

New bis(phosphines) derived from *N,N'*-substituted ethylenediamine derivatives. Synthesis and transition metal chemistry of $X_2PN(R)CH_2CH_2(R)NPX_2$ ($R = CH_2Ph$ or Ph , $X = Ph$; $R = CH_2Ph$, $X_2 = O_2C_6H_4$). The crystal and molecular structure of $Ph_2PN(CH_2Ph)CH_2CH_2(CH_2Ph)NPPh_2$ and *cis*-[PtCl₂Ph₂PN(CH₂Ph)CH₂CH₂(CH₂Ph)NPPh₂]

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The bis(phosphines) of the type $X_2PN(R)CH_2CH_2(R)NPX_2$ ($R = Ph$ or CH_2Ph , $X = Ph$; $R = CH_2Ph$, $X_2 = O_2C_6H_4$) with the ethylenediamine framework were prepared by reaction of X_2PCl with the corresponding *N,N'*-substituted ethylenediamine derivatives. These ligands readily formed complexes with Group 6 metals and Ru^{II}, Ni^{II}, Pd^{II} and Pt^{II}. All complexes were characterised by elemental analysis, IR and NMR spectroscopic methods of which ³¹P-¹H is most valuable. The structures of the bis(phosphine) ligand $Ph_2PN(CH_2Ph)CH_2CH_2(CH_2Ph)NPPh_2$ and its platinum(II) complex *cis*-[PtCl₂{PPh₂N(CH₂Ph)CH₂CH₂(CH₂Ph)NPPh₂}] were determined by X-ray crystallography. The ligand crystallises in the extended conformation with both the nitrogen atoms nearly planar and the bond angles around them close to 120°. The P–N distances are shorter than normally accepted P–N single bond lengths (*ca.* 1.77 Å) suggesting some degree of P–N π bonding. The seven-membered chelate ring in the platinum complex is non-planar but the metal atom is in a typical square planar environment with two phosphorus atoms and two chlorine atoms in a mutually *cis* disposition and the ethylenediamine bridge is folded with respect to the plane in an “open envelope” fashion.

Introduction

Synthesis of new bis(phosphine) ligand systems to stabilise transition metal chelates in low valent states is considered to be a most challenging task in view of their potential usefulness in a variety of metal-mediated organic transformations.¹ To date, a number of such systems with a variety of backbone frameworks have been synthesized and their transition metal chemistry has been explored. Amongst the most significant ones are those with the P–C–P framework,² *e.g.* dppm,³ dppe,⁴ dmpm,⁵ *etc.* In the last fifteen years, the metal chemistry of the P–N–P framework has been significantly developed because of its flexibility and the relatively easy and high yield synthetic methodologies.⁶ As a part of our interest⁷ and that of others⁸ in designing new ligand systems for complexation studies, catalytic⁹ and medicinal applications,¹⁰ we report here the synthesis of a new bis(phosphine) system having heteroatoms in the backbone framework. The bis(phosphines), derived from the *N,N'*-substituted ethylenediamine derivatives of the type $X_2PN(R)CH_2CH_2(R)NPX_2$ ($R = CH_2Ph$; $X = Ph$ **I**; $R = X = Ph$ **II**) form stable seven-membered metallacycles with Group 6 and platinum metals respectively. Two examples, the bisphosphine, **I** and its platinum complex, were structurally characterised.

Experimental

All experimental manipulations were performed under an atmosphere of dry nitrogen. Standard Schlenk and vacuum line techniques were used.¹¹ Solvents were dried and distilled prior to use. The compound [Ni(CO)₂(PPh₃)₂] was obtained from Strem Chemical Co., *N,N'*-dibenzylethylenediamine, 1,2-di-

anilinoethane and PPh₃ from Lancaster Synthesis Ltd., and used without further purification; [Cr(CO)₄(NBD)],¹² [Mo(CO)₄(NBD)],¹³ [M(CO)₄(pip)₂]¹⁴ ($M = Mo$ and W , pip = piperidine), [Ru(η⁵-C₅H₅)Cl(PPh₃)₂],¹⁵ [M(COD)Cl₂] ($M = Pd^{16}$ or Pt^{17}) and (C₆H₄O₂)PCl¹⁸ were prepared according to published procedures or with minor modifications thereof. The ¹H and ³¹P NMR spectra were recorded on a VXR 300S spectrometer operating at the appropriate frequencies using tetramethylsilane and 85% H₃PO₄ as internal and external references respectively; CDCl₃ was used as both solvent and internal lock. Positive shifts lie downfield in all cases. Infrared spectra were recorded on a Nicolet Impact 400 FT IR instrument in Nujol mull or KBr disk, mass spectra on a HP Vectra VL2 instrument. Microanalyses were performed by the Microanalytical Laboratory in the Department of Chemistry at the Indian Institute of Technology, Bombay.

