

Preparation and organometallic complexes of the new unsymmetrical ligand: $\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2^\star$

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Abstract

Deprotonation of (2-diphenylphosphino)benzeneamine with BuLi followed by reaction with ClPPh_2 in THF gave $\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2$ in good yields. The new unsymmetrical ligand has been incorporated into a number of complexes $[\text{Rh}\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\}(\text{cod})][\text{ClO}_4]$ **2**, $\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-}P_{(N)}\}$ **3**, $[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-}P_{(N)}, P\}][\text{Cl}]$ **4**, $\text{IrCl}_2(\eta^5\text{-C}_5\text{Me}_5)\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-}P_{(N)}\}$ **5**, $\text{RuCl}_2(\eta^6\text{-MeC}_6\text{H}_4\text{Pr})\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-}P_{(N)}\}$ **6**, $[\text{RuCl}(\eta^6\text{-MeC}_6\text{H}_4\text{Pr})\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-}P_{(N)}, P\}][\text{BF}_4]$ **7**, $\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-}P_{(N)}\}$ **8**, $[\text{RuCl}(\eta^6\text{-C}_6\text{Me}_6)\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-}P_{(N)}, P\}][\text{BF}_4]$ **9**, $\text{RuCl}_2(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-}P_{(N)}\}$ **10**, $\text{OsCl}_2(\eta^6\text{-MeC}_6\text{H}_4\text{Pr})\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-}P_{(N)}\}$ **11** to demonstrate its coordination behaviour as a monodentate or as a chelate ligand. The X-ray structures of for **5**, **9** and **10** are reported. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Phosphine; X-ray structure; Heterocycle; Transition metal; Complex

1. Introduction

We have recently reported a number of syntheses of new P–N–P ligands [1–3] and phosphines [4–6] via simple P–N bond forming reactions. Apart from ligand systems with totally non-carbon backbones we have been able to synthesise the first six-membered true heterocycles [7]. Surprisingly, there have been few reports on non-carbon spacers between the carbon backbone and the adjacent phosphine centres in bidentate phosphine, we have been able to prepare simple bidentate systems from reactions with diaminotoluene [8]. Here we report on the formation of a simple unsymmetric bis-phosphines obtained from the reaction of (2-diphenylphosphino)benzeneamine [9] with BuLi followed by Ph_2PCl . We decided to investigate these sys-

tems so as to establish whether the difference in the basicity/bulkiness of the phosphines could be employed to enable the ligands to be switched between monodentate and bidentate coordination behaviour, i.e. to generate ‘hemilabile’ bisphosphines with properties similar to other reported examples [10–12].

2. Experimental

2.1. General

Diethyl ether, petroleum ether (60–80°C) and THF were purified by reflux over sodium and distillation under nitrogen. Dichloromethane was heated to reflux over powdered calcium hydride and distilled under nitrogen. $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$ [13], $[\{\text{MCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2]$ M = Rh, Ir [14], $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-MeC}_6\text{H}_4\text{Pr})\}_2]$ [15], $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-C}_6\text{Me}_6)\}_2]$ [15], and $[\{\text{RuCl}(\mu\text{-Cl})(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\}_2]$ [16] were prepared as described in the literature. IR spectra were recorded

* Dedicated to Alan Cowley, on the occasion of his 65th birthday. Although we were only briefly colleagues, Alan has been a significant influence on much of our work.

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from KBr discs on a Perkin–Elmer system spectrometer; ^{31}P -NMR spectra on a Jeol FX90Q operating at 36.21 MHz; ^1H -, ^{13}C - and ^{31}P -NMR spectra on a Bruker AC250 operating at 250, 62.9 and 101.3 MHz, respectively. Fast atom bombardment mass spectra were carried out by the Swansea mass spectrometer service.

2.1.1. $\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2$ **1**

A solution of 2.43 M $n\text{BuLi}$ (13 cm³, 31.6 mmol) in hexane was added dropwise over a period of 10 min to a cooled (-78°C cardice/acetone) stirred solution of (2-diphenylphosphino)benzeneamine [9] (8.7 g, 31.4 mmol) in freeze/thaw degassed THF (350 cm³). The clear pale orange solution was warmed to room temperature (r.t.) and stirred for 30 min giving a light, white precipitate. The reaction was cooled once more to -78°C (cardice/acetone) and a solution of chlorodiphenylphosphine (5.7 cm³, 7.0 g, 31.7 mmol) in freeze/thaw degassed THF (50 cm³) was added dropwise over a period of 5 min and the mixture was allowed to warm to r.t., then stirred for 1 h. The solvent was removed in vacuo and the pale brown oil was taken up in a minimum amount of acetone (ca. 50 cm³). Distilled water was added dropwise (ca. 20 cm³) to precipitate the product. The colourless solid was collected by suction filtration, washed with ice cold methanol (20 cm³) and dried overnight in vacuo. Yield 10.5 g, 73%. Microanalysis: Found (Calc. for $\text{C}_{30}\text{H}_{25}\text{NP}_2$). C, 78.08 (76.99); H, 5.46 (5.53); N, 3.04 (3.35)%. $^{31}\text{P}\{\text{H}\}$ -NMR (CDCl_3): $\delta(\text{P}_\text{A})$ $-19.5(\text{d})$,

