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Organometallics of diphosphazanes

VI *. Reactions of bicyclo-1,3,2-λ^3,4-λ^3-diazadiphosphetidines (bicyclic diphosphazenes) with Group 6 metal carbonyls and palladium and platinum(II) complexes

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Abstract

The reactions of the bicyclic 1,3,2-λ^3,4-λ^3-diazadiphosphetidines $(PhNP)_2(XCH_2CH_2Y)$ (X = Y = O (1); X = O, Y = NMe (2)) with Group 6 metal carbonyl derivatives give the mononuclear complexes $M(CO)_4L_2$ and $M(CO)_3L_3$ in which the cyclodiphosphazane ligand (L) exhibits η^1-mode of coordination through one of its phosphorus atoms. Reactions of 1 with $M_2Cl_4(PEt_3)_2$ (M = Pd or Pt) yield both mononuclear and dinuclear complexes, $MCl_2(PEt_3)$ (1) and $M_2Cl_4(PEt_3)_2$ (1) in which the cyclodiphosphazane ligand is bound to the metal in monodentate and bridged bidentate fashion, respectively. Treatment of 1 with $PdCl_2(COD)$ gives a complex of composition $[PdCl_2(1)]_n$ in which the cyclodiphosphazane functions as a bridging bidentate ligand. Structures of the compounds have been elucidated by ^1H and ^{31}P NMR spectroscopic studies.

Introduction

It is well established that λ^3-cyclodiphosphazanes coordinate to transition metals through their phosphorus atoms in an η^1 or bridged bidentate fashion [1–3]. There is no structural or spectroscopic evidence for a bidentate chelating mode of complexation of a cyclodiphosphazane [4]. Recently Kumaravel *et al.* [5] have determined the structures of bicyclodiphosphazanes of type I (see below) and shown that in these compounds the puckering of the P–N ring occurs in a manner opposite to that observed for *cis*-cyclodiphosphazanes, $(RNPX)_2$. With the objec-

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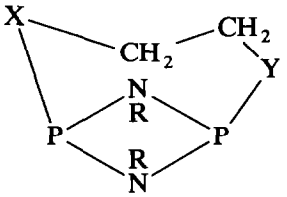
* For part 5, see ref. 3c.

tive of investigating the effect of this novel structural feature on the behaviour of I as ligands towards transition metals, we have carried out the reactions of I [X = Y = O (1); X = O, Y = NMe(2)] with Group 6 metal carbonyl, palladium(II) and platinum(II) complexes, and the results are reported below.



(I)

X = Y = O, R = Ph (1)

X = O, Y = NMe, R = Ph (2)

Experimental

All manipulations were carried out under dry nitrogen by standard Schlenk and vacuum line techniques [6]. Solvents were purified by usual methods and degassed with dry N_2 prior to use. The NMR spectra were recorded on Bruker WH-270, WP 80, WMB 60, ACF 250 and Varian FT-80A spectrometers. ^{31}P chemical shifts are quoted relative to 85% H_3PO_4 as an external reference, with upfield shifts negative. ^1H chemical shifts are expressed on the δ scale relative to tetramethylsilane. Infrared spectra were recorded on Perkin–Elmer model 457 and 1430 spectrometers. Elemental analyses for the complexes were carried out at Sussex University, and at the City University, London, UK through the kind offices of Dr. S.A. Matlin.

Metal hexacarbonyls $M(CO)_6$ (M = Mo or W) were purchased from Strem Chemicals, USA. The hexacarbonyls were converted into the norbornadiene, piperidine or acetonitrile derivatives, $M(CO)_4(C_7H_8)$ (M = Mo) [7], $M(CO)_4(NHC_5H_{10})_2$ (M = Mo, W) [8] or *fac*-$[M(CO)_3(NCMe)_3]$ (M = Mo, W) [9] by published procedures or modifications thereof. The platinum and palladium complexes $[MCl_2(COD)]$, $[M_2Cl_4(PEt_3)_2]$ (M = Pt or Pd) and $[Pt_2Cl_4(PMe_2Ph)_2]$ were prepared by published methods [10,11]. Bicyclic diphosphazane ligands were prepared as described by Kumaravel *et al.* [5].

Reactions of the bicyclic derivatives 1 and 2 with cis-*$[M(CO)_4(NHC_5H_{10})_2]$ (M = Mo,W) and* cis-*$[M(CO)_4(C_7H_8)]$, (M = Mo)*

A mixture of *cis*-$[Mo(CO)_4(NHC_5H_{10})_2]$ (0.2 g, 0.53 mmol) and **2** (0.34 g, 1.06 mmol) was heated under reflux in 25 cm^3 of CH_2Cl_2 for 1.5 h. The solution was cooled to 25°C and passed through a silica gel column to remove some decomposition product. The eluent was concentrated to 5 cm^3 methanol (10 cm^3) was added, and the solution cooled at 0°C (5 h) to yield the light yellow complex *cis*-$[Mo(CO)_4\{(PhNP)_2(N(Me)CH_2CH_2O)\}_2]$ (**3**) in 60% yield. Anal. Found: C, 48.5; H, 4.0; N, 9.8. $C_{34}H_{34}MoN_6O_6P_4$ calc.: C, 48.6; H, 4.1; N, 9.9%. The analogous tungsten complex **4** was prepared from *cis*-$[W(CO)_4(NHC_5H_{10})_2]$ (0.25 g, 0.54

mmol) and **2** (0.34 g, 1.07 mmol) in 65% yield. Anal. Found: C, 43.6; H, 3.5; N, 9.1. $C_{34}H_{34}N_6O_6P_4W$ calc.: C, 44.0; H, 3.7; N, 9.0%.