Syntheses

Ph₂PN(CH₂Ph)CH₂CH₂(CH₂Ph)NPPh₂, I. A solution of PPh₂Cl (3.95 g, 17.95 mmol) in dry diethyl ether (20 cm³) was added with stirring to one of *N,N'*-dibenzylethylenediamine (2.05 g, 8.51 mmol) and triethylamine (1.72 g, 16.99 mmol) in dry diethyl ether (20 cm³) at 0 °C. The reaction mixture was stirred for 24 h at room temperature, then filtered and the white solid obtained consecutively washed with water, methanol and diethyl ether and dried under vacuum. The compound was crystallised from CH₂Cl₂–hexane (1 : 1) (4.35 g, 84%), mp 146–148 °C (Found: C, 78.83; H, 6.30; N, 4.57. C₂₀H₁₉NP requires C, 78.92; H, 6.29; N, 4.60%); δ_H(CDCl₃) 7.52–7.89 (30 H, m, Ph), 3.93 (4 H, d, CH₂Ph,³ J_{P–H} 8.6 Hz) and 2.83 (4 H, m, CH₂CH₂); δ_P(CDCl₃) 65.9 (2 P, s).

Ph₂PN(Ph)CH₂CH₂(Ph)NPPh₂ II. A solution of PPh₂Cl (2.18 g, 9.89 mmol) in dry diethyl ether (20 cm³) was added with stirring to one of 1,2-dianilinoethane (1.00 g, 4.71 mmol) and triethylamine (0.95 g, 9.42 mmol) in dry diethyl ether (20 cm³) at 0 °C. The reaction mixture was treated, and the white solid obtained as above (1.86 g, 68%), mp 184–187 °C (Found: C, 78.53; H, 5.89; N, 4.79. C₁₉H₁₇NP requires C, 78.65; H, 5.90; N, 4.82%); δ_H(CDCl₃) 6.82–7.41 (30 H, m, Ph) and 3.28 (4 H, s, CH₂CH₂); δ_P(CDCl₃) 61.9 (2 P, s).

(C₆H₄O₂)PN(CH₂Ph)CH₂CH₂(CH₂Ph)NP(C₆H₄O₂) III. A solution of (C₆H₄O₂)PCL (1.76 g, 10.08 mmol) in dry diethyl ether (20 cm³) was added with stirring to one of *N,N'*-dibenzylethylenediamine (1.21 g, 5.03 mmol) and triethylamine (1.02 g, 10.08 mmol) in dry diethyl ether (20 cm³) at –98 °C. The reaction mixture was stirred for 24 h at room temperature then filtered and solvent was removed under reduced pressure to obtain a white solid. The compound was crystallised from CH₂Cl₂–hexane (2.18 g, 84%), mp 146–148 °C (Found: C, 65.01; H, 5.03; N, 5.32. C₁₄H₁₃NO₂P requires C, 65.11; H, 5.03; N, 5.42%); δ_H(CDCl₃) 6.84–7.32 (18 H, m, Ph), 3.94 (4 H, d, CH₂Ph, ³J_{P-H} 9 Hz) and 2.72 (4 H, m, CH₂CH₂); δ_P(CDCl₃) 148.5 (2 P, s); *m/z* 515 (*M*⁺).

[M(CO)₄{(Ph₂PN(R)CH₂CH₂(R)NPPh₂)}] (M = Cr, R = CH₂Ph 1 or Ph 2; M = Mo, R = CH₂Ph 3 or Ph 4). A mixture of compound I (0.12 mmol) and [M(CO)₄(NBD)] (0.12 mmol) was heated under reflux in dry hexane (15 cm³) for 24 h after which it was filtered hot. The filtrate was then cooled to 0 °C to give analytically pure crystalline product in good yield.

Compound 1 (0.057 g, 64%), mp 170 °C(decomp.) (Found: C, 68.41; H, 4.88; N, 3.55. C₄₄H₃₈CrN₂O₄P₂ requires C, 68.39; H, 4.95; N, 3.62%); IR ν̄(CO)/cm⁻¹ 1993s and 1879w; δ_H(CDCl₃) 6.86–7.73 (30 H, m, Ph), 3.77 (4 H, s, CH₂Ph) and 3.29 (4 H, t, CH₂CH₂, ³J_{P-H} 8.4 Hz); δ_P(CDCl₃) 112.9 (2 P, s). Complex 2 (0.07 g, 85%), mp 194–196 °C(decomp.) (Found: C, 61.82; H, 4.50; N, 3.69. C₄₂H₃₄CrN₂O₄P₂ requires C, 61.29; H, 4.60; N, 3.76%); IR ν̄(CO)/cm⁻¹ 2019s, 1926s, 1900s and 1880s; δ_H(CDCl₃) 6.60–7.70 (30 H, m, Ph) and 4.53 (4 H, m, CH₂CH₂); δ_P(CDCl₃) 111.7 (2 P, s). Complex 3 (0.09 g, 65%), mp 148 °C(decomp.) (Found: C, 64.77; H, 4.77; N, 3.58. C₄₄H₃₈MoN₂O₄P₂ requires C, 64.73; H, 4.69; N, 3.43%); IR ν̄(CO)/cm⁻¹ 2029s, 1926s and 1887w; δ_H(CDCl₃) 6.80–7.73 (30 H, m, Ph), 3.78 (4 H, s, CH₂Ph) and 3.32 (4 H, m, CH₂CH₂); δ_P(CDCl₃) 94.2 (2 P, s). Complex 4 (0.05 g, 71%), mp 120 °C(decomp.) (Found: C, 57.25; H, 4.29; N, 3.42. C₄₂H₃₄MoN₂O₄P₂ requires C, 57.87; H, 4.34; N, 3.55%); IR ν̄(CO)/cm⁻¹ 2071s, 2032s, 1986s and 1940s; δ_H(CDCl₃) 6.64–7.80 (m, 30 H, Ph) and 4.57 (m, 4 H, CH₂CH₂); δ_P(CDCl₃) 93.3 (2 P, s).