$\delta(\text{P}_\text{X})$ 29.6(d) ppm. $^4J(^{31}\text{P}_\text{A}^{31}\text{P}_\text{X})$ 3.7 Hz. FAB⁺ MS: m/z 461, $[\text{M}]^+$. IR (KBr): 3300vs, 3059m, 1587s, 1566s, 1474s, 1433s, 1372s, 1286m, 1261m, 1090m, 1025vs, 997vs, 891s, 849s, 781vs, 755vs, 743m, 696s, 545s, 516vs, 496m, 469vs 447s, 419s, 393s, 282vs cm⁻¹.

2.1.2. $[\text{Rh}\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\}(\text{cod})][\text{ClO}_4]$ **2**

Care: perchlorate salts may be explosive. $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$ (0.126 g, 0.26 mmol) and AgClO_4 (0.107 g, 0.52 mmol) were weighed into a 50 cm³ round bottomed Schlenk flask. The flask was evacuated, then filled with N_2 . Degassed acetone (30 cm³) was added and the mixture was stirred for 30 min giving AgCl as a white precipitate. The solution was transferred by a filter stick to a second flask (also filled with N_2) containing **1** (0.238 g, 0.52 mmol). The mixture was stirred under an N_2 atmosphere for 1 h and concentrated in vacuo to ca. 15 cm³. Light petroleum (25 cm³) was added to precipitate the product and the flask was stored at -4°C over night. The dark orange solid was collected by suction filtration washed with light petroleum (2×15 cm³) and dried in vacuo. Yield 0.32 g, 81%. Microanalysis: Found (Calc. For $\text{C}_{38}\text{H}_{37}\text{ClNO}_4\text{P}_2\text{Rh}$). C, 59.01 (59.12); H, 4.62 (4.83); N, 1.47 (1.81)%. $^{31}\text{P}\{\text{H}\}$ -NMR (CDCl_3): $\delta(\text{P}_\text{A})$ 17.5(dd) ppm. $^1J(^{103}\text{Rh} - ^{31}\text{P}_\text{A})$ 136 Hz. $\delta(\text{P}_\text{X})$ 71.9(dd) ppm. $^1J(^{103}\text{Rh} - ^{31}\text{P}_\text{X})$ 158 Hz. $^2J(^{31}\text{P}_\text{A} - ^{31}\text{P}_\text{X})$ 52.8 Hz. FAB⁺ MS: m/z 672, $[\text{M}]^+$. IR (KBr): 3248br, 3056s, 1697br, 1625br, 1591s, 1482vs, 1437vs, 1311m, 1271m, 1228m, 1096br, 998s, 938s, 750s, 727vs, 695vs, 623vs, 527br, 497s cm⁻¹.

Table 1
Details of the crystal data and refinements

Compound	5	9	10
Empirical formula	$\text{C}_{40.75}\text{H}_{41.5}\text{Cl}_{3.5}\text{IrNP}_2$	$\text{C}_{42.5}\text{H}_{43.5}\text{BCl}_{2.5}\text{F}_4\text{N}_2\text{P}_2\text{Ru}$	$\text{C}_{40}\text{H}_{41}\text{Cl}_2\text{NP}_2\text{Ru}$
Formula weight	923.5	920.7	769.7
Colour	Yellow	Yellow	Yellow
Size (mm)	$0.2 \times 0.25 \times 0.3$	$0.01 \times 0.06 \times 0.08$	$0.4 \times 0.35 \times 0.2$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1$
a (Å)	10.4389(2)	15.3659(3)	13.3780(2)
b (Å)	17.1933(2)	17.7795(2)	10.3410(1)
c (Å)	22.7357(1)	16.0576(3)	13.5412(1)
β (°)	103.117(1)	100.633(1)	102.951(1)
V (Å ³)	3974	4311	1826
Z	4	4	2
D_{calc} (g cm ⁻³)	1.54	1.42	1.40
$\mu(\text{Mo-K}\alpha)$ (mm ⁻¹)	3.70	0.64	0.69
$F(000)$	1838	1880	792
Independent reflections	9220	6166	8098
Observed reflections	9171	6100	4852
Final R_1 [$I > 2\sigma(I)$]	0.0344	0.0852	0.0330
wR_2	0.0827	0.1805	0.0839
Goodness of fit on F^2	0.922	1.038	0.944
Largest difference peak/hole (e Å ⁻³)	1.18 and -0.87	0.96 and -0.74	0.49 and -0.23

