the interactions between these ligands and hydrogen atoms disappear. The lack of such interaction could allow the chelate ring in **6** to adopt a chair conformation. However, this chair form is distorted (almost into a half-chair form). In order to minimize the “eclipsed” interaction between chlorides and phenyl groups, the dihedral angles of Cl–Ni–P2–C11 and Cl–Ni–P2–

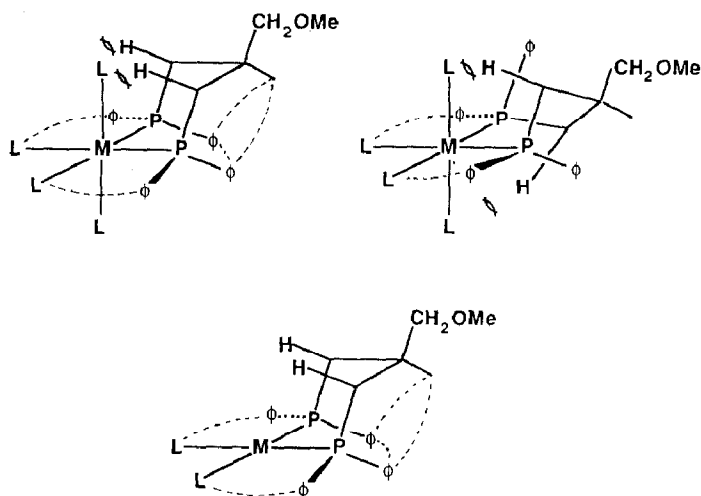


Fig. 5. Major interactions in (a) chair form and (b) twist-boat form in $M(P_2O)L_4$, and (c) chair form in $M(P_2O)L_2$.

C21 become $-51.8(1)$ and $68.0(1)^\circ$ respectively. In addition the larger P–Ni–P [$95.49(7)^\circ$], angle helps to relieve the 1,3-diaxial interaction between the phenyl groups.

Experimental

Proton magnetic resonance spectra were recorded on either a Varian EM-390, a Bruker AC-E 200 or a Bruker AM-300WB spectrometer. Proton-decoupled phosphorus-31 NMR spectra were determined on a Bruker AC-E 200 or a Bruker AM-300WB spectrometer at 81.01 MHz and 121.49 MHz respectively. Chemical shifts are given in parts per million relative to 85% H_3PO_4 for ^{31}P NMR spectra in $CDCl_3$, unless otherwise noted.

Infrared and UV/Vis spectra were obtained on a Perkin Elmer 1310 or 983G and a Perkin Elmer Lambda 3B instrument, respectively. Elemental analyses were carried out on Perkin Elmer 240C instrument.

All of the reactions, manipulations and purification steps involving phosphines were performed under dry nitrogen or argon. Air-sensitive liquids were transferred by Teflon flex-needles under nitrogen pressure or by syringe. Toluene and xylene were distilled from sodium metal under nitrogen. Acetone was dried over 4A molecular sieves. $NiCl_2 \cdot DME$ was prepared according to the literature method [13]. Other solvents and chemicals from commercial sources were used without further purification, unless otherwise stated.

General procedures for preparation of 4a–4c. A flask equipped with refluxing condenser and containing tripod ligand **3** and equimolar amounts of metal carbonyl in aromatic solvent [toluene for $Mo(CO)_6$ and $W(CO)_6$, xylene for $Cr(CO)_6$], was heated to reflux under nitrogen. The progress of each reaction was monitored by IR spectroscopy in the range of metal-carbonyl absorptions. The crude reaction mixture was then chromatographed on silica gel with a mixture of hexane, dichloromethane and ethyl acetate as eluant. The fraction containing the

desired product was collected and recrystallized from a solution of methylene chloride and methanol. All spectroscopic and analytical data are listed in Table 1.

[2,2-Bis(diphenylphosphinomethyl)-1-methoxypropane]nickel(II) chloride (6). A mixture of **3** (24.3 mg, 0.052 mmol) and NiCl₂ · DME (11.4 mg, 0.052 mmol) in dry acetone (10 ml) was heated at reflux for 2 h. After removal of solvent, the residue was recrystallized from hexane/dichloromethane to give the desired complex **6** as a brown crystalline solid (22.3 mg, 72%): mp (dec.) 196 °C; ¹H NMR δ 8.10 (d, *J* = 7.5 Hz, 4 H), 7.95 (d, *J* = 7.5 Hz, 4 H), 7.58–7.39 (m, 12 H), 3.21–2.56 (br, 4 H), 2.86 (s, 3 H), 2.59 (s, 2 H), 0.56 (s, 3 H); UV/Vis (CH₂Cl₂) 466, 312, 283, 276, 239 nm.