[W(CO)₄{(Ph₂PN(R)CH₂CH₂(R)NPPh₂)}] (M = W, R = CH₂Ph 5 or Ph 6). A mixture of compound I or II (0.11 mmol) and [W(CO)₄(pip)₂] (0.11 mmol) was heated under reflux in dry dichloromethane (10 cm³) for 6 h. The solution was concentrated to about 5–7 cm³ under reduced pressure and diluted with 3 cm³ of hexane. Cooling to 0 °C gave analytically pure samples of 5 or 6. Complex 5 (0.05 g, 54%), mp 140–142 °C (Found: C, 57.24; H, 4.25; N, 2.91. C₄₄H₃₈N₂O₄P₂W requires C, 58.42; H, 4.23; N, 3.09%); IR ν̄(CO)/cm⁻¹ 2015s, 1893s and 1826w; δ_H(CDCl₃) 6.80–7.80 (30 H, m, Ph), 3.80 (4 H, s, CH₂Ph) and 3.35 (4 H, m, CH₂CH₂); δ_P(CDCl₃) 77.5 (2 P, s, ¹J_{PW} 258.5 Hz). Complex 6 (0.09 g, 83.17%), mp 148–150 °C(decomp.) (Found: C, 57.25; H, 4.29; N, 3.42. C₄₂H₃₄N₂O₄P₂W requires C, 57.87; H, 4.34; N, 3.55%); IR ν̄(CO)/cm⁻¹ 2025s, 1887s and 1782w; δ_H(CDCl₃) 6.80–7.80 (30 H, m, Ph) and 4.58 (4 H, m, CH₂CH₂); δ_P(CDCl₃) 74.5 (2 P, s, ¹J_{PW} 253.6 Hz).

[RuCpCl{Ph₂PN(CH₂Ph)CH₂CH₂(CH₂Ph)NPPh₂}] 7. A

mixture of compound I (0.03 g, 0.05 mmol) and [RuCpCl(PPh₃)₂] (0.04 g, 0.05 mmol) in toluene was heated to 80 °C for 8 h. A clear solution was obtained at the end of the reaction to which 3 cm³ of *n*-hexane were added. The orange-yellow product, which precipitated, was isolated by filtration and then dried under vacuum (0.03 g, 69%), mp 174–176 °C (Found: C, 66.10; H, 5.09; N, 3.40. C₄₅H₄₃ClN₂P₂Ru requires C, 66.70; H, 5.34; N, 3.45%); δ_H(CDCl₃) 6.90–8.07 (30 H, m, Ph), 4.06 (5 H, s, Cp), 3.97 (4 H, m, CH₂Ph) and 2.76 (4 H, m, CH₂CH₂); δ_P(CDCl₃) 105.4(2 P, s).

[Ni(CO)₂{Ph₂PN(CH₂Ph)CH₂CH₂(CH₂Ph)NPPh₂}] 8. A mixture of compound I (0.04 g, 0.06 mmol) and [Ni(CO)₂(PPh₃)₂] (0.04 g, 0.06 mmol) was stirred at room temperature in dry dichloromethane (10 cm³) for 5–6 h. Solvent was removed under reduced pressure and the residue extracted with dry hexane (15 cm³) to remove PPh₃. The remaining residue was dried completely under reduced pressure (0.03 g, 60%), mp 170 °C(decomp.) (Found: C, 72.77; H, 5.81; N, 4.20. C₄₂H₃₈N₂–NiO₂P₂ requires C, 72.96; H, 5.53; N, 4.05%); IR ν̄(CO)/cm⁻¹ 2005s and 1933s; δ_H(CDCl₃) 7.02–7.75 (m, 30 H, Ph), 3.82 (d, 4 H, CH₂Ph, ³J_{PH} 9.9 Hz) and 3.08 (m, 4 H, CH₂CH₂); δ_P(CDCl₃) 31.6(2 P, s).