A mixture of 0.2 g (0.53 mmol) of *cis*-$[Mo(CO)_4(NHC_5H_{10})_2]$ and 0.32 g (1.1 mmol) of **1** was heated under reflux in 25 cm^3 of CH_2Cl_2 for 3 h. Solvent was removed under reduced pressure and the oily residue extracted with 25 cm^3 EtOH to yield a mixture of products, one of them *cis*-$[Mo(CO)_4\{(PhNP)_2(OCH_2CH_2O)\}_2]$ (**5**), which was identified spectroscopically. A similar product was obtained from the reaction of *cis*-$[Mo(CO)_4(C_7H_8)]$ with **1**.

The tungsten analogue of **5**, *cis*-$[W(CO)_4(\mathbf{1})_2]$ (**6**) was also obtained as a mixture of products from the reaction of *cis*-$[W(CO)_4(NHC_5H_{10})_2]$ (0.23 g, 0.49 mmol) with **1** (0.3 g, 0.98 mmol).

Preparation of fac-*[M(CO)$_3$\{(PhNP)$_2$(OCH$_2$CH$_2$O)\}$_3$] (M = Mo (7), W (8))*

The bicyclic diphosphazane, (**1**) (1.07 g, 3.52 mmol) was added to a solution of *fac*-$[Mo(CO)_3(NCMe)_3]$ (1.17 mmol) in 25 cm^3 acetonitrile. The mixture was heated under reflux for 8 h and cooled to 25°C. Solvent was removed under reduced pressure and the residue extracted with 150 cm^3 of diethyl ether. The ether extract was passed through a Celite column and the solution concentrated and cooled at 0°C (24 h) to give yellow crystals of *fac*-$[Mo(CO)_3\{(PhNP)_2(OCH_2CH_2O)\}_3]$ (**7**) in 70% yield. Anal. Found: C, 49.6; H, 4.9; N, 7.4. $C_{45}H_{42}MoN_6O_9P_6$ calc.: C, 49.6; H, 3.9 and N, 7.7%. The analogous tungsten complex **8** was prepared similarly in 65% yield. Anal. Found: C, 45.6; H, 4.1; N, 6.9. $C_{45}H_{42}N_6O_9P_6W$ calc.: C, 45.8; H, 3.6; N, 7.1%.

Reaction of 2 with fac-*[Mo(CO)$_3$(NCMe)$_3$]*

A mixture of *fac*-$[Mo(CO)_3(NCMe)_3]$ (0.38 mmol) and **2** (0.26 g, 1.14 mmol) was heated under reflux for 0.5 h. The mixture was cooled to 25°C and solvent removed under reduced pressure. The residue was extracted with 150 cm^3 of diethyl ether, and the extract concentrated to 5 cm^3 to give a brown crystalline material which was highly sensitive to chlorine-containing solvents. IR spectroscopic evidence suggested it was *fac*-$[Mo(CO)_3(\eta^1\text{-}\mathbf{2})_3]$ (**9**), but no further data could be obtained because of its instability.

Reaction of MCl$_2$(COD) (M = Pd, Pt) with 1

An equimolar mixture of $PdCl_2(COD)$ (0.4 g, 1.40 mmol) and the bicyclic diphosphazane (**1**) (0.43 g, 1.40 mmol) was stirred in 25 cm^3 of CH_2Cl_2 for 6 h. Solvent was removed under reduced pressure and the residue extracted with 150 cm^3 of acetonitrile. The extract was concentrated to 10 cm^3 and 30 cm^3 of petroleum ether (b.p. 60–80°C) was added, to yield the yellow palladium(II) complex $[Pd(\mu\text{-}\mathbf{1})Cl_2]_n$ ($n = 2/3/4$) (**10**) in 25% yield. Anal. Found: C, 35.2; H, 3.0; N, 5.6. $C_{14}H_{14}Cl_2N_2O_2P_2Pd$ calc.: C, 34.9; H, 2.9; N, 5.8%.

The reaction of $PtCl_2(COD)$ (0.3 g, 0.8 mmol) and **1** (0.24 g, 0.8 mmol) in 25 cm^3 of CH_2Cl_2 for 10 h gave only an insoluble colourless product, m.p. 220°C.