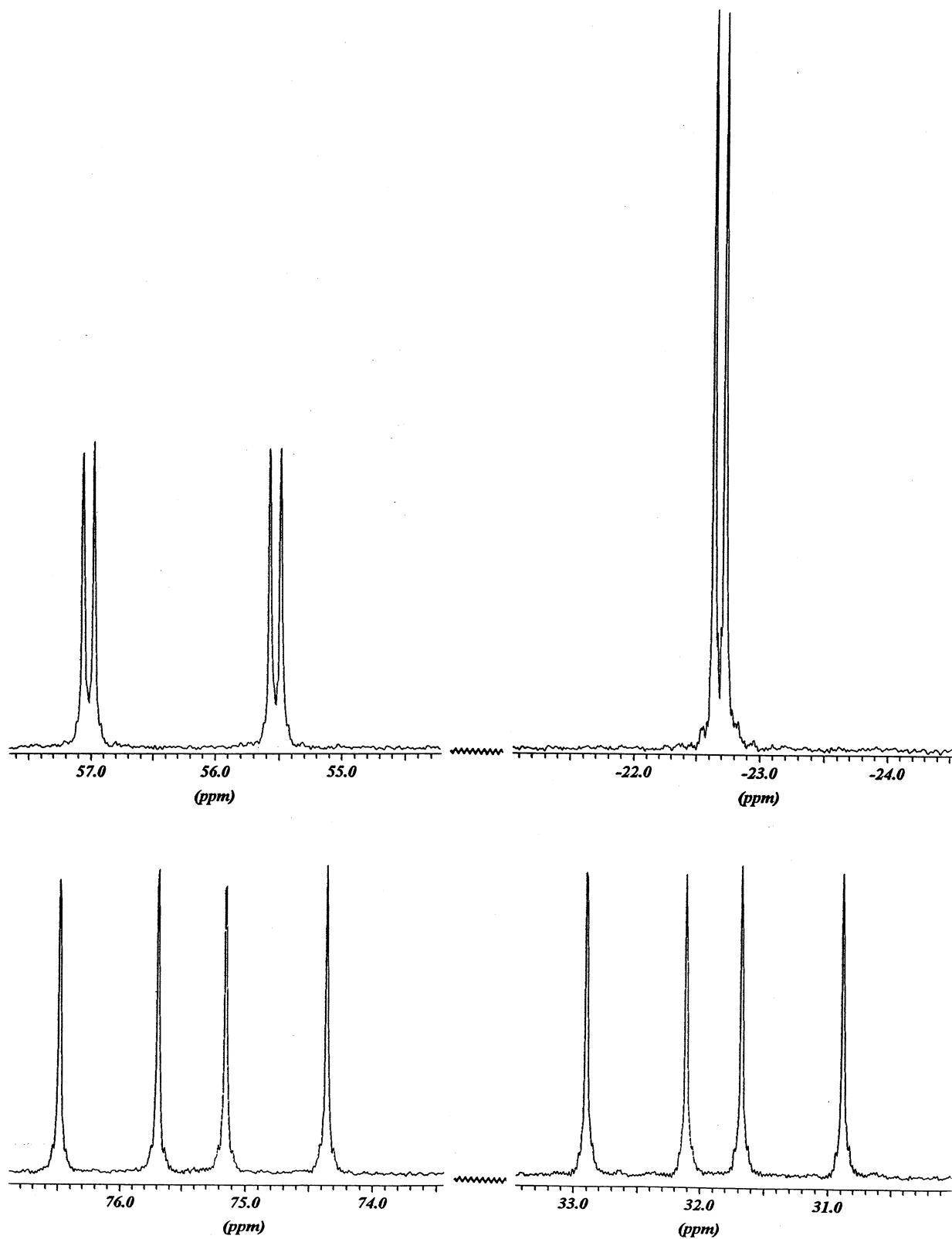


Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ -NMR of complexes 3 (top) and 4 (bottom).

2.1.3. $\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-P}_{(N)}\}$ 3

$[\{\text{RhCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2]$ (0.090 g, 0.15 mmol) was suspended in THF (1.5 cm^3). To the stirred suspension

was added 1 (0.140 g, 0.30 mmol) as a solid. The suspension dissolved and the product 3 precipitated. After stirring for ca. 90 min, the dark red solid was

Table 2

Comparison of ^{31}P -NMR spectroscopic data for monodentate and chelate complexes

Monodentate ligand				Chelating ligand			
	δP_A	δP_X	$^4J\{^{31}\text{P}-^{31}\text{P}\}$		δP_A	δP_X	$^2J\{^{31}\text{P}-^{31}\text{P}\}$
3	−22.7	56.3	8.8	4	31.9	75.4	80.3
5	−22.6	23.8	7.6	a	−6.4	37.7	48.4
6	−21.8	53.1	8.5	7	34.8	81.6	75.7
8	−24.5	56.7	8.9	9	35.8	81.2	83.6
11	−21.6	11.4	8.6	a	−10.8	36.8	48.4