[MCl₂{Ph₂PN(R)CH₂CH₂(R)NPPh₂}] (M = Pd, R = CH₂Ph 9 or Ph 10; M = Pt, R = CH₂Ph 11 or Ph 12). A mixture of Ph₂PN(R)CH₂CH₂(R)NPPh₂ (0.09 mmol) and [M(COD)Cl₂] (0.09 mmol) in dry dichloromethane was stirred at room temperature for 6–7 h. Yellow crystals were obtained when the concentrated solution was diluted with 2–3 cm³ of hexane and allowed to evaporate slowly at room temperature. Complex 9 (0.03 g, 50%), mp 150 °C(decomp.) (Found: C, 56.59; H, 5.30; N, 2.85. C₄₀H₃₈Cl₂N₂P₂Pd requires C, 56.62; H, 5.38; N, 2.90%); δ_H(CDCl₃) 7.17–7.18 (30 H, m, Ph), 3.70 (4 H, m, CH₂Ph) and 3.15 (4 H, m, CH₂CH₂); δ_P(CDCl₃) 82.2 (2 P, s). Complex 10 (0.06 g, 82.27%), mp 192–194 °C(decomp.) (Found: C, 60.80; H, 4.37; N, 3.60. C₃₈H₃₄Cl₂N₂P₂Pd requires C, 60.21; H, 4.52; N, 3.69%); δ_H(CDCl₃) 6.61–8.13 (30 H, m, Ph) and 3.87 [pseudo triplet (pt), 4 H, CH₂CH₂, ³J_{PH} 6.2 Hz]; δ_P(CDCl₃) 85.1(2 P, s). Complex 11 (0.05 g, 72%), mp 200 °C(decomp.) (Found: C, 51.30; H, 4.44; N, 2.97. C₄₀H₃₈Cl₂N₂P₂Pt·0.5CH₂Cl₂·H₂O requires C, 51.72; H, 4.42; N, 2.98%); δ_H(CDCl₃) 6.77–7.82 (30 H, m, Ph), 3.72 (4 H, d, CH₂Ph, ³J_{PH} 4.5) and 3.16 (4 H, d, CH₂CH₂, ³J_{PH} 8.1 Hz); δ_P(CDCl₃) 59.1 (2 P, s, ¹J_{PPt} 4047.8 Hz). Complex 12 (0.07 g, 85%), mp 276–278 °C(decomp.) (Found: C, 49.28; H, 4.00; N, 2.95. C₃₈H₃₄Cl₂N₂P₂Pt·CH₂Cl₂·H₂O requires C, 49.32; H, 4.03; N, 2.94%); δ_H(CDCl₃) 6.63–8.12 (30 H, m, Ph) and 3.84 (4 H, m, CH₂CH₂); δ_P(CDCl₃) 59.3 (2 P, s, ¹J_{PPt} 4210.8 Hz).

X-Ray crystallography

Crystals of compounds I and 11 obtained as described above were mounted on Pyrex filaments with epoxy resin. General procedures for crystal alignment, unit cell determination and refinement and collection of intensity data on the Enraf-Nonius CAD-4 diffractometer have been published.²⁰ Details specific to the present study are presented in Table 2. The initial monoclinic cells obtained by the CAD-4 software were confirmed by the observation of 2/*m* diffraction symmetry. Systematic absences observed for I uniquely determined the space group while for 11 the space group was determined from both systematic absences and intensity statistics. In both instances, periodic monitoring of check reflections showed stability of the intensity data. The data were corrected for Lorentz-polarisation effects (XCAD 4²¹) and in the case of 11 for absorption using ψ scans on several reflections with χ near 90°. Initial solutions for I and 11 were obtained, respectively, from direct methods (SIR 88²¹) and from a sharpened Patterson function with the remainder of the structures

Table 1 Proton and ^{31}P NMR spectroscopic data ^a for the ligands and their metal complexes