Reactions of 1 with M$_2$Cl$_4$(phosphine)$_2$ (M = Pt or Pd)

Preparation of mononuclear complexes. A solution of $(PhNP)_2O_2C_2H_4$ (0.12 g, 0.385 mmol) in dichloromethane (2 cm^3) was treated with a solution of

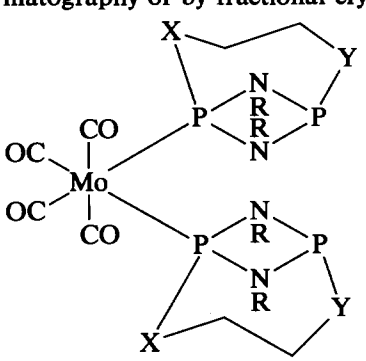
$[Pt_2Cl_4(PEt_3)_2]$ (0.15 g, 0.19 mmol) in dichloromethane (2 cm^3) at room temperature and the mixture stirred for 1 h. Monitoring by ^{31}P NMR spectroscopy showed that the reaction was complete. The solution was reduced to dryness *in vacuo* to afford *cis*-$[PtCl_2(PEt_3)\{(PhNP)_2O_2C_2H_4\}]$ (**11**) as off-white crystals. Yield 0.25 g, (94%). Anal. Found: C, 35.5; H, 4.4; N, 3.7. $C_{20}H_{29}Cl_2N_2O_2P_3Pt$ calc.: C, 35.0; H, 4.2; N, 4.1%. Similarly prepared were the complexes *cis*-$[PtCl_2(PMe_2Ph)\{(PhNP)_2O_2C_2H_4\}]$ (**12**) and *cis*-$[PdCl_2(PEt_3)\{(PhNP)_2O_2C_2H_4\}]$ (**13**) (yields 87% and 91% respectively). Compound **12** was characterised by ^{31}P NMR spectroscopy (see Table 1); satisfactory analytical data were obtained for **13** (Anal. Found: C 38.4; H, 4.6; N, 4.1. $C_{20}H_{29}Cl_2N_2O_2P_3Pd$ calc.: C, 40.1; H, 4.8; N, 4.7%).

Preparation of dinuclear complexes. Treatment of the mononuclear complexes **11** or **13** with the appropriate $[M_2Cl_4(PEt_3)_2]$ complex in 2:1 molar ratio in dichloromethane gave the dinuclear complexes $[MCl_2(PEt_3)]_2[(PhNP)_2O_2C_2H_4]$ [M = Pt (**14**) or Pd (**15**)] (yield 70%). C,H,N analytical data for **14**: Anal. Found: C, 28.4; H, 3.7; N, 2.1. $C_{26}H_{44}Cl_4N_2O_2P_4Pt_2$ calc.: C, 29.2; H, 4.1; N, 2.6%. For **15**: Anal. Found: C, 33.4; H, 5.2; N, 2.4. $C_{26}H_{44}Cl_4N_2O_2P_4Pd_2$ calc.: C, 35.0; H, 4.9; N, 3.1%.

Results and discussion

Reactions of the bicyclic derivatives 1 and 2 with cis-*$[M(CO)_4(NHC_5H_{10})_2]$ (M = Mo, W) and* cis-*$[Mo(CO)_4(C_7H_8)]$*

Thermal reactions of the bicyclic diphosphazanes **1** and **2** with Group 6 metal carbonyls in toluene gave decomposition products and no identifiable metal carbonyl phosphine complex could be isolated. However, complexes of the type *cis*-$[M(CO)_4\{(PhNP)_2N(Me)CH_2CH_2\}_2]$ (M = Mo, **3**; M = W, **4**) were obtained in 60–65% yields by heating a mixture of *cis*-$[M(CO)_4(NHC_5H_{10})_2]$ (M = Mo, W), and the asymmetrical bicyclic ligand **2** in dichloromethane. In contrast, reactions of the bicyclic ligand **1** with *cis*-$[M(CO)_4(NHC_5H_{10})_2]$ (M = Mo, W) or *cis*-$[Mo(CO)_4(C_7H_8)]$ yielded a mixture of products, of which *cis*-$[M(CO)_4\{(PhNP)_2(OCH_2CH_2O)\}_2]$ (M = Mo, **5**; M = W, **6**) was the major component. All attempts to separate these compounds from the reaction mixture either by column chromatography or by fractional crystallisation failed.