^a NMR only—sample not isolated.

collected by suction filtration and washed with diethyl ether ($2 \times 10 \text{ cm}^3$) and dried in vacuo. Yield 0.20 g, 89%. Microanalysis: Found (Calc. for $\text{C}_{40}\text{H}_{40}\text{Cl}_2\text{NP}_2\text{Rh}$). C, 62.10 (62.35); H, 5.61 (5.23); N 1.97 (1.82)%. $^{31}\text{P}\{\text{H}\}$ -NMR (toluene/ C_6D_6): $\delta(\text{P}_\text{A})$ −22.7(d) ppm. $\delta(\text{P}_\text{X})$ 56.3(dd) ppm. $^1J(^{103}\text{Rh}-^{31}\text{P}_\text{X})$ 151.1 Hz. $^4J(^{31}\text{P}_\text{A}-^{31}\text{P}_\text{X})$ 8.8 Hz. IR (KBr): 3279m, 3051s, 2910m, 2863s, 1585vs, 1570vs, 1503m, 1476vs, 1435vs, 1383vs, 1277vs, 1216s, 1186m, 1159m, 1093s, 1062vs, 1025m, 909vs, 773m, 750vs, 701vs, 619vs, 613vs, 522vs, 492s, 473vs, 449s, 397br cm^{-1} .

2.1.4. $[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-P}_{(\text{N})}\text{P}\}][\text{Cl}]$ **4**

Compound **3** (0.103 g, 0.13 mmol) was stirred in chloroform (4 cm^3) for 2 h, diethyl ether (25 cm^3) was added to precipitate a bright orange coloured solid. The product was collected by suction filtration washed with diethyl ether ($2 \times 10 \text{ cm}^3$) and dried in vacuo. Yield 0.91 g, 91%. Microanalysis: Found (Calc. for $\text{C}_{40}\text{H}_{40}\text{Cl}_2\text{NP}_2\text{Rh}$). C, 62.67 (62.35); H, 5.74 (5.32); N, 1.66 (1.82)%. $^{31}\text{P}\{\text{H}\}$ -NMR (CDCl_3): $\delta(\text{P}_\text{A})$ 31.9(dd) ppm. $^1J(^{103}\text{Rh}-^{31}\text{P}_\text{A})$ 124.2 Hz. $\delta(\text{P}_\text{X})$ 75.4(dd) ppm. $^1J(^{103}\text{Rh}-^{31}\text{P}_\text{X})$ 135.2 Hz. $^2J(^{31}\text{P}_\text{A}-^{31}\text{P}_\text{X})$ 80.3 Hz. FAB⁺ MS: m/z 734 corresponds to $[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)\{\text{Ph}_2\text{PC}_6\text{H}_4\text{NHPPH}_2\}]^+$, 699 corresponds to $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\{\text{Ph}_2\text{PC}_6\text{H}_4\text{NHPPH}_2\}]^+$. IR (KBr): 3052s, 1624br, 1590vs, 1503s, 1457s, 1435vs, 1376s, 1318m, 1260m, 1225m, 1188s, 1158m, 1134m, 1096vs, 1074s, 1018m, 999vs, 868br, 749vs, 696vs, 602m, 537vs, 523vs, 511vs, 483vs, 446br, 374br cm^{-1} .

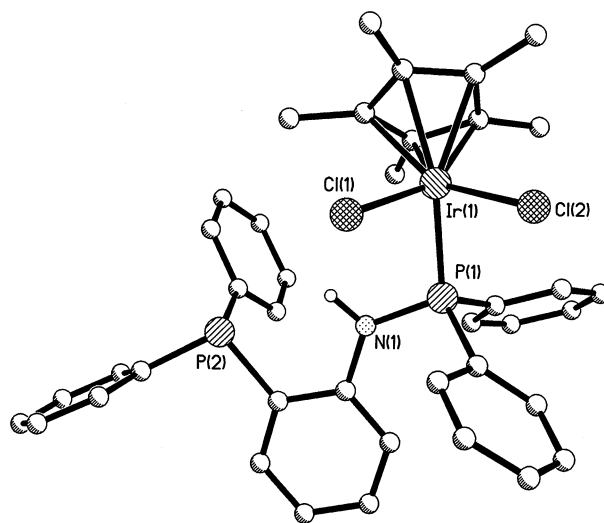
2.1.5. $\text{IrCl}_2(\eta^5\text{-C}_5\text{Me}_5)\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-P}_{(\text{N})}\}$ **5**