Compound	^{31}P δ , J/Hz	$\Delta\delta^b$	^1H	
			CH_2CH_2	N(R)
I $\text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2(\text{CH}_2\text{Ph})\text{NPPh}_2$	65.9	—	2.83 (m)	3.93 (d)
II $\text{Ph}_2\text{PN}(\text{Ph})\text{CH}_2\text{CH}_2(\text{Ph})\text{NPPh}_2$	61.9	—	3.28 (s)	—
III $(\text{C}_6\text{H}_4\text{O}_2)\text{PN}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2(\text{CH}_2\text{Ph})\text{NP}(\text{C}_6\text{H}_4\text{O}_2)$	148.5	—	2.72 (m)	3.94 (d)
1 $[\text{Cr}(\text{CO})_4\{\text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2(\text{CH}_2\text{Ph})\text{NPPh}_2\}]$	112.9	47	3.29 (t)	3.77 (s)
2 $[\text{Cr}(\text{CO})_4\{\text{Ph}_2\text{PN}(\text{Ph})\text{CH}_2\text{CH}_2(\text{Ph})\text{NPPh}_2\}]$	111.7	49.8	4.53 (m)	—
3 $[\text{Mo}(\text{CO})_4\{\text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2(\text{CH}_2\text{Ph})\text{NPPh}_2\}]$	94.2	28.3	3.32 (m)	3.78 (s)
4 $[\text{Mo}(\text{CO})_4\{\text{Ph}_2\text{PN}(\text{Ph})\text{CH}_2\text{CH}_2(\text{Ph})\text{NPPh}_2\}]$	93.3	31.4	4.57 (m)	—
5 $[\text{W}(\text{CO})_4\{\text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2(\text{CH}_2\text{Ph})\text{NPPh}_2\}]$	77.5	11.6	3.35 (m)	3.80 (s)
6 $[\text{W}(\text{CO})_4\{\text{Ph}_2\text{PN}(\text{Ph})\text{CH}_2\text{CH}_2(\text{Ph})\text{NPPh}_2\}]$	$^1J_{\text{WP}} = 258.5$	12.6	4.58 (m)	—
	74.5			
7 $[\text{Ru}(\text{Cp})\text{Cl}\{\text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2(\text{CH}_2\text{Ph})\text{NPPh}_2\}]$	$^1J_{\text{WP}} = 253.6$	39.5	2.76 (m)	3.97 (m)
	105.4			
8 $[\text{Ni}(\text{CO})_2\{\text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2(\text{CH}_2\text{Ph})\text{NPPh}_2\}]$	31.6	-34.3	3.08 (m)	3.82 (d)
9 $[\text{PdCl}_2\{\text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2(\text{CH}_2\text{Ph})\text{NPPh}_2\}]$	82.2	16.3	3.15 (m)	3.70 (m)
10 $[\text{PdCl}_2\{\text{Ph}_2\text{PN}(\text{Ph})\text{CH}_2\text{CH}_2(\text{Ph})\text{NPPh}_2\}]$	85.1	23.2	3.87 (pt)	—
11 $[\text{PtCl}_2\{\text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2(\text{CH}_2\text{Ph})\text{NPPh}_2\}]$	59.1	-6.8	3.16 (d)	3.72 (d)
	$^1J_{\text{PtP}} = 4047.8$	-2.6	3.84 (m)	—
59.3				
12 $[\text{PtCl}_2\{\text{Ph}_2\text{PN}(\text{Ph})\text{CH}_2\text{CH}_2(\text{Ph})\text{NPPh}_2\}]$	$^1J_{\text{PtP}} = 4210.8$	—	—	—
	59.3			

^a In CDCl_3 ; $\delta(^{31}\text{P})$ in ppm vs. 85% H_3PO_4 . ^b $\Delta\delta = (\delta_{\text{complex}} - \delta_{\text{ligand}})$ in ppm.

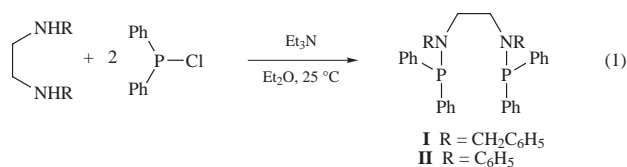
developed by full-matrix, least-squares refinement followed by calculation of a difference map. In the late stages of refinement for **11**, a molecule of solvent dichloromethane located on a twofold axis and a molecule of water disordered approximately equally over two sites were located and successfully refined. Hydrogen atoms were included in calculated positions as riding atoms with isotropic displacement parameters 20% larger than those of the attached atoms. All calculations were performed with the SHELXTL PLUS²² program package.

CCDC reference number 186/1372.

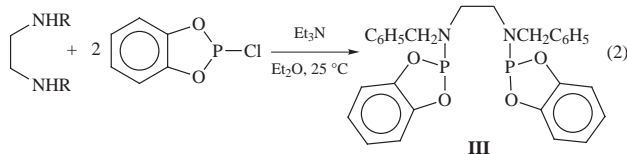
See <http://www.rsc.org/suppdata/dt/1999/1407/> for crystallographic files in .cif format.

Results and discussion

N,N'-Substituted ethylenediamine derivatives react with two moles of chlorodiphenylphosphine in the presence of triethylamine to afford the expected compounds in good yield as shown in eqn. 1. The analogous catechol derivative **III**



