

0277-5387(95)00561--7

ORGANOMETALLIC CHEMISTRY OF DIPHOSPHAZANES— 13.¹ PALLADIUM COMPLEXES OF UNSYMMETRICAL DIPHOSPHAZANES Ph₂PN(Prⁱ)PYY'

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(Received 20 October 1995; accepted 22 November 1995)

Abstract—Unsymmetrical diphosphazanes $Ph_2PN(Pr^i)PYY'$ [$YY' = O_2C_{12}H_8$ (L^1), $O_2C_{20}H_{12}$ (L^2); Y = Ph and $Y' = OC_6H_4Br-4$ (L^3), OC_6H_4Me-4 (L^4), $OC_6H_3Me_2-3,5$ (L^5), $N_2C_3HMe_2-3,5$ (L^6)] react with *cis*-[PdCl₂(COD)] (COD = cycloocta-1,5-diene) giving the chelate complexes of the type *cis*-[PdCl₂{ $\eta^2-Ph_2PN(Pr^i)PYY'$ }] [$YY' = O_2C_{12}H_8$ (1), $O_2C_{20}H_{12}$ (2); Y = Ph and $Y' = OC_6H_4Br-4$ (3), OC_6H_4Me-4 (4), $OC_6H_3Me_2-3,5$ (5), $N_2C_3HMe_2-3,5$ (6)]. The P—N bond in 3 and 5 undergoes a facile cleavage in methanol solution to give *cis*-[PdCl₂{ $\eta^1-Ph_2P(OMe)$ }{ $\eta^1-PhP(NHPr^i)(Y')$ }] [$Y' = OC_6H_4Br-4$ (7), $OC_6H_3Me_2-3,5$ (8)]. Reactions of $Pd_2(dba)_3 \cdot CHCl_3$ (dba = dibenzylideneacetone) with the diphosphazanes $Ph_2PN(Pr^i)PPhY'$ [$Y' = OC_6H_4Me-4$ (L^4), $N_2C_3HMe_2-3,5$ (L^6), $N_2C_3H_3$ (L^7)] in the presence of MeI yields *cis*-[PdI₂{ $\eta^2-Ph_2PN(Pr^i)PPhMe$ }] (9); the P—O or P—N(pyrazolyl) bond of the starting ligands is cleaved and a P—C(Me) bond is formed. An analogous oxidative addition reaction in the presence of $Ph_2PN(Pr^i)PPh_2$ (L^8) yields *cis*-[PdI(Me)(η^2 - L^8)] (10) and *cis*-[PdI₂(η^2 - L^8)] (11). The structures of 8 and 9 have been determined by X-ray diffraction. Copyright © 1996 Elsevier Science Ltd

Although symmetrical diphosphazane ligands of the type $X_2PN(R)PX_2$ have attracted much attention, studies on unsymmetrical and heterofunctional ligands containing the P-N-P skeleton are limited.² Transition metal complexes of heterofunctional ligands are of considerable current interest because of their potential applications as catalysts for various organic transformations.3-5 Our earlier work on palladium chemistry of diphosphazanes was focused on the complexes of the diphosphazanes, symmetrically substituted $(PhO)_2N(R)P(OPh)_2$ (R = Me or Ph).⁶ In this paper we report the syntheses and structural characterization of palladium(II) complexes of several unsymmetrical diphosphazanes of the type Ph₂PN(Prⁱ)PYY' and also oxidative addition of methyl iodide to the palladium(0) complex

 $Pd_2(dba)_3 \cdot CHCl_3$ in the presence of diphosphazane ligands. Platinum(II) complexes of $Ph_2PN(R)PPh_2$ (R = S-CHMePh) were reported by Payne and Stephan⁷ and Pt^{II} complexes of $Ph_2PN(R)PPh_2$ (R = Hor Me) have been subject of recent studies by Farrar, Woollins and their respective co-workers.^{8–10}

EXPERIMENTAL

The general experimental procedure and details of spectroscopic measurements were as reported previously.¹ The diphosphazane ligands¹¹ and the palladium precursor complexes, cis-[PdCl₂ (COD)],¹² trans-[PdCl₂(PhCN)₂]¹³ and [Pd₂(dba)₃] · CHCl₃¹⁴ were prepared by published procedures.

The physical properties, micro analyses and spectroscopic data are given in Tables 1 and 2.