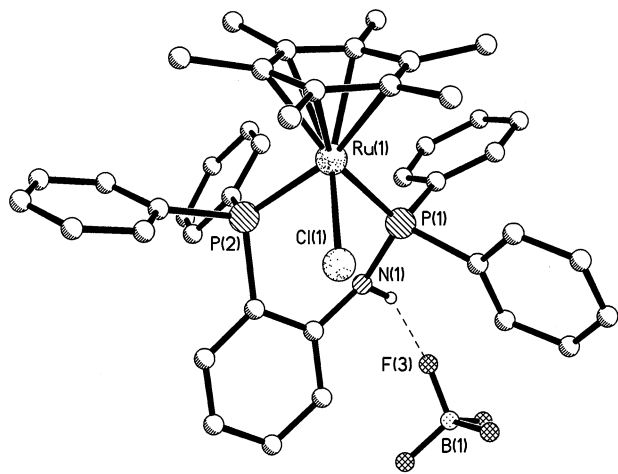
This was prepared in the same way as the rhodium compound **3** using $[\{\text{IrCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2]$ (0.070 g, 0.09 mmol) in THF (1.5 cm^3) and **1** (0.084 g, 0.18 mmol) to give a bright orange solid. Yield 0.13 g, 87%. Microanalysis: Found (Calc. for $\text{C}_{40}\text{H}_{40}\text{Cl}_2\text{IrNP}_2$). C, 55.71 (55.88); H, 4.82 (4.69); N, 1.80 (1.63)%. $^{31}\text{P}\{\text{H}\}$ -NMR (CDCl_3): $\delta(\text{P}_\text{A})$ −22.6(d), $\delta(\text{P}_\text{X})$ 23.8(d) ppm. $^4J(^{31}\text{P}_\text{A}-^{31}\text{P}_\text{X})$ 7.6 Hz. FAB⁺ MS: m/z 858, $[\text{M}-\text{H}]^-$. IR (KBr): 3286s, 3052s, 2975m, 2911m, 2862m, 1585s, 1568s, 1475s, 1435s, 1383s, 1278vs, 1217s, 1186s, 1160s,

1095s, 1062s, 1026s, 999s, 910s, 779m, 749vs, 701s, 620vs, 613vs, 526vs, 513vs, 494vs, 474vs, 441s, 297s, 273s cm^{-1} .

2.1.6. $\text{RuCl}_2(\eta^6\text{-MeC}_6\text{H}_4\text{Pr})\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-P}_{(\text{N})}\}$ **6**

This was prepared in the same way as the rhodium compound **3** using $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-MeC}_6\text{H}_4\text{Pr})\}_2]$ (0.074 g, 0.12 mmol) in THF (1.5 cm^3) and **1** (0.115 g, 0.25 mmol). The red/brown product was collected by suction filtration, dissolved in CH_2Cl_2 (5 cm^3) and filtered through celite to remove some insoluble material. Light petroleum (25 cm^3) was added and the volume was reduced in vacuo to ca. 10 cm^3 . The orange/red product was collected by suction filtration and dried in vacuo. Yield 0.15 g, 83%. Microanalysis: Found (Calc. for $\text{C}_{40}\text{H}_{39}\text{Cl}_2\text{NP}_2\text{Ru}$). C, 62.69 (62.58); H, 5.37 (5.12); N, 1.92 (1.82)%. $^{31}\text{P}\{\text{H}\}$ -NMR (CDCl_3): $\delta(\text{P}_\text{A})$ −21.8(d), $\delta(\text{P}_\text{X})$ 53.1(d) ppm. $^4J(^{31}\text{P}_\text{A}-^{31}\text{P}_\text{X})$ 8.5 Hz. FAB⁺ MS: m/z 768, $[\text{M}+\text{H}]^+$. IR (KBr): 3242s, 3048s, 3033s, 2956s, 2868m, 1585s, 1567s, 1478vs, 1437vs, 1401vs, 1287vs, 1228m, 1183m, 1161vs, 1125s, 1093vs, 1071s, 1056s, 1027vs, 999vs, 925m, 875vs, 783s,

Fig. 2. The X-ray structure of **5**.

Fig. 3. The X-ray structure of **9**.

745vs, 697vs, 612vs, 523vs, 490vs, 472vs, 452s, 430m, 299br cm^{-1} .