Anal. Found: C, 54.68; H, 5.11. C₃₀H₃₂OP₂Cl₂Ni · CH₂Cl₂ calcd.: C, 54.30; H, 5.00%.

[2,2-Bis(diphenylphosphinomethyl)-1-methoxypropane]palladium(II) chloride. A solution of **3** (75.5 mg, 16.06 mmol) and PdCl₂ (28.3 mg, 15.96 mmol) in dichloromethane (2.5 ml) and methanol (2.5 ml) was stirred at room temperature overnight. After removal of the solvents, the yellow solid was collected and recrystallized from dichloromethane and methanol. The desired product was isolated as a light yellow solid (45 mg, 43 %): mp (dec.) 218 °C; ¹H NMR δ 8.00–7.60 (m, 8 H), 7.5–7.4 (m,

Table 7

Crystal data for **4b**, **4c** and **6** ^{a,b}

	4b	4c	6
Formula	MoP ₂ C ₃₄ H ₃₂ O ₅	WP ₂ C ₃₄ H ₃₂ O ₅	NiP ₂ C ₃₁ H ₃₄ Cl ₄ O
Crystal size(mm)	0.30 × 0.30 × 0.20	0.50 × 0.50 × 0.45	0.2 × 0.2 × 0.15
Lattice	Monoclinic	Monoclinic	Monoclinic
Specific gravity	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>m</i>
<i>a</i> (Å)	11.346(4)	11.330(5)	9.173(4)
<i>b</i> (Å)	17.481(3)	17.422(3)	17.726(15)
<i>c</i> (Å)	16.493(4)	16.446(5)	10.693(2)
β (°)	100.97(3)	101.06(3)	110.13(2)
<i>V</i> (Å ³)	3211(2)	3185(2)	1632(3)
<i>Z</i>	4	4	2
<i>F</i> (000)	1263.71	1363.69	1084
Temperature	300	300	300
μ (mm ⁻¹)	0.53	3.83	1.74
Transmission	0.92-1.00	0.74-1.00	0.90-1.00
2θ _{max} (°)	49.9	49.9	50
<i>h</i> , <i>k</i> , <i>l</i>	13, 20, ±19	±13, 20, 19	10, 21, ±12
λ(Mo-Kα) (Å)	0.7093	0.7093	0.7093
No. of reflections	5649	5599	3153
No. of observed reflections	4439[<i>I</i> > 2σ(<i>I</i>)]	3970[<i>I</i> > 2σ(<i>I</i>)]	1936[<i>I</i> > 2σ(<i>I</i>)]
No. of variables	378	378	190
<i>R</i> (<i>F</i>)	0.042	0.033	0.040
<i>R</i> _w (<i>F</i>)	0.044	0.026	0.032
<i>S</i>	4.504	2.092	1.963

^a Unit cell parameters were obtained by least-squares refinement of the setting of 24 reflections with 18.25 < 2θ < 21.40° for **4b**; 25 reflections with 18.66 < 2θ < 21.58° for **4c** and 11.7 < 2θ < 32.56° for **6**.

^b Relevant expressions are as follows, *F*_o and *F*_c represent respectively the observed and calculated structure factor amplitudes; *R*(*F*) = Σ|*F*_o - *F*_c|/Σ*F*_o; *R*_w(*F*) = [Σw(*F*_o - *F*_c)²/Σw*F*_o²]^{1/2}; *S* = [Σw(*F*_o - *F*_c)²/(*m* - *n*)]^{1/2}, *m* = No. of reflections, *n* = No. of variables.

12 H), 2.81 (s, 3 H), 2.73 (s, 2 H), 2.48 (dd, $J = 15$ and 9 Hz, 2 H), 2.22 (dd, $J = 15$ and 9 Hz, 2 H), 0.58 (s, 3 H); ^{31}P NMR δ 16.93; UV/Vis (CH_2Cl_2) 320 ($\epsilon = 5300$), 382 ($\epsilon = 460$) nm.

Anal. Found: C, 52.90; H, 5.08. $\text{C}_{30}\text{H}_{32}\text{OP}_2\text{Cl}_2\text{Pd} \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ calcd.: C, 53.07; H, 4.82%.

X-Ray data collection. Cell parameters were determined on a CAD-4 diffractometer by a least-squares treatment. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography [14]. The NRCC SDP VAX Program package [15] was used. Relevant data are listed in Table 7. Tables of atomic coordinates and thermal parameters, anisotropic thermal parameters, complete bond distances and bond angles, and structure factors are available from the authors.