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		Elemental analyses Found (Calc.) (%)				
Compound	M.pt ^a (°C)	С	Н	N	IR data" {only v_{Pd-x} (x = Cl or I)} (cm ⁻¹)	
$\frac{1}{\left[PdCl_{2}\left\{\eta^{2}-Ph_{2}PN(Pr^{i})P(O_{2}C_{12}H_{8})\right\}\right]}$ (1)	240	50.6	3.5	1.9		
	(md)	(51.1)	(4.0)	(2.2)	312w, 278w	
$[PdCl_{2}\{\eta^{2}-Ph_{2}PN(Pr^{i})P(O_{2}C_{20}H_{12})\}] (2)$	210	56.3	3.2	1.5	318w, 294w	
		(57.2)	(4.0)	(1.9)		
$[PdCl_{2}{\eta^{2}-Ph_{2}PN(Pr^{i})PPh(OC_{6}H_{4}Br-4)}] (3)$	236	46.6	4.1	1.7	307w, 284w	
	(md)	(46.3)	(3.8)	(2.0)		
$[PdCl_{2}{n^{2}-Ph_{2}PN(Pr^{i})PPh(OC_{6}H_{4}Me-4)}] (4)$	228	51.6	4.2	1.9	311w, 278w	
	(d)	(53.0)	(4.6)	(2.2)		
$[PdCl_{2}{n^{2}-Ph_{2}PN(Pr^{i})PPh(OC_{6}H_{3}Me_{2}-3.5)}]$ (5)	238	52.4	5.1	1.8	312w, 282m	
		(53.7)	(4.8)	(2.2)		
$[PdCl_{2}{n^{2}-Ph_{2}PN(Pr^{i})PPh(N_{2}C_{3}HMe_{2}-3,5)}]$ (6)	205	49.8	4.4	5.5	312w, 287w	
		(50.2)	(4.7)	(6.8)		
$[PdCl_2{n^1-Ph_2P(OMe)}{\eta^1-$	195	46.4	4.5	2.2	289 br. w	
PhP(NHPr ⁱ)(OC ₆ H ₄ Br-4)}] (7)		(46.0)	(4.1)	(1.9)		
$[PdCl_{3}{n^{1}-Ph_{2}P(OMe)}{n^{1}-}$	190	53.5	5.6	2.4	316w, 289w	
PhP(NHPr ⁱ)(OC ₆ H ₃ Me ₂ -3,5)}] (8)		(52.9)	(5.2)	(2.1)		
$[PdI_{2}{n^{2}-Ph_{2}PN(Pr^{i})PPhMe}]$ (9)	245	35.3	3.4	2.6	278w, 239w	
		(36.4)	(3.5)	(1.9)		
$[PdI_{2}{n^{2}-Ph_{2}PN(Pr^{i})PPh_{2}}]$ (11)	240	41.7	3.7	2.2	278w	
		(41.2)	(3.5)	(1.8)		

Table 1. Melting point, microanalyses and IR data for palladium complexes

 $^{a}d = decomposed, md = melted with decomposition.$

^{*b*}Nujol mull; v_{NH} for 7 and 8 are 3259 and 3255 cm⁻¹, respectively.

Synthesis of cis- $[PdCl_2\{\eta^2-Ph_2PN(Pr^i)PYY'\}]$ [YY' = $O_2C_{12}H_8$ (1), $O_2C_{20}H_{12}$ (2), Y = Ph and Y' = OC_6H_4Br-4 (3), OC_6H_4Me-4 (4), $OC_6H_3Me_2-3,5$ (5), $N_2C_3HMe_2-3,5$ (6)]

A mixture of *cis*-[PdCl₂(COD)] (0.100 g, 3.5×10^{-4} mol) and Ph₂PN(Prⁱ)PYY' [YY' = O₂C₁₂H₈ (L¹); 0.160 g; YY' = O₂C₂₀H₁₂ (L²), 0.195 g]; Y = Ph and Y' = OC₆H₄Br-4 (L³), 0.183 g; Y = Ph and Y' = OC₆H₄Me-4 (L⁴), 0.160 g; Y = Ph and Y' = OC₆H₃Me₂-3,5 (L⁵), 0.165 g; Y = Ph and Y' = N₂C₃HMe₂-3,5 (L⁵), 0.156 g; (3.5 × 10⁻⁴ mol) was dissolved in dichloromethane (10 cm³) and stirred at 25°C for 10 min. Evaporation of the solvent *in vacuo* gave an oily residue, which was washed twice with hot petrol to remove cyclo-octadiene and crystallized from dichloromethane/petrol (60–80°C; 3:1) mixture to obtain the title complexes as pale yellow crystalline solids. Yield 85–90%.

Treatment of the ligands with *trans*- $[PdCl_2(PhCN)_2]$ also yielded the same complexes **1–6**.