M = Mo, X = O, Y = NMe (**3**)

M = W, X = O, Y = NMe (**4**)

M = Mo, X = Y = O (**5**)

M = W, X = Y = O (**6**)

Table 1

Spectroscopic data for bicyclic diphosphazane complexes

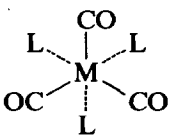
Complex	ν(CO) or ν(M–Cl) [a] (cm^{-1})	^1H NMR [b]	^{31}P NMR [c]
cis-[Mo(CO)$_4${(PhNP)$_2$NMe(CH$_2$)$_2$O}$_2$] (3)	2040(vs) 1940(vs,br)	2.69d(12)(NMe); 3.17d(12)(NCH$_2$); 3.80br(OCH$_2$)	178.3d(7) [d] 140.6d(7) [e]
cis-[W(CO$_4$){(PhNP)$_2$NMe(CH$_2$)$_2$O}$_2$] (4)	2050(vs) 1920(vs,br)	2.69d(12)(NMe); 3.19d(12)(NCH$_2$); 3.85br(OCH$_2$)	170.2d(6) [d] 136.7d(6) [e]
cis-[Mo(CO)$_4${(PhNP)$_2$O(CH$_2$)$_2$O}$_2$] (5)	2050(vs) 1920(vs,br)	3.2–4.0br(OCH$_2$)	185.2d(15.5) [f] 151.0d(15.5) [g]
cis-[W(CO)$_4${(PhNP)$_2$O(CH$_2$)$_2$O}$_2$] (6)	2050(vs) 1920(vs,br)	3.2–4.0br(OCH)$_2$	162.0d(16.0) [f] 145.2d(16.0) [g]
fac-[Mo(CO)$_3${(PhNP)$_2$O(CH$_2$)$_2$O}$_3$] (7)	1970(vs) 1890(vs) 1850(vs)	3.84–3.89m(OCH$_2$)	194.4m [f] 148.9m [g]
fac-[W(CO)$_3${(PhNP)$_2$O(CH$_2$)$_2$O}$_3$] (8)	1970(vs) 1895(vs) 1850(vs)	3.84–3.89m(OCH$_2$)	167.4m [f,h] 140.8m [g]
[Pd{μ-(PhNP)$_2$O(CH$_2$)$_2$O}Cl$_2$]$_4$ (10)	–	4.25br(OCH$_2$)	69.7s
cis-[PtCl$_2$(PEt$_3$){(PhNP)$_2$O$_2$C$_2$H$_4$}] (11)	330(m), 310(m)	0.80(q, 9H, 3CH$_3$) 1.80(t, 6H, 3CH$_2$) 3.84(m, 4H, 2OCH$_2$)	*303 K*: 16(3211), 12(3213) 96(5247), 92(5258) 119 *193 K*: 21(3205), 18(3209) 96(5202), 92(5262) 114
cis-[PtCl$_2$(PMe$_2$Ph){(PhNP)$_2$O$_2$C$_2$H$_4$}] (12)	–	–	−8(3193), −12(3198) 92(5546), 89
cis-[PdCl$_2$(PEt$_3$){(PhNP)$_2$O$_2$C$_2$H$_4$}] (13)	330(m), 300(m)	1.1(m, 9H, 3CH$_3$) 1.9(m, 6H, 3CH$_2$) 4.3(m, 4H, 2OCH$_2$)	*293 K*: 46,39,129,128,132
[{PtCl$_2$(PEt$_3$)}$_2${(PhNP)$_2$O$_2$C$_2$H$_4$}] (14)	330(m), 300(m)		*303 K*: 20(3291), 83(5791)
[{PdCl$_2$(PEt$_3$)}$_2${(PhNP)$_2$O$_2$C$_2$H$_4$}] (15)	325(m), 305(m) 285(m)	1.01(m, 18H, 6CH$_3$) 2.02(m, 12H, 6CH$_2$) 4.5(d, 4H, 2OCH$_2$)	*203 K*: 52, 47, 119, 113

[a] Recorded in Nujol mull; vs, very strong; br, broad. [b] **3–6** in $CDCl_3$ solution and **7–10** in CD_3CN solution; in ppm; ^3J(PH) in Hz in parentheses; d, doublet; t, triplet; q, quartet; br, broad; m, multiplet; δ of phenyl protons omitted. [c] **3–6** in CH_2Cl_2 solution and **7–10** in CD_3CN solution; in ppm relative to 85% H_3PO_4; ^2J(PP) in Hz in parentheses; for Pt complexes, the large values in parentheses are ^1J(PtP) couplings. [d] P attached to OCH_2. [e] P attached to NMe. [f] P coordinated to Mo or W. [g] uncoordinated phosphorus. [h] ^1J(WP) = 369.8 Hz.

The IR spectra of complexes **3–6** indicate the presence of an $M(CO)_4$ moiety bonded to strong π-acceptor phosphorus ligands, and the expected $\nu(CO)$ absorptions (Table 1) are observed in the range 2050–1920 cm^{-1}. Other spectroscopic data are listed in Table 1. The ^{31}P NMR spectra of **3** and **4** show the expected two resonances, one for the coordinated phosphorus and the other for the uncoordinated phosphorus. From a comparison of the ^{31}P chemical shifts of the complexes **3** and **4** with those of the free ligand, it is inferred that the phosphorus that is attached to the oxygen atom of the $-OCH_2$ group is coordinated to the metal and the ^{31}P resonance is deshielded upon complexation. The ^{31}P NMR spectra of **5** and **6** are also of the AB type, with the coordinated phosphorus nucleus being deshielded relative to the uncoordinated phosphorus. The spectra of **5** and **6** show other minor peaks at δ_P 192.0 and 170.2 for the molybdenum and tungsten complexes, respectively, which may be tentatively assigned to a symmetrical complex of the type $[(OC)_4M(\mu\text{-}\mathbf{1})_2M(CO)_4]$. Weak resonances observed at δ_P 131.5 and 122.0, respectively, for the molybdenum and tungsten complexes could not be assigned.