2.1.7. $[\text{RuCl}(\eta^6\text{-MeC}_6\text{H}_4\text{Pr})\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-P}_{(N)}\}][\text{BF}_4]$ **7**

Compound **6** (0.114 g, 0.15 mmol) and AgBF_4 (0.029 g, 0.15 mmol) were weighed into a Schlenk tube. The tube was sealed with a septum evacuated then filled with nitrogen. Degassed dichloromethane (5 cm^3) was added and the mixture was stirred for 5 h. AgCl was removed by filtration through a Celite pad and the volume was reduced to ca. 1–2 cm^3 . Addition of diethyl ether (20 cm^3) gave a brown precipitate. The crude product was recrystallised from a minimum of chloroform and the red crystalline material was collected by suction filtration and dried in vacuo. Yield 0.75 g, 62%. Microanalysis: Found (Calc. for $\text{C}_{40}\text{H}_{39}\text{BCl}_2\text{FNP}_2\text{Ru}$). C, 58.94 (58.66); H, 4.96 (4.80); N, 1.77 (1.71)%. $^{31}\text{P}\{\text{H}\}$ -NMR (CDCl_3): $\delta(\text{P}_A)$ 35.4(d), $\delta(\text{P}_X)$ 82.5(d) ppm. $^2J(^{31}\text{P}_A - ^{31}\text{P}_X)$ 78.1 Hz. FAB⁺ MS: m/z 732, $[\text{M}]^+$. IR (KBr): 3283br, 3056m, 2965m, 1625br, 1587vs, 1568vs, 1479vs, 1437vs, 1390s, 1288s, 1231s, 1187s, 1164s, 1097m, 1083m, 1061br, 998s, 915m,

Table 3
Comparative selected bond lengths (Å) and angles (°) for **5**, **9** and **10**

	5	9	10
Bond length (Å)			
M–P(1)	2.3113(11)	2.331(3)	2.440(1)
P(1)–N(1)	1.691(3)	1.681(8)	1.671(3)
N(1)–C(1)	1.423(5)	1.435(13)	1.421(6)
C(1)–C(2)	1.427(6)	1.394(14)	1.406(6)
C(2)–P(2)	1.841(4)	1.823(10)	1.832(5)
M–P(2)	–	2.307(3)	–
M–Cl(1)	2.425(1)	2.382(3)	2.422(1)
M–Cl(2)	2.401(1)	–	2.406(1)
Bond angle (°)			
M–P(1)–N(1)	110.3(1)	115.6(3)	112.1(1)
P(1)–N(1)–C(1)	130.0(3)	127.2(7)	130.1(3)
N(1)–C(1)–C(2)	118.7(4)	120.4(9)	119.2(4)
C(1)–C(2)–P(2)	118.8(3)	117.4(8)	117.9(3)
C(2)–P(2)–M	–	115.1(3)	–
P(2)–M–P(1)	–	85.0(1)	–

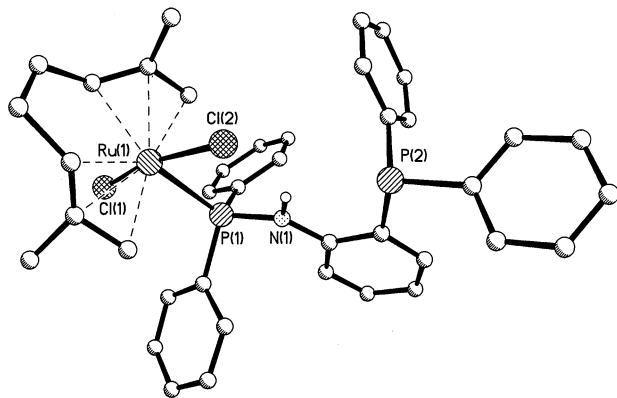
862br, 799vs, 749vs, 696vs, 612vs, 528vs, 476vs, 457s cm^{-1} .

2.1.8. $\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-P}_{(N)}\}$ **8**

This was prepared in the same way as the rhodium compound **3** using $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-C}_6\text{Me}_6)\}_2]$ (0.090 g, 0.13 mmol) in THF (3 cm^3) and **1** (0.126 g, 0.27 mmol). The mixture was stirred for 18 h. The brown solid was collected by suction filtration, dissolved in DCM (5 cm^3) and filtered through celite to remove some black insoluble material. Light petroleum (25 cm^3) was added and the volume was reduced in vacuo to ca. 10 cm^3 . The red product was collected by suction filtration and dried in vacuo. Yield 0.19 g, 90%. Microanalysis: Found (Calc. for $\text{C}_{42}\text{H}_{43}\text{Cl}_2\text{NP}_2\text{Ru}$). C, 63.66 (63.40); H, 5.71 (5.45); N, 1.98 (1.76)%. $^{31}\text{P}\{\text{H}\}$ -NMR (CDCl_3): $\delta(\text{P}_A)$ –24.5(d), $\delta(\text{P}_X)$ 56.7(d) ppm. $^4J(^{31}\text{P}_A - ^{31}\text{P}_X)$ 8.9 Hz. FAB⁺ MS: m/z 760, $[\text{M} - \text{Cl}]^+$. IR (KBr): 3261m, 34051m, 2914br, 1622vs, 1586vs, 1569vs, 1478vs, 1435vs, 1385vs, 1281vs, 1220m, 1184m, 1162m, 1102s, 1090s, 1070vs, 1072vs, 903m, 783s, 744vs, 695s, 620vs, 537vs, 524vs, 490vs, 470vs, 455vs, 436s cm^{-1} .