Isolation of cis-[PdCl₂{ η^1 -Ph₂P(OMe)}{ η^1 -PhP(NH Prⁱ)(Y')}] [Y' = OC₆H₄Br-4 (7), OC₆H₃Me₂-3,5 (8)]

The palladium dichloride complex *cis*-[PdCl₂{ η^2 -Ph₂PN(Prⁱ)PPhY'}] [Y' = OC₆H₄Br-4 (3), 0.100 g; 1.43 × 10⁻⁴ mol; or OC₆H₃Me₂-3,5 (5), 0.100 g, 1.54 × 10⁻⁴ mol] was dissolved in methanol (10 cm³) and the solution kept at 25°C for 24 h. Concentration of the solution *in vacuo* to *ca* 5 cm³ and cooling at 0°C overnight gave pale yellow crystals of the title complexes. Yield 7 0.094 g, 90%; 8 0.089 g, 85%.

Reaction of $Ph_2PN(Pr')PYY'$ with $[Pd_2(dba)_3]$. CHCl₃

A mixture of $[Pd_2(dba)_3] \cdot CHCl_3$ (0.1 g, 9.66 × 10⁻⁵ mol) and Ph₂PN(Prⁱ)P(O₂C₂₀H₁₂) (L²), (0.161 g, 2.89 × 10⁻⁴ mol) or Ph₂PN(Prⁱ)PPhY' [Y' = OC₆H₄Me-4 (L⁴), 0.133 g, or N₂C₃HMe₂-3,5 (L⁶), 0.129 g; 2.89 × 10⁻⁴ mol] was dissolved in toluene at -70° C. The solution was slowly warmed

	¹ H N!	³¹ P NMR δ (ppm)					
	δ (ppm)						
Compound	CH ₃ ^c	CH ^c (NCH)	δ_{A} (YY')	$\Delta\delta$	δ_{X} (Ph ₂)	$\Delta\delta$	² <i>J</i> (PP)
$[PdCl_{2}\{\eta^{2}-Ph_{2}PN(Pr')P(O_{2}C_{12}H_{8})\}] (1)$	0.88	3.4	64.9	-83.7	43.6	15.7	31.0
$[PdCl_2{\eta^2-Ph_2PN(Pr^i)P(O_2C_{20}H_{12})}]$ (2)	0.75, 0.69	3.22	67.5	-80.8	44.2	15.9	34.0
$[PdCl_{2}\{\eta^{2}-Ph_{3}PN(Pr^{i})PPh(OC_{6}H_{4}Br-4)\}] (3)$	1.15, 0.59	3.46	63.6	-65.5	35.8	-3.6	18.0
$[PdCl_{2}\{\eta^{2}-Ph_{2}PN(Pr^{i})PPh(OC_{6}H_{4}Me-4)\}] (4)$	1.13, 0.58 2.40 ^d	3.45	61.6	-65.8	35.3	-4.2	17.0
$[PdCl_{2}\{\eta^{2}-Ph_{2}PN(Pr^{i})PPh(OC_{6}H_{3}Me_{2}-3,5)\}] $ (5)	1.14, 0.59 2.31	3.5	60.8	-65.5	34.9	-3.7	17.0
$[PdCl_{2}\{\eta^{2}-Ph_{2}PN(Pr^{i})PPh(N_{2}C_{3}HMe_{2}-3,5)\}] (6)$	1.02, 0.43 $2.64^{e}, 2.34^{e}$	3.9	33.0	-38.6	31.0	- 12.8	30.0
$[PdCl_{2}{\eta^{1}-Ph_{2}P(OMe)}{\eta^{1}-$ PhP(NHPr ⁱ)(OC ₆ H ₄ Br-4)} ¹ (7)	1.01, 0.86 2.86 ^g	3.0	107.9		83.8	—	30.8
$[PdCl_{2}{\eta^{1}-Ph_{2}P(OMe)}{\eta^{1}-Ph_{2}P($	1.03, 0.85 $2.26^d, 2.86^g$	3.0	106.5	—	82.6		29.0
$[PdI_2{\eta^2-Ph_2PN(Pr^i)PPhMe}] (9)$	0.99, 0.55 2.61 ^h	3.4	17.5		18.3		15.0
$[\mathbf{PdI}(\mathbf{Me})\{\eta^2 - \mathbf{Ph}_2\mathbf{PN}(\mathbf{Pr}^i)\mathbf{PPh}_2\}]^i (10)$	0.66 0.57 [/]	3.6			52.1 42.3	3.3 - 6.5	80.0
$[PdI_{a}{n^{2}-Ph_{a}PN(Pr^{i})PPh_{a}}]$ (11)	0.63	35	_		19.3	-29.5	
$[PdC]_{n} \{n^{2}-Ph_{n}PN(Pr^{i})PPh_{n}\}^{18}$		_			28.9	-19.9	
$[PdCl_{2}{\eta^{2}-(PhO)_{2}PN(Me)_{1}}]^{6}$	—	_	65.5	-69.6			
$[ruCl_2(\eta - rn_2rCn_2rrn_2)]^{-1}$		_			- 55.7	- 52.1	

Table 2. Proton NMR ^a and	³¹ ₽	H^{\prime}	NMR [*]	data fo	r palladium	complexes
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^a Recorded at 200.1 MHz in CDCl₃; for 10 only, spectrum recorded in acetone-d₆.