Reactions of fac-$M(CO)_3(NCMe)_3$] *(M = Mo or W) with 1 and 2*

Reactions of the tris-acetonitrile tricarbonyl complexes *fac*-$[M(CO)_3(NCMe)_3]$ (M = Mo or W) with the bicyclic diphosphazane ligands afford the mononuclear complexes, $[M(CO)_3L_3]$ (**7–9**), (L = bicyclic diphosphazane), in which three diphosphazane ligands are coordinated to the metal in an η^1-fashion and occupy *facial* positions of an octahedron around the metal. Complexes **7–9** are very sensitive to air and moisture, and decompose rapidly in chlorine-containing solvents. Decomposition is particularly marked for complex **9**, and so satisfactory elemental analyses and NMR spectra could not be obtained, and it was identified only by IR spectroscopy.



M = Mo, L = **1** (**7**)
M = W, L = **1** (**8**)
M = Mo, L = **2** (**9**)

The ^{31}P NMR spectra of **7** and **8** clearly establish their structures, and the spectrum of **8** is illustrated in Fig. 1. The spectrum is consistent with a symmetrical $[AX]_3$ spin system. The coordinated and the uncoordinated phosphorus nuclei exhibit resonances at δ 194.4 and 148.9 for **7**, and δ 167.4 and 140.8 for **8** respectively; $^1J(WP)$ for **8** is 369 Hz. A more complex spectrum (four different resonances with an intensity ratio of 2:2:1:1 and a complex splitting pattern), would be expected for a meridional arrangement of the diphosphazane ligands.

The IR spectra of **7–9** show three strong $\nu(CO)$ absorptions (1850–1970 cm^{-1}), indicating the presence of a $[M(CO)_3]$ moiety consistent with a distorted facial arrangement arising from the presence of the three bulky diphosphazane ligands.

Reactions of $MCl_2(COD)$ *(M = Pd, Pt) with 1*

Treatment of $PtCl_2(COD)$ with **1** gives a colourless product (m.p. > 220°C), which is insoluble in common organic solvents. On the other hand, $PdCl_2(COD)$ reacts with **1** to give a product of the composition $[PdCl_2\{(PhNP)_2OCH_2CH_2O\}_2]$ (**10**), which can be separated from the reaction mixture by extraction with acetoni-

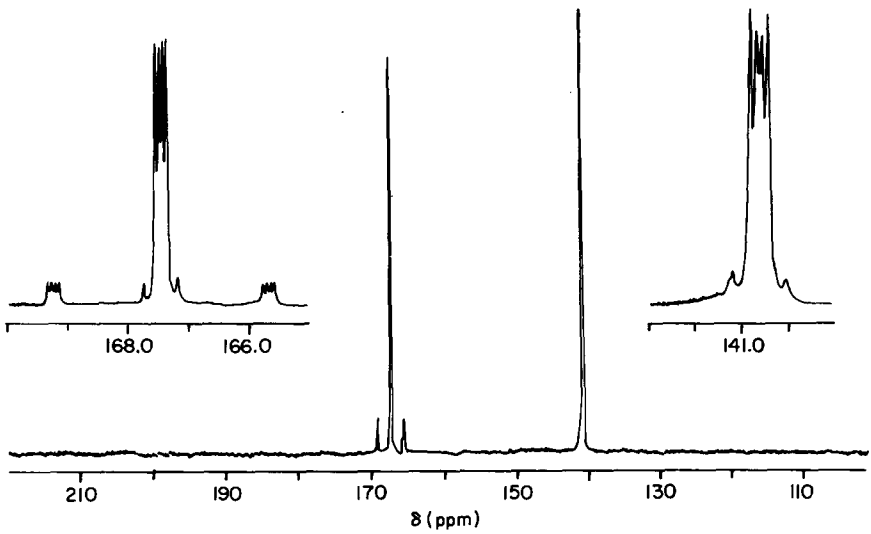


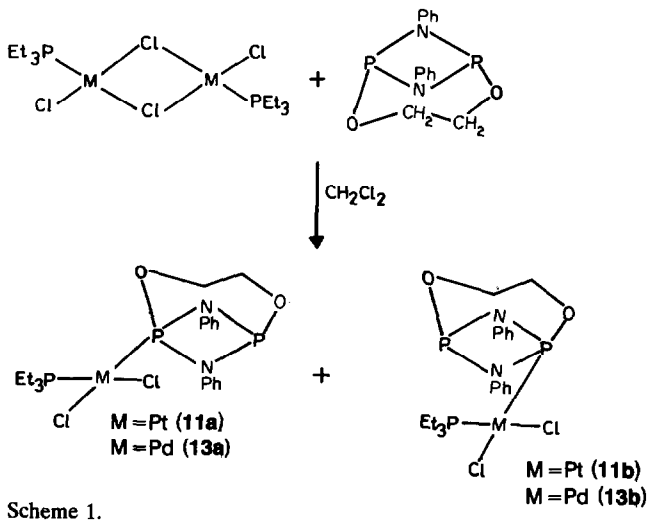
Fig. 1. ^{31}P NMR spectrum (101.5 MHz/CD_3CN) of *fac*-[$W(CO)_3$[$(PhNP)_2O_2$-C_2H_4}$_3$] (**8**).

trile. The yield of this product is low (< 25%), and the major product is an insoluble material, as is the case for the analogous reaction with the platinum derivative.