2.1.9. $[\text{RuCl}(\eta^6\text{-C}_6\text{Me}_6)\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-P}_{(N)}, \text{P}\}][\text{BF}_4]$ **9**

This was prepared in the same way as the ruthenium compound **7** using **8** (0.119 g, 0.15 mmol) and AgBF_4 (0.029 g, 0.15 mmol). The crude product was recrystallised from the minimum of chloroform and the orange crystalline product was collected by suction filtration and dried in vacuo. Yield 0.83 g, 66%. Microanalysis: Found (Calc. for $\text{C}_{42}\text{H}_{43}\text{BCl}_2\text{FP}_2\text{Ru}$). C, 59.77 (59.55); H, 5.47 (5.12); N, 1.60 (1.65)%. $^{31}\text{P}\{\text{H}\}$ -NMR (CDCl_3): $\delta(\text{P}_A)$ 36.3(d), $\delta(\text{P}_X)$ 82.5(d) ppm. $^2J(^{31}\text{P}_A - ^{31}\text{P}_X)$ 73.6 Hz. FAB⁺ MS: m/z 760, $[\text{M}]^+$. IR (KBr): 3299m, 3056m, 1618br, 1587s, 1483vs, 1450vs, 1437vs,

Fig. 4. The X-ray structure of **10**.

1387m, 1316m, 1295s, 1280m, 1232s, 1188m, 1164m, 1096s, 10765br, 914vs, 873s, 801m, 763vs, 747vs, 728s, 699s, 647s, 595m, 538vs, 520vs, 486vs, 458s, 443s, 356br cm^{-1} .

2.1.10. $\text{RuCl}_2(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-P}_{(N)}\}$ **10**

This was prepared in the same way as the rhodium compound **3** using $[\{\text{RuCl}(\mu\text{-Cl})(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\}_2]$ (0.117 g, 0.19 mmol) and **1** (0.175 g, 0.38 mmol) in THF (4 cm^3). The mixture was stirred for 2 h giving a dark yellow solution which was filtered through a small celite plug and precipitated by the slow addition of diethyl ether (40 cm^3). The yellow product was collected by suction filtration and dried in vacuo. Yield 0.222 g, 87%. Microanalysis: Found (Calc. for $\text{C}_{40}\text{H}_{41}\text{Cl}_2\text{NP}_2\text{Ru}$). C, 61.97 (62.42); H, 5.31 (5.37); N, 1.63 (1.82)%. $^{31}\text{P}\{\text{H}\}$ -NMR (CDCl_3): $\delta(\text{P}_A)$ –20.3(d), $\delta(\text{P}_X)$ 34.6(d) ppm. $^2J(^{31}\text{P}_A - ^{31}\text{P}_X)$ 13.2 Hz. FAB⁺ MS: m/z 858, $[\text{M} + \text{H}]^+$. IR (KBr): 3170br, 3050vs, 2912m, 2855m, 1583vs, 1568vs, 1475vs, 1435vs, 1383vs, 1220s, 1089s, 1026vs, 915s, 856m, 785s, 760vs, 749vs, 698s, 611vs, 526vs, 469vs, 420s, 390s, 331m, 310s, 229vs, 224vs cm^{-1} .

2.1.11. $\text{OsCl}_2(\eta^6\text{-MeC}_6\text{H}_4\text{Pr})\{\text{Ph}_2\text{NHPC}_6\text{H}_4\text{PPh}_2\text{-P}_{(N)}\}$ **11**

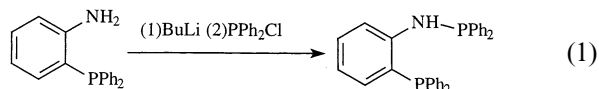
This was prepared in the same way as the rhodium compound **3** using $[\{\text{OsCl}(\mu\text{-Cl})(\eta^6\text{-MeC}_6\text{H}_4\text{Pr})\}_2]$ (0.051 g, 0.065 mmol) in THF (2 cm^3) and **1** (0.060 g, 0.13 mmol). The mixture was stirred for 18 h. Light petroleum (15 cm^3) was added to further precipitate the product. The orange solid was collected by suction filtration and dried in vacuo. Yield 0.10 g, 90%. Microanalysis: Found (Calc. for $\text{C}_{40}\text{H}_{39}\text{Cl}_2\text{NOsP}_2$). C, 56.41 (56.07); H, 4.42 (4.59); N, 1.47 (1.63)%. $^{31}\text{P}\{\text{H}\}$ -NMR (CDCl_3): $\delta(\text{P}_A)$ –21.6(d), $\delta(\text{P}_X)$ 11.4(d) ppm. $^4J(^{31}\text{P}_A - ^{31}\text{P}_X)$ 8.6 Hz. FAB⁺ MS: m/z 734, $[\text{M} - \text{H}]^+$. IR (KBr): 3243m, 3046s, 3026s, 2956s, 1585vs, 1567vs, 1479vs, 1437vs, 1402vs, 1288s, 1183m, 1160s, 1094vs, 1027vs, 924s, 879vs, 745vs, 697vs, 613vs, 525vs, 490vs, 473vs, 451vs, 433s, 399s, 305vs, 279s, 229vs cm^{-1} .