^{*b*} Recorded at 81 MHz in CH₂Cl₂ solvent for 1–10 and in DMSO for 11; $\Delta \delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$ the ligand values taken from ref. 11.

^c CH₃ (Prⁱ) resonances are doublets with ${}^{3}J(HH) \approx 7$ Hz, CH(Prⁱ) resonances are multiplets.

^dCH₃ on the aryl ring.

^e Pyrazolyl methyls.

¹NH resonances are doublet of doublets centred at 6.26 for 7 and 6.21 for 8 with a ${}^{2}J(PH) \approx 20$ Hz and a ${}^{3}J(HH) \approx 10$ Hz.

^{*g*} Methoxy resonances are doublets with ³*J*(PH) \approx 12 Hz.

^hmethyl group resonance attached to phosphorus atom is a doublet with ${}^{2}J(PH) = 12$ Hz.

^{*i*}Not isolated.

¹ Methyl group resonance attached to palladium atom is a doublet of doublet with ${}^{3}J(PH)$ of 9.5 and 3.3 Hz.

to 25°C with stirring and stirring continued for 10 h. The solvent was evaporated *in vacuo* to obtain an oily residue. Attempts to crystallize the oily product from toluene/petrol (1:1) or dichloromethane/ petrol (1:1) mixture were unsuccessful. The ³¹P NMR spectrum of the reaction mixture showed broad unresolved multiplets in the region 10–120 ppm.

Reaction of $Ph_2PN(Pr^i)PYY'$ with $[Pd_2(dba)_3]$. CHCl₃ in the presence of MeI

A solution of $[Pd_2(dba)_3] \cdot CHCl_3$ (0.2 g, 1.93 × 10⁻⁴ mol) in toluene (25 cm³) was cooled to -70°C. Solid Ph₂PN(Prⁱ)PPhY' [Y' = OC₆H₄Me-4 (L⁴), 0.177 g, Y' = N₂C₃HMe₂-3,5 (L⁶), 0.172 g, or Y' = N₂C₃H₃ (L⁷), 0.161 g; 3.86 × 10⁻⁴ mol] was added to the solution followed by dropwise addition of MeI (0.12 cm³, 1.93×10^{-3} mol). The solution was slowly warmed to 25°C with stirring; during this period, the colour of the solution changed from purple to reddish brown. The stirring was continued for 8 h. Solvent was evaporated in vacuo and the resultant oily residue was washed with hot petrol to remove dba and free ligand. Crystallization of the residue using dichloromethane/petrol mixture (3:1) gave cis-[PdI₂{ η^2 - $Ph_2PN(Pr^i)PPhMe$] (9); yield: 0.085 g, 30% (based on $[Pd_2(dba)_3] \cdot CHCl_3$) as deep red crystals. The ³¹P NMR spectrum (CH₂Cl₂) of the reaction mixture showed a major doublet of doublets for 9 (Table 2); in addition, resonances spread over the range 6-100 ppm were observed and these could not be assigned.

Reaction of Ph₂PN(Prⁱ)PPh₂ (L⁸) with [Pd₂(dba)₃] · CHCl₃ in the presence of MeI

The reaction of $[Pd_2(dba)_3] \cdot CHCl_3$ (0.150 g, 1.45×10^{-4} mol) in toluene (25 cm³) with L⁸ (0.124) g, 2.89×10^{-4} mol) and MeI (0.09 cm³, 1.45×10^{-3} mol) was carried out at -70° C as described above. The reaction mixture was slowly warmed to 25°C and stirring continued for 8 h. A yellowish-brown solid was precipitated during this period. The solid was isolated by filtration. The ³¹P NMR spectrum (CH_2Cl_2) of the solid showed a pair of doublets [52.1 and 42.3 ppm; ${}^{2}J(PP) = 80$ Hz] and a singlet (20.6 ppm). The doublets were assigned to the alkyl palladium iodo complex cis-[PdI(Me){ η^2 -Ph₂ $PN(Pr^{i})PPh_{2}$ (10) and the singlet peak was assigned to $[PdI_2{\eta^2-Ph_2PN(Pr^i)PPh_2}]$ (11). The relative yields of the two products 10 and 11 were 5:3, as estimated from the integrated intensities of the doublets and singlet observed for these complexes. Recrystallization of the solid from dichloromethane/petrol mixture (4:1) yielded an air-stable red crystalline palladium diiodo complex, cis-[PdI₂{ η^2 -Ph₂PN(Prⁱ)PPh₂}] (11). Yield 11: 0.075 g, 34%. Compound 10 could not be isolated in a pure state as it decomposed slowly in solution to give the diiodo complex **11** (¹H NMR evidence).