Complex **10** has been characterised by elemental analysis, IR and proton and ^{31}P NMR spectroscopic data. The ^{31}P NMR spectrum shows a single resonance at δ 69.7, indicating that the cyclodiphosphazane acts as a bridging ligand. Verkade and coworkers [12] have reported the isolation of dimeric complexes of the type [$(OC)_5M(P-P)\ M(CO)_5$], (M = Cr, Mo and W; P–P = $P(OCH_2)_3P$) and tetrameric complexes of the type *cyclo*-[$(OC)_4M(P-P)]_4$, (M = Cr, Mo or W), in which the bicyclic ligand, $P(OCH_2)_3P$ bridges the two metal centres. The parent ion corresponding to the tetrameric structure was observed in the FAB mass spectrum for the tungsten complex. In the present study no mass spectral data for **10** could be obtained. However, by analogy with the results of Verkade and coworkers [12], a tetrameric structure is tentatively assigned to **10**. A dinuclear structure with two bridging bicyclic diphosphazane ligands will be sterically more encumbered than a tetranuclear complex.

Reactions of trans-*[$M_2Cl_4L_2$] (M = Pt or Pd, L = PEt_3 or PMe_2Ph)*

Treatment of the chloro-bridged dimer, *trans*-[$M_2Cl_4L_2$] (M = Pt, L = PEt_3 or PMe_2Ph; M = Pd, L = PEt_3) with the bicyclodiphosphazane **1** gives the mononuclear complexes *cis*-[MCl_2(L)(**1**)] (**11–13**), which were isolated as colourless solids. The ^{31}P NMR spectra clearly indicate that these complexes exist in solution as two isomers, as shown in Scheme 1. The ^{31}P NMR data are summarised in Table 1. The spectrum of *cis*-[$PtCl_2(PEt_3)$(**1**)] at 303 K is illustrated in Fig. 2. The intense set of peaks marked A, B and C are assigned to the major isomer (**11a**). Peak A is due to PEt_3 bound to platinum (^1J(PtP) = 3211, ^2J(PP) = 17 Hz). Peak B arises from the phosphorus coordinated to platinum, which shows a large ^1J(PtP) value of 5207 Hz in addition to coupling to PEt_3 and the uncoordinated P of the



Scheme 1.

bicyclodiphosphazane (^2J(PP) = 17; ^2J(PP) = 7 Hz). The signal from the uncoordinated phosphorus of the bicyclodiphosphazane is at 119 ppm (peak C) and exhibits no platinum satellites. The less intense set of peaks D and E (which exhibit

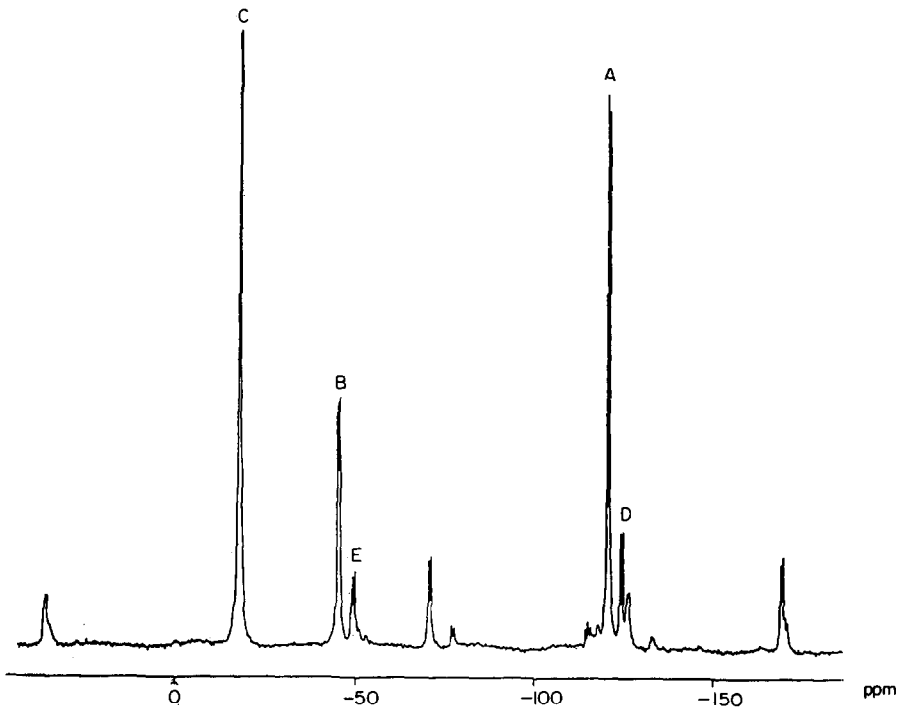


Fig. 2. ^{31}P NMR (32.4 MHz) spectrum (CH_2Cl_2/303 K) of *cis*-[$PtCl_2(PEt_3)$]($PNPh)_2O_2C_2H_4$}] (11). The shifts are with reference to $P(OMe)_3$.