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References

- 1 For recent review on tripodal polytertiary phosphines see: (a) L. Sacconi and F. Mani, in G.A. Melson and B.N. Figgis (Eds.), *Transition Metal Chemistry*, Vol. 8, Marcel Dekker, New York, 1982, p. 179, (b) D.W. Meek, in L.H. Pignolet (Ed.), *Homogeneous Catalysis by Metal Phosphine Complexes*, Plenum, New York, 1983, p. 257.
- 2 (a) A. Albinati, F. Demartin, P. Janser, L.F. Rhodes, L.M. Venanzi, *J. Am. Chem. Soc.*, 111 (1989) 2115; N. Kuhn, M. Winter, E. Zimmer, *J. Organomet. Chem.*, 344 (1988) 401; J.R. Bleeker, M.K. Hays, R.J. Wittenbrink, *Organometallics*, 7 (1988) 1417; G.V. Goeden, J.C. Hoffman, K.G. Caulton, *Inorg. Chem.*, 25 (1986) 2484; M.D. Vaira, M. Peruzzini, P. Stoppioni, *Polyhedron*, 5 (1986) 945; P. Peringer, M. Lusser, *Inorg. Chim. Acta*, 117 (1986) L25; S.C. Abrahams, A.P. Ginsberg, T.F. Koetzle, P. Marsh, C.R. Sprinkle, *Inorg. Chem.*, 25 (1986) 2500; S.I. Hommeltoft, A.D. Cameron, T.A. Shackleton, M.E. Fraser, S. Fortier, M. C. Baird, *Organometallics*, 5 (1986) 1380; O.J. Scherer, R. Walter, W.S. Sheldrick, *Angew. Chem. Int. Ed. Engl.*, 24 (1985) 525; F. Cecconi, C.A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini, M. Bacci, *J. Chem. Soc., Chem. Commun.*, (1985) 731; J. Rimmelin, P. Lemoine, M. Gross, A.A. Bahsoun, J.A. Osborn, *Nouv. J. Chim.*, 9 (1985) 181; D.J. Darensbourg, D.J. Zalewski, *Organometallics*, 4 (1985) 92; R.B. King, P.N. Kapoor, R.N. Kapoor, *Inorg. Chem.*, 10 (1971) 1841; J. Chatt, F.A. Hart, H.R. Watson, *J. Chem. Soc.*, (1962) 2537, and references therein.
- 3 A.A. Ismail, I.S. Butler, *J. Organomet. Chem.*, 346 (1988) 185.
- 4 C. Bianchini, D. Masi, D. Mealli, A. Meli, M. Sabat, F. Vizza, *Inorg. Chem.*, 27 (1988) 3716; C. Bianchini, F. Laschi, A. Meli, M. Peruzzini, P. Zanello, P. Frediani, *Organometallics*, 7 (1988) 2575; C. Bianchini, D. Masi, A. Meli, M. Peruzzini, F. Zanobini, *J. Am. Chem. Soc.*, 110 (1988) 6411, and references therein.
- 5 R. Davis, J.E. Fergusson, *Inorg. Chim. Acta*, 4 (1970) 23.
- 6 S.-T. Liu, C.-H. Yieh, H.-J. Lu, *Phosphorus, Sulfur and Silicon*, 44 (1989) 261.
- 7 S.-T. Liu, H.-E. Wang, M.-C. Cheng, S.-M. Peng, *J. Organomet. Chem.*, 376 (1989) 333.
- 8 A.J. McAlees, R. McCrindle, A.R. Woon-Fat, *Inorg. Chem.* 15 (1976) 1065.
- 9 P.E. Garrou, *Chem. Rev.*, 81 (1981) 229.
- 10 D. Berglund, Ph.D. dissertation, Ohio State University, 1969; also see reference 1a.
- 11 J.R. Gollgoly, C.J. Hawkins, *Inorg. Chem.*, 11 (1972) 156.
- 12 M.R. Churchill, A.L. Rheingold, R.L. Keiter, *Inorg. Chem.*, 20 (1981) 2730.
- 13 L.G.L. Ward, *Inorg. Synth.*, 13 (1972) 154.
- 14 International Tables for X-Ray Crystallography. Vol. IV, Kynoch Press, Birmingham, 1974.
- 15 E.J. Gabe, F.L. Lee, *Acta Crystallogr.*, A37 (1981) S 339.