X-ray structural analysis of cis-[PdCl₂{ η^1 -Ph₂ P(OMe)}{ η^1 -PhP(NHPrⁱ)(OC₆H₃Me₂-3,5)}] (8) and cis-[PdI₂{ η^2 -Ph₂PN(Prⁱ)PPhMe}] (9)

Single crystals of the compounds 8 and 9 suitable for X-ray analysis were grown from methanol or dichloromethane/petrol (3:1), respectively. A suitable crystal of each compound was glued to a glass

fibre and coated with paraffin oil to protect it from air and moisture. Data were collected on an Enraf-Nonius CAD-4 diffractometer. The details pertaining to data collection and refinement and listed in Table 3. Absorption correction was applied for 9 using the DIFABS program.¹⁵ The structures were solved by conventional Patterson and Fourier techniques and refined by full-matrix least-squares treatment.^{16,17} All the non-hydrogen atoms were refined anisotropically except the isopropyl methyl groups of 8, which showed positional disorder. The positions of these two carbon atoms were refined isotropically with partial occupancies. The N-H proton of compound 8 was located from a difference Fourier map and refined isotropically; the positions of all other hydrogen atoms were calculated and their contributions in structure factor calculations were included.

Additional material available from the Cambridge Crystallographic Data Centre comprises atom coordinates, thermal parameters, bond lengths and bond angles.

RESULTS AND DISCUSSION

Synthetic and spectroscopic aspects

Reactions of cis-[PdCl₂(COD)] with 1:1 molar proportion of the unsymmetrical diphosphazanes, $Ph_2PN(Pr^i)PYY' [YY' = O_2C_{12}H_8 (L^1), O_2C_{20}H_{12}]$ (L²), Y = Ph; Y' = OC₆H₄Br-4 (L³), OC₆H₄Me-4 (L^4) , OC₆H₃Me₂-3,5 (L⁵), N₂C₃HMe₂-3,5 (L⁶)] in dichloromethane at 25°C give the complexes cis- $[PdCl_{2}\{\eta^{2}-Ph_{2}PN(Pr^{i})PYY'\}] [YY' = O_{2}C_{12}H_{8} (1),$ $O_2C_{20}H_{12}$ (2), Y = Ph; Y' = OC_6H_4Br-4 (3), OC_6H_4Me-4 (4), $OC_6H_3Me_2-3,5$ (5), $N_2C_3HMe_2-3,5$ (6)] (Scheme 1). These complexes are pale yellow or colourless air-stable solids with high melting points $(>200^{\circ}C)$. The reactions of *trans*-[PdCl₂(PhCN)₂] with 1:1 molar proportion of the diphosphazane ligands also give the same *cis*-chelate complexes. Even when the reaction is carried out with a metal precursor to ligand ratio of 1:2, only the cis-chelate complexes are obtained. As reported previously, diphosphazane ligands have a pronounced tendency to form stable four-membered chelates.²

These complexes have been characterized by elemental analyses and IR, ¹H and ³¹P NMR spectroscopic studies. The IR spectra of these complexes show two distinct bands v_{M-CI} in the region 280– 310 cm⁻¹ (Table 1). In the ¹H NMR spectrum of 1 the methyl(Prⁱ) resonances are observed as a doublet; in all other cases two different resonances are observed owing to the presence of an adjacent phosphorus chiral centre (Table 2). These methyl(Prⁱ)

Parameter	8	9
Empirical formula	$C_{30}H_{35}Cl_2NO_2P_2Pd$	C ₂₂ H ₂₅ I ₂ NP ₃ Pd
Molecular weight	680.9	725.6
Colour	Pale yellow	Reddish brown
Crystal size (mm)	0.20 imes 0.23 imes 0.08	$0.13 \times 0.20 \times 0.30$
Crystal system	Triclinic	Monoclinic
<i>a</i> (Å)	9.011(1)	12.126(3)
b (Å)	10.522(1)	16.524(2)
<i>c</i> (Å)	17.580(3)	12.897(3)
α (°)	81.47(1)	—
β (°)	84.50(1)	93.54(2)
γ (°)	73.87(1)	
V (Å ³)	1580.9(4)	2579.4(8)
Space group	PĪ	$P2_{1}/n$
Ζ	2	4
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.43	1.87
<i>F</i> (000)	692	1384
Temperature (°C)	20	20
Decay (%)	<1	<1
Linear absorption coefficient, μ (cm ⁻¹)	8.26	32.3
Absorption correction	None	Semi-empirical
Min., max. transmission	_	0.97-10.2
Radiation (graphite monochromator)	Mo- K_{α} (0.7107 Å)	Mo- K_{α} (0.7107 Å)
Scan technique	$\omega/2 heta$	$\omega/2 heta$
2θ range (°)	2-50	2-50
Total number of reflections	6261	5165
Unique reflections	5545	4534
Observed reflections	4493 $[F_{o} > 5\sigma(F_{o})]$	$3851 [F_{o} > 5\sigma(F_{o})]$
No. of parameters	349	253
R^a	0.039	0.054
$R_{w}^{b,c}$	0.044	0.060
Residual peak in final diff. map (e $Å^{-3}$)	0.76	1.67
$(\Delta/\sigma)_{ m max}$	0.194	0.122