platinum satellites), are ascribed to PEt_3 and the coordinated P of the bicyclodiphosphazane ligand of the minor isomer (**11b**). The resonance of the unbound phosphorus atom of the $(PhNP)_2O_2C_2H_4$ ligand (**1**) appears at the same chemical shift, peak C, for both isomers which is perhaps not surprising. The ratio of intense peaks to weak peaks changes when the spectrum is recorded at lower temperature (213 K), implying that the two isomers are in dynamic equilibrium with each other although the critical temperature for fluxional exchange has not been reached at 213 K. Values of chemical shifts and coupling constants (Table 1) are similar but not identical, suggesting that at room temperature the onset of fluxional behaviour is being approached. The ^{31}P spectra of the complexes *cis*-$[PtCl_2(PMe_2Ph)\{(PhNP)_2O_2C_2H_4\}]$ (**12**) and *cis*-$[PdCl_2[PEt_3](\mathbf{1})]$ are similar to the spectrum discussed above. However, in contrast to the *cis*-$[PtCl_2(PEt_3)(\mathbf{1})]$ complex, the equilibrium between the major and minor isomers for *cis*-$[PdCl_2(PEt_3)(\mathbf{1})]$ is highly temperature dependent.

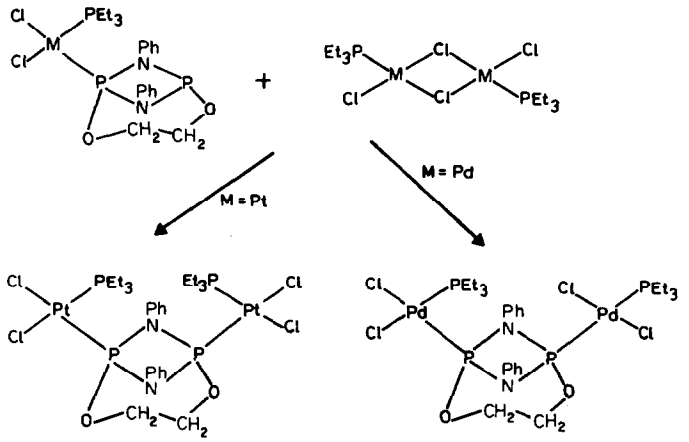
Spectroscopic evidence thus clearly points to the presence of two structural isomers of **11–13**, both possessing a *cis* configuration. In the absence of a single-crystal study, any postulated structures for these isomers can only be tentative, but the spectroscopic data suggest that the isomers differ only in respect of the rotational conformation about the Pt–$P(N_2O)$ bond and the most likely conformation would be one with the (P_2N_2) ring perpendicular to the square-plane containing the metal atom (as found for the related complexes which have been crystallographically characterised) [13]. The more abundant isomer (**11–13**) would then have the oxygen atom (bound to P) *cis* to the phosphine ligand and the minor isomer would have that oxygen atom *trans* to the phosphine ligand (Scheme 1).

The ^1H NMR spectra of the above complexes (**11** and **13**) are entirely consistent with the proposed structures and spectroscopic data are given in Table 1. The far IR spectra of these complexes show two bands, in each case at 330 and 310 cm^{-1} for the Pt complex **11** and 330 and 300 cm^{-1} for the Pd complex **13**, attributable to M–Cl stretching vibrations.

Dinuclear Pd and Pt complexes

Treatment of *cis*-$[MCl_2(PEt_3)\{(PhNP)_2O_2C_2H_4\}]$ with $M_2Cl_4(PEt_3)_2$ in dichloromethane yields the dinuclear complexes $[M_2Cl_4(PEt_3)_2\{\mu\text{-}(PhNP)_2O_2C_2H_4\}]$, (M = Pt or Pd), (Scheme 2). Phosphorus-31 NMR data (Table 1) confirm the identities of the two products, and also indicate that the diplatinum complex has a *cis,cis* configuration of the PEt_3 groups whereas the dipalladium complex has a *cis,trans* configuration. The ^{31}P spectra of the diplatinum complex **14** recorded at 303 K and 203 K suggest the presence of a small amount of the *cis*-$[PtCl_2(PEt_3)\{(PhNP)_2O_2C_2H_4\}]$ starting material, which undergoes a facile exchange with the dimeric complex **14**.