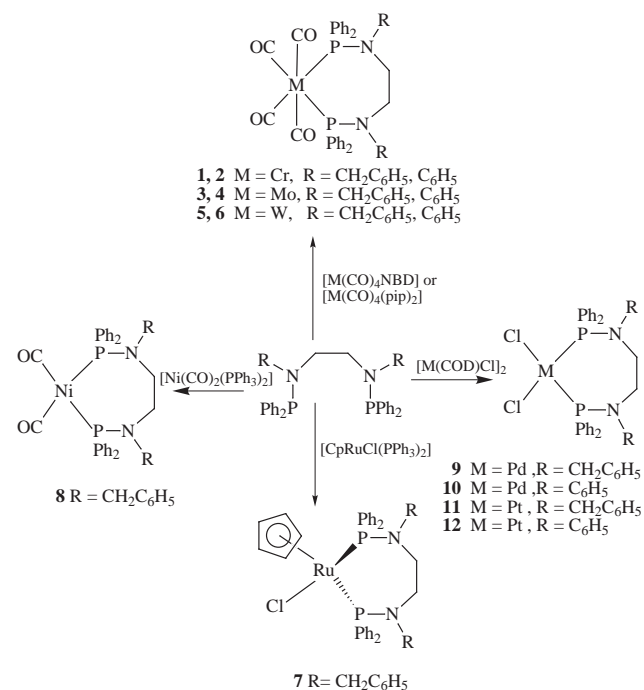
was prepared by treating *N,N'*-dibenzylethylenediamine with $(\text{C}_6\text{H}_4\text{O}_2)\text{P}(\text{Cl})$ in the ratio 1 : 2 in diethyl ether in the presence of triethylamine as shown in eqn. 2.



The ^1H and ^{31}P NMR spectroscopic data for the newly synthesized ligands and their compounds are listed in Table 1. The ^{31}P NMR spectra for **I–III** show singlets at δ 65.9, 61.9 and 148.5 respectively, indicating the symmetric nature of the ligands. The ^1H NMR spectrum of **I** shows a doublet for the benzylic protons at δ 3.93 and a doublet of doublets at δ 2.83 for the backbone (CH_2CH_2) protons. A similar pattern is

observed in the spectrum of **III**: a doublet for the benzylic protons at δ 3.94 and a doublet of doublets for the (CH_2CH_2) protons at δ 2.72. By contrast, the spectrum of **II** displays a singlet at δ 3.28 for the bridging (CH_2CH_2) protons.

All the ligands are crystalline white solids, moderately air stable and soluble in dichloromethane, chloroform and toluene. Their co-ordinating properties were studied by treating them with various Group 6 metal carbonyl and platinum metal derivatives containing one or two labile ligands. The reactions of ligands **I** and **II** with various transition metal derivatives are shown in Scheme 1.



Scheme 1

The mononuclear metal tetracarbonyl derivatives *cis*- $[\text{M}(\text{CO})_4\{\text{Ph}_2\text{PN}(\text{R})(\text{CH}_2)_2(\text{R})\text{NPPh}_2\}]$ have been prepared by displacement either of the co-ordinated olefins or piperidine from the corresponding tetracarbonyl derivatives as shown in Scheme 1. The seven-membered metallacycles **1–6** were

characterised by elemental analysis, infrared and NMR spectroscopic data (see Table 1). The infrared spectra exhibit strong $\nu(\text{CO})$ absorptions in the range $1780\text{--}2071\text{ cm}^{-1}$, characteristic of the bis(phosphine)s bound to the $[\text{M}(\text{CO})_4]$ moiety in the *cis* fashion.²³ The ^{31}P NMR spectra exhibit a single resonance, which is considerably deshielded compared to that of the "free" ligand. The ^{31}P co-ordination chemical shifts decrease on going from chromium to tungsten and the trend is comparable with those for analogous bis(phosphine) complexes.^{24,25} The reaction of **I** with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2]$ in toluene solution in a ratio of 1:1 at 80°C gives a yellow crystalline complex **7** in 69% yield. The ^{31}P NMR spectrum shows a singlet at δ 105.4 indicating that both the PPh_3 ligands have been replaced by $\text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2(\text{CH}_2\text{Ph})\text{NPPh}_2$ which is acting as a bidentate chelating ligand.^{3a,7a} The ^1H NMR spectrum is consistent with the structure proposed.

The reaction of compound **I** with an equimolar ratio of the nickel(0) derivative $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$ afforded a seven-membered chelating dicarbonyl nickel derivative, **8** with the elimination of two PPh_3 groups. The IR spectrum shows two $\nu(\text{CO})$ bands at 2005 and 1933 cm^{-1} indicating the presence of two *cis* carbonyl groups. The ^{31}P NMR spectrum shows a single resonance at δ 31.6 with a co-ordination shift of -34.3 ppm which is in accord with the data reported for analogous complexes.^{26,27} Treatment of $[\text{M}(\text{COD})\text{Cl}_2]$ ($\text{M} = \text{Pd}$ or Pt) with 1:1 molar proportion of the ligand **I** or **II** in dichloromethane yields the chelate complexes **9–12**. Their ^{31}P NMR spectra show single resonances that are downfield of the signals for the corresponding "free" ligands. Although the deshielding is more pronounced in the case of palladium complexes of ligand **II**, it is comparable with that of ligand **I** in the case of platinum complexes. The $^1J_{\text{P-P}}$ couplings for complexes **11** and **12** are comparable, with values of 4047.8 and 4210.8 Hz respectively that are consistent with the proposed *cis* geometry.²⁸ The structures of the "free" ligand **I** and the complex **11** have been established by single crystal X-ray analysis.