Table 3. Crystal data and details of structure solution for $[PdCl_2\{\eta^1-Ph_2P(OMe)\}\{\eta^1PhP(NHPr)(OC_6H_3Me_2-3,5)\}$
(8) and $[PdI_2\{\eta^2-Ph_2PN(Pr^i)PPhMe\}]$ (9)

$${}^{a}R = \frac{\Sigma(\|F_{o}| - |F_{c}\|)}{\Sigma|F_{o}|}.$$
$${}^{b}R_{w} = \left(\frac{\Sigma w(|F_{o}| - |F_{c}|)^{2}}{\Sigma w|F_{o}|^{2}}\right)^{1/2}$$

^c w for $\mathbf{8} = 1.5774/[\sigma^2(F) + 0.000467F^2]$ and for $\mathbf{9} = 3.3428/[\sigma^2(F) + 0.000724F^2]$.

resonances are shielded compared to the free ligand chemical shifts, one of them much more so than the other.

The ³¹P NMR spectra of the complexes shows an AX pattern; the chemical shifts are shifted considerably upfield compared with those of the free ligands. The coordination shifts ($\Delta \delta = \delta_{complex} - \delta_{ligand}$) are given in Table 2. It is evident that the

shielding of the coordinated >P—N ($\Delta\delta$) is dependent on the electronegativity of the substituents attached to the phosphorus centre and decreases in the order O₂P—N > OCP—N > NCP—N > CCP—N. The PYY' (O₂P—N) of 1 and 2 show the highest shielding, presumably due to the formation of a seven-membered ring through the oxygen atoms; the corresponding PPh₂ res-

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Scheme 1. (i) [PdCl₂(COD)]; (ii) MeOH.

onances are shifted downfield (see Table 2). The same type of shielding effect is observed for the other diphosphazane complexes^{2,8,9,18} and also for the diphosphinoalkane complexes such as *cis*-[MCl₂{ η^2 -Ph₂P(CH₂)PPh₂}] (M = Pd, Pt) and *cis*-[PdMe₂{ η^2 -Ph₂P(CH₂)PPh₂}].^{19,20} However, the coordination shifts for five- and six-membered chelate complexes, *cis*-[MCl₂{ η^2 -Ph₂P(CH₂)₂PPh₂}] (M = Pd, Pt) and *cis*-[PtCl₂{ η^2 -Ph₂P(CH₂)₃PPh₂}] (M = Pd, Pt) show the normal downfield shifts with respect to their free ligands.²⁰ The presence of the four-membered ring may be one of the factors contributing to the observed high shielding, but it is evident (Table 2) that the ³¹P NMR resonances are more dependent on the electronic factors.

The palladium(II) diphosphazane complexes cis- $[PdCl_2\{\eta^2 - Ph_2PN(Pr^i)PPhY'\}] [Y' = OC_6H_4Br-4$ (3), $OC_6H_3Me_2-3.5$ (5)] are reasonably air-stable, but on dissolution in methanol they undergo a facile P-N bond cleavage at room temperature to yield cis-[PdCl₂{ η^1 -Ph₂P(OMe)}{ η^1 -PhP(NHPrⁱ)(Y')}] $[Y' = OC_6H_4Br-4$ (7), $OC_6H_3Me_2-3,5$ (8)] (Scheme 1). In contrast, the free diphosphazane ligands are unaffected in methanol at ambient temperatures for several days or when heated under reflux for 3 h. The structure of complex 8 has been determined by X-ray crystallography (see below). Recently Browning and Farrar¹⁰ have reported that the P-N bond of $[Pt{Ph_2P(NMe)PPh_2}_2]Cl_2$ is readily cleaved by MeOH to give $[Pt{Ph_2P(NMe)}]$ PPh_2 { $Ph_2P(OMe)$ } { $Ph_2P(NHMe)$ }] Cl_2 .