The ^{31}P NMR spectra of the dipalladium complex **15** at 203 K, which is illustrated in Fig. 3, consists of three sets of peaks. The most intense set (H–K) features an AB quartet (H and I) in the coordinated $(PhNP)_2O_2C_2H_4$ region and two different resonances J and K in the coordinated PEt_3 region. Analysis of the AB quartet gives $\delta(P_H)$ and $\delta(P_I)$ as 119 and 113 respectively with a $^2J(PP)$ value of 39 Hz. Further doublet splitting of the quartet arises because of coupling to PEt_3 phosphorus. The peak (H) has a $^2J(PP)$ of 10 Hz mirrored in the doublet K, and I has a doublet splitting of 14 Hz mirrored in the doublet J. These spectral



14 15

Scheme 2.

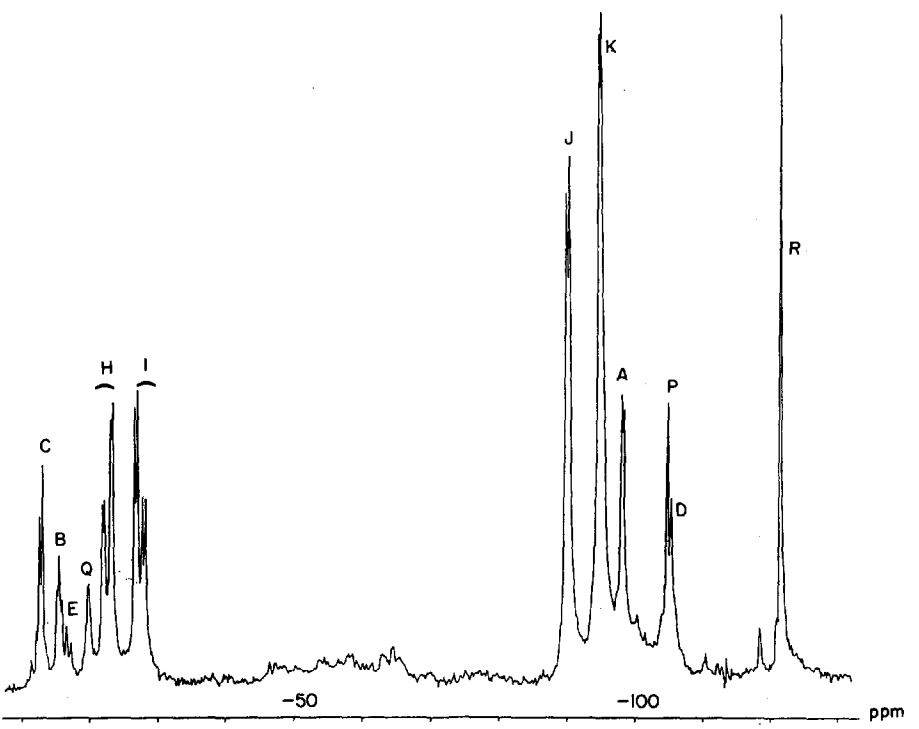


Fig. 3. ^{31}P NMR (32.4 MHz) spectrum (CH_2Cl_2 /203 K) of *cis*-[{$PdCl_2(PEt_3)$}$_2${$(PNPh)_2O_2C_2H_4$}] (**15**). The shifts are with reference to $P(OMe)_3$.

features are compatible only with an unsymmetrical dimeric structure for the principal product, and this is assumed to be *cis,trans*-[{$PdCl_2(PEt_3)$}$_2${$(PhNP)_2O_2C_2H_4$}] (**15**). The ^{31}P spectrum also shows two weak singlets marked P and Q which may be attributed to the presence of a small amount of the symmetrical *cis,cis*-[{$PdCl_2PEt_3$}$_2${$(PhNP)_2O_2C_2H_4$}] having the same structure as that of the Pt complex **14**. In addition, the ^{31}P spectrum of **15** shows a weak set of peaks A–E which can be easily recognised as arising from the two isomers of the mononuclear complex (**13a, b**) and a peak (R) due to triethyl phosphine oxide.

Surprisingly, the reaction between *trans*-$[Pt_2Cl_4(PEt_3)_2]$ and $(PhNP)_2O_2C_2H_4$ in tetrahydrofuran proceeded entirely differently from that in CH_2Cl_2. Monitoring of the reaction by ^{31}P NMR spectroscopy during several weeks showed that the reaction mixture contains the starting material *trans*-$[Pt_2Cl_4(PEt_3)_2]$ and the platinum dimer **14**, which subsequently decomposes to *trans*-$[Pt_2Cl_4(PEt_3)_2]$ and the bicyclodiphosphazane ligand.

The ^1H NMR spectra of the dimeric complexes (**14, 15**) are entirely consistent with the proposed structures. The far IR spectra of the diplatinum complex (**14**) shows two ν(PtCl) absorptions at 330 and 300 cm^{-1}; the dipalladium complex (**15**) shows three peaks at 325, 305 and 285 cm^{-1} in line with its unsymmetrical structure.

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