The ^1H and ^{31}P NMR spectra for all the compounds were studied. The resonances due to the bridging ethylene protons in the ^1H NMR spectra of the complexes **1–6** appear in the range δ 3.29–4.58 as multiplets with virtual coupling. Complexes **1**, **3** and **5** exhibit single resonances in the range δ 3.77–3.80 for the CH_2 protons in the benzyl substituent, surprisingly with lower $^3J_{\text{P-H}}$ values when compared to that of the "free" ligand. The bridging ethylene protons are more deshielded in the complexes **1–6** when compared to those of the respective "free" ligands.

However the methylene (CH_2Ph) proton chemical shift values for the benzyl derivative do not show any significant difference between the co-ordinated and the "free" ligand.

The structures of ligand **I** and its platinum complex **11** were determined by single crystal X-ray diffraction studies. Perspective views of the molecules and the numbering schemes are shown in Figs. 1 and 2 with selected bond lengths and interbond angles in Table 3. The ligand **I** crystallises in the extended conformation and possesses crystallographically imposed centrosymmetry. The P–N bond length of 1.680 \AA is shorter than the normally accepted value for a single bond (1.77 \AA)³⁰ but compares well with those found in a variety of complexes of $\text{MeN}[\text{P}(\text{OMe})_2]_2$ ³¹ suggesting a degree of P–N π bonding. Consistent with this, the nitrogen atom is nearly planar as evidenced by the sum of angles about N being 358.7° . The platinum complex **11** did not give any X-ray quality crystals in very dry solvents. However, when air was bubbled for a few seconds through a dichloromethane–hexane (1:1) solution of the complex followed by cooling to 0°C , colourless cubes crystallised which contained both dichloromethane and water of solvation. No significant inter-

Table 2 Crystallographic data for $\text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2(\text{CH}_2\text{Ph})\text{NPPh}_2$ **I** and $[\text{PtCl}_2\{\text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2(\text{CH}_2\text{Ph})\text{NPPh}_2\}]$ **11**

	I	11
Formula	$\text{C}_{40}\text{H}_{38}\text{N}_2\text{P}_2$	$\text{C}_{40.50}\text{H}_{41.50}\text{Cl}_3\text{N}_2\text{O}_{1.25}\text{P}_2\text{Pt}$
<i>M</i>	608.66	939.64
Crystal size/mm	$0.53 \times 0.33 \times 0.30$	$0.50 \times 0.33 \times 0.27$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
<i>a</i> /Å	10.6559(4)	21.101(2)
<i>b</i> /Å	9.2138(10)	21.7015(10)
<i>c</i> /Å	17.3676(8)	19.9911(13)
$\beta/^\circ$	94.835(4)	119.33(3)
<i>V</i> /Å ³	1699.1(2)	7981.1(9)
<i>Z</i>	2	8
<i>D</i> _f /g cm ⁻³	1.190	1.564
μ/mm^{-1}	0.158	3.832
<i>T</i> /K	293(2)	293(2)
Total no. reflections	3194	7288
No. unique reflections	3023	7085
<i>R</i> _{int}	0.0269	0.0506
<i>R</i>	0.0356	0.0581
<i>R</i> '	0.0873	0.1670
Goodness of fit	1.008	1.062

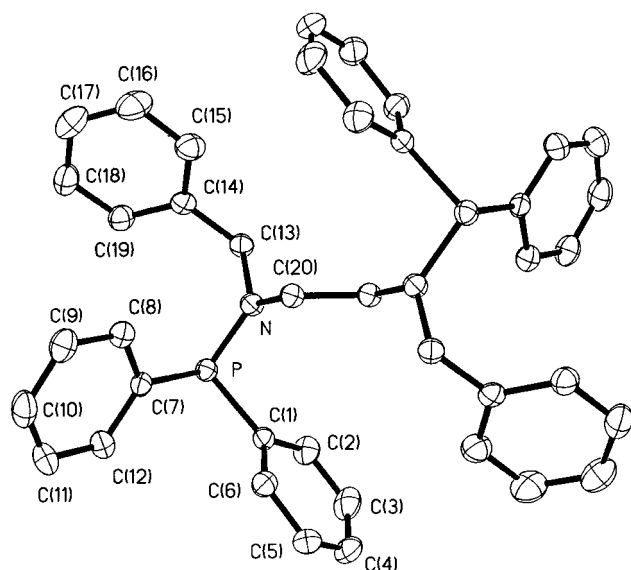


Fig. 1 An ORTEP²⁹ plot of a perspective view of $\text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2(\text{CH}_2\text{Ph})\text{NPPh}_2$ **I** showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