The IR spectra of 7 and 8 show a band near 3260

cm⁻¹, which can be assigned to the N---H stretching vibration (Table 1). The ¹H NMR spectra show resonances similar to those of the parent complex, in addition to the resonances for methoxy and the amino group protons (Table 2). The methine resonance is shielded by ca 0.5 ppm compared with its position in the spectra of the parent complexes (3 and 5). The methoxy protons appear as a doublet at 2.86 ppm with a ${}^{3}J(PH)$ of ~12 Hz. The NH proton resonance is observed around 6.2 ppm as a doublet of doublets owing to coupling with the methine proton and the phosphorus nucleus. The ³¹P NMR spectra show an AX pattern owing to the non-equivalence of the phosphorus nuclei; the chemical shifts are very much downfield compared with those for the precursor chelate complexes 3 and 5 (see Table 2).

Attempts to prepare Pd⁰ derivatives of the ligands Ph₂PN(Prⁱ)PYY' [YY' = $O_2C_{20}H_{12}$ (L²), Y = Ph and Y' = OC_6H_4Me-4 (L⁴), Y = Ph and Y' = $N_2C_3HMe_2-3,5$ (L⁶)] by their treatment with [Pd₂(dba)₃·CHCl₃ in dry toluene were unsuccessful (see Experimental). However, when Pd₂(dba)₃· CHCl₃ is treated with MeI (10-fold excess) in the presence of the ligands Ph₂PN(Prⁱ)PPhY' [Y' = OC_6H_4Me-4 (L⁴), $N_2C_3HMe_2-3,5$ (L⁶) or $N_2C_3H_3$ (L⁷)], the Pd¹¹ complex *cis-*[PdI₂{ η^2 -Ph₂PN(Prⁱ)PPhMe}] (9) is obtained as the major product (Scheme 2) besides several other side-products (see Experimental). The structure of 9 is confirmed by single-crystal X-ray diffraction (see below). There is a cleavage of the P—N(pyrazolyl)



Scheme 2. (i) $Ph_2PN(Pr^i)PPhY'$ [Y' = OC_6H_4Me-4 (L⁴), $N_2C_3HMe_2-3,5$ (L⁶) or $N_2C_3H_3$ (L⁷)]; (ii) $Ph_2PN(Pr^i)PPh_2$ (L⁸).

or P—O bond and the formation of the P—C(Me)bond with concomitant oxidation of the metal from zero to divalent state. The details of the mechanism of formation of 9 in these reactions are not clear. An analogous oxidative addition reaction with the symmetrical diphosphazane ligand Ph₂PN(Prⁱ)PPh₂ (L^8) vields palladium(II) complexes the $[PdI(Me)(\eta^2-L^8)]$ (10) and $[PdI_2(\eta^2-L^8)]$ (11) (see Experimental). These complexes are characterized by ¹H and ³¹P NMR spectroscopic data. The ³¹P{¹H} NMR spectrum of **10** displays an AB pattern (Table 2) as both the phosphorus nuclei would be different (one is *cis* to the methyl group and the other is trans to methyl). The protons of the methyl group coordinated to palladium give rise to a doublet of doublets centred at 0.57 ppm $[{}^{3}J(PH) = 9.5$ and 3.3 Hz]. The NMR chemical shifts and coupling constants are close to those observed for the methyl platinum chloro complex [PtCl(Me){ η^2 -Ph₂PN $(*CHMePh)PPh_2$].⁷ The methyl (CHMe₂) resonance is shielded compared with the free ligand value; this trend is also observed for complexes 1-6 (Table 2). The ³¹P resonance of the diiodo complex 11 is a singlet; the chemical shift lies upfield to that for the corresponding dichloro complex (Table 2).18

X-ray crystal structures of cis-[PdCl₂{ η^1 -Ph₂P (OMe)}{ η^1 -PhP(NHPrⁱ)(OC₆H₃Me₂-3,5)}] (8) and cis-[PdI₂{ η^2 -Ph₂PN(Prⁱ)PPhMe)] (9)

The crystal structures of 8 and 9 are shown in Figs 1 and 2. Selected bond lengths and bond angles

are listed in Table 4. The palladium atom in 8 displays a square-planar geometry with the two monophosphane ligands oriented *cis* to each other. The geometry around the two phosphorus atoms is tetrahedral and that around the nitrogen [N(1)] is The P(1)—Pd(1)—P(2) bond angle planar. $[94.05(5)^{\circ}]$ is much higher than that in the diphosphazane chelate complexes in which it is usually $\sim 70^{\circ}$ (see below). Two different Pd—P bond lengths are observed; the M-P distance connected to the methoxy-substituted phosphorus is 2.232(1) Å, whereas the other M—P distance is 2.248(1) Å. It is interesting to note that methanolysis has occurred to cleave the P-N bond connected to the PPh₂ end; the other P-N bond is not affected because of the presence of an electron-withdrawing aryloxy group on the phosphorus. An intramolecular N(1)—H(1')···Cl(2) hydrogen bond [N(1)··· Cl(2) distance 3.043(4) Å] between the NH proton and a chloride anion is observed. There are no significant intermolecular contacts. The palladium diiodo complex *cis*-[PdI₂{ η^2 -Ph₂PN(Prⁱ)PPhMe}] (9) is structurally similar to that of other palladium(II) and the platinum(II) diphosphazane complexes reported so far.^{2,8,9} The diphosphazane ligand is coordinated in a chelating fashion. The P(1)-N(1)-P(2) bond angle $[100.1(3)^{\circ}]$ is considerably less than the tetrahedral or trigonal angle and indicates considerable strain in the four-membered PdP₂N ring. The related bond angle at the metal, P(1)—Pd(1)—P(2), is 71.14(5)°, which