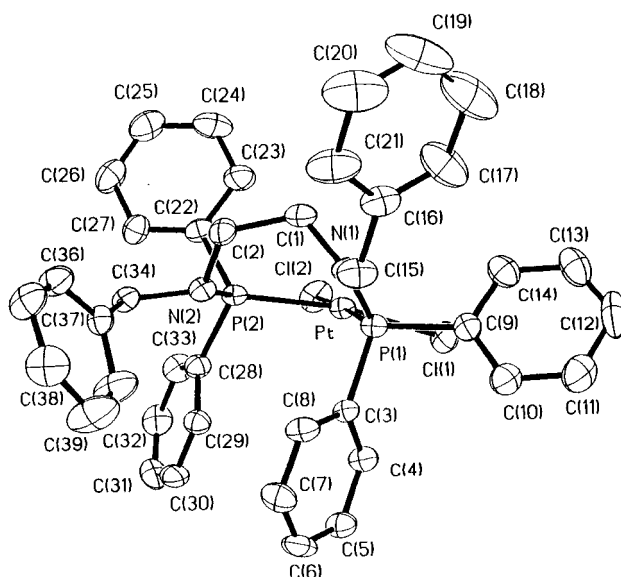


Fig. 2 An ORTEP²⁹ plot of a perspective view of $[\text{PtCl}_2\{\text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2(\text{CH}_2\text{Ph})\text{NPPh}_2\}]$ **11** showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

Table 3 Selected bond distances (Å) and angles (°) for compounds **I** and **11**

I			
P–N	1.680(2)	N–P–C(7)	106.56(9)
N–C(20)	1.462(2)	N–P–C(1)	103.04(8)
N–C(13)	1.474(2)	C(7)–P–C(1)	101.08(9)
C(13)–C(14)	1.508(3)	C(20)–N–C(13)	116.3(2)
C(20)–C(20) ^a	1.523(4)	C(20)–N–P	124.91(13)
		C(13)–N–P	117.52(13)
		N–C(20)–C(20) ^a	112.1(2)
11			
Pt–P(1)	2.233(3)	P(1)–Pt–P(2)	96.39(10)
Pt–P(2)	2.249(3)	P(1)–Pt–Cl(1)	90.34(11)
Pt–Cl(1)	2.346(3)	P(2)–Pt–Cl(1)	168.49(11)
Pt–Cl(2)	2.364(3)	Cl(1)–Pt–Cl(2)	87.14(12)
P(1)–N(1)	1.671(8)	P(1)–Pt–Cl(2)	176.79(11)
P(2)–N(2)	1.702(9)	P(2)–Pt–Cl(2)	85.78(11)
N(1)–C(1)	1.423(14)	C(1)–N(1)–P(1)	121.6(7)
N(1)–C(15)	1.478(14)	C(2)–N(2)–P(2)	117.2(7)
N(2)–C(2)	1.458(13)	C(1)–N(1)–C(15)	115.8(9)
N(2)–C(34)	1.496(14)	C(15)–N(1)–P(1)	122.1(7)
		C(2)–N(2)–C(34)	108.7(8)
		C(34)–N(2)–P(2)	116.0(7)

^a Symmetry transformation used to generate equivalent atoms: $-x, -y + 1, -z + 1$.

action of either solvent molecules with the complex appears to be present.

As expected, complex **11** contains the ligand chelating to platinum which, with the two chloride ligands, gives an approximately (within 0.09 Å) square planar geometry. The deviations from planarity are in the form of a slight tetrahedral distortion. The Pt–Cl and Pt–P distances (Table 3) are within the ranges found previously³² for similar complexes with the former being near the long end of the range because of the *trans* influence of the phosphine. The Pt–P distances are significantly different ($\Delta\sigma = 5.3$) as are the Pt–Cl distances ($\Delta\sigma = 6$) with the shorter Pt–P distance paired with the longer Pt–Cl distance and *vice versa* but there is no obvious explanation. That there is only a single ³¹P NMR resonance in solution suggests that the observed differences may result from packing or other solid-state effects. As with the “free” ligand, N(1) is virtually planar (sum of angles = 359.9°) but here N(2) is distinctly pyramidal (sum of angles = 341.9°). Accompanying this is a slight lengthening of the P(2)–N(2) distance as compared with the P(1)–N(1) distance although the difference is just above the threshold of crystallographic significance. It would, however, be consistent with a smaller degree of π character in this bond. Finally, the ligand backbone is in the “open envelope” conformation.

Conclusion

Owing to the presence of a long backbone in this type of ligand, phosphorus–phosphorus coupling through the backbone is less likely. Hence, this type of ligand with asymmetric phosphorus centres would be well suited for the study of phosphorus–phosphorus coupling through the metal in its chelate complexes. Also, metal complexes of this class of bis-(phosphine) can be used as potential catalysts for alkylation of various allylic acetates and other different organic transformations. Further studies in this direction are in progress.

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