Fig. 1. Molecular structure of $[PdCl_2\{\eta^1-Ph_2P(OMe)\}\{\eta^1-PhP(NHPr^i)(OC_6H_3Me_2-3,5)\}]$ (8).



Fig. 2. Molecular structure of $[PdI_2{\eta^2-Ph_2PN(Pr^i)PPhMe}]$ (9).

Table 4. Selected bond distances (Å) and bond angles (°) in $[PdCl_2\{\eta^1-Ph_2P(OMe)\}\{\eta^1-PhP(NHPr^i)(OC_6H_3Me_2-3,5)\}]$ (8) and $[PdI_2\{\eta^2-Ph_2PN(Pr^i)PPhMe\}]$ (9)

(a) $[PdCl_2\{\eta^1-Ph_2P(\eta^2)\}]$	$OMe)$ { η^{1} -PhP(MH	$HPr^{i}(OC_{6}H_{3}Me_{2}-3,5)\}]$ (8)	I)
Pd(1)Cl(1)	2.337(1)	P(1) - Pd(1) - P(2)	94.05(5)
Pd(1)Cl(2)	2.3696(9)	Cl(1)— $Pd(1)$ — $Cl(2)$	90.14(5)
Pd(1) - P(1)	2.2320(9)	Pd(1) - P(1) - O(1)	110.4(1)
Pd(1) - P(2)	2.248(1)	Pd(1) - P(2) - N(1)	109.8(1)
P(1) - O(1)	1.589(3)	Pd(1) - P(2) - O(2)	120.2(1)
P(1) - C(11)	1.805(4)	P(1) - O(1) - C(1)	124.6(3)
P(1) - C(21)	1.804(5)	P(2) - O(2) - C(31)	126.5(3)
P(2)—O(2)	1.604(3)	P(2) - N(1) - H(1')	114(3)
P(2) - N(1)	1.635(3)	P(2) - N(1) - C(2)	125.2(4)
P(2)—C(41)	1.809(6)	C(2) - N(1) - H(1')	121(3)
O(1) - C(1)	1.457(5)	$N(1) - H(1') \cdots Cl(2)$	139(4)
O(2)—C(31)	1.392(5)		
N(1)—C(2)	1.474(6)		
N(1)H(1')	0.95(5)		
$N(1) \cdots Cl(2)$	3.043(4)		
(b) $[PdI_2\{\eta^2-Ph_2PN($	Pr ⁱ)PPhMe}] (9)		
Pd(1) - I(1)	2.6363(9)	P(1) - Pd(1) - P(2)	71.14(5)
Pd(1) - I(2)	2.6540(8)	Pd(1) - P(1) - C(14)	118.5(2)
Pd(1) - P(1)	2.222(2)	Pd(1) - P(1) - N(1)	94.4(2)
Pd(1) - P(2)	2.230(2)	Pd(1) - P(2) - N(1)	94.4(2)
P(1) - N(1)	1.694(5)	P(1) - N(1) - P(2)	100.1(3)
P(1) - C(8)	1.802(7)	P(2) - N(1) - C(20)	132.0(5)
P(1) - C(14)	1.801(6)	P(1) - N(1) - C(20)	127.7(5)
P(2) - N(1)	1.686(6)		
P(2) - C(1)	1.801(10)		
P(2) - C(2)	1.795(7)		
N(1)C(20)	1.499(10)		

represents considerable distortion from the 90° expected from a square-planar configuration. The geometry around the nitrogen atom is trigonal planar and that of the phosphorus atoms is tetrahedral. The presence of a methyl instead of a phenyl group does not alter the P—N bond lengths, which are almost the same [1.686(6) and 1.694(5) Å].

The P—N distance in **8** is 1.635(3) Å, which is considerably shorter than the P—N distances in **9** [1.686(6) and 1.694(5) Å]. These P—N distances are shorter than the usually accepted value for a P—N single bond (1.77 Å).²¹ These trends can be explained on the basis of "negative hyper-conjugation" involving the overlap of the lone pair on the nitrogen with a P—X (X = O or C) σ^* orbitals.²²

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Acknowledgement—Thanks are due to the Department of Science and Technology, New Delhi, for financial support.

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