2.2. Crystallography

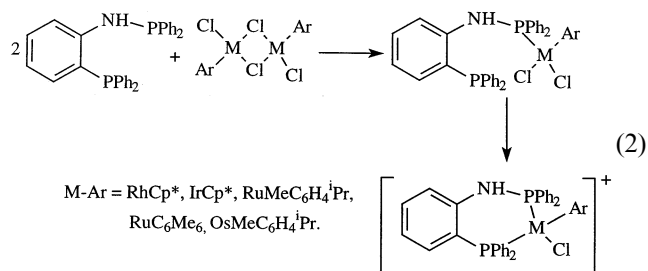
Crystallography was performed using a Siemens SMART diffractometer; full hemisphere of data with 0.3° 'slices', r.t., Mo– K_α radiation and empirical absorption corrections. In **9** the half weight chloroform solvate was refined in two occupancies with 30 and 20% occupancies with the lower occupancy sites being refined isotropically, all of the other non-H atoms were refined anisotropically. In **10** the chirality was established from the Flack parameter [0.02(3)]. All calculations employed the SHELXTL program system [17]. Details of crystal data and refinement for compounds **5**, **9** and **10** are shown in Table 1.

3. Results and discussion

The synthesis of bidentate phosphine ligands with aromatic backbones/spacer groups is well established [18]. However, rather less is known about diphosphines with non-organic backbones. Baker and Pringle have described the preparation of a chiral metal phosphite ligand starting from phosphinolphenol [19]. We have previously described the synthesis of a symmetric bis-phosphine from diamino-toluene [8] and there has been a report on the cyclisation of anilino-phosphine to give 1,2,3-benzadiphosphole [20]. Here we report on the facile synthesis of an unsymmetric diphosphine together with demonstrative organometallic complexes. Thus deprotonation of (2-diphenylphosphino)benzeneamine with BuLi followed by reaction with PPh_2Cl (Eq. 1) in THF gave $\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2$ **1** in a good yield (73%).



The new phosphine gave the expected AX type ^{31}P -NMR and we assign P_A ($\delta = -19.5$ ppm) as the triaryl phosphine [(2-diphenylphosphino)benzeneamine has $\delta = 21$ ppm] and P_X ($\delta = 29.6$ ppm) as the N– PPh_2 group end of the molecule (cf. $\text{MeC}_6\text{H}_4(\text{NHPPH}_2)_2$ which has $\delta = 33.3, 30.4$ ppm). Reaction of **1** with a range of organometallic halo complexes proceeds smoothly (Eq. 2). All of the new complexes gave satisfactory microanalyses, mass spectral data (including isotopomer distributions) and ^{31}P - and ^1H -NMR data. Interestingly, not all of the initial products obtained involve bidentate coordination of **1**. Thus, while bridge cleavage of $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$ gave the anticipated product $[\text{Rh}\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\}(\text{cod})][\text{ClO}_4]$ **2**, the reaction with $[\{\text{RhCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2]$ gave $\{\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{PPh}_2\text{-P}_{(N)}\}\}$ **3**, which only involves coordination via the N– PPh_2 end of the bis-phosphine. Similar results were obtained with $[\{\text{IrCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2]$, $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-MeC}_6\text{H}_4\text{Pr})\}_2]$, $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-C}_6\text{Me}_6)\}_2]$, $[\{\text{RuCl}(\mu\text{-Cl})(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\}_2]$ and $[\{\text{OsCl}(\mu\text{-Cl})(\eta^6\text{-MeC}_6\text{H}_4\text{Pr})\}_2]$. Stirring the monodentate rhodium complex **3** in chloroform for a few hours results in conversion to the corresponding bidentate complex while the other monodentate complexes undergo the analogous conversion (Eq. 2, Fig. 1) when stirred in $\text{MeOH}/\text{CHCl}_3$.



Alternatively, bidentate coordination can be induced by removal of a coordinated chloride using Ag^+ . Selected NMR parameters for the monodentate and bidentate complexes are given in Table 2. We suppose that the monodentate complexes prefer to use the N–PPh₂ phosphine for coordination on simple steric grounds, though we cannot exclude any electronic effects. The observation of initial monodentate coordination supports the idea that these unsymmetrical ligands could be used as ‘hemilabile’ systems.

As part of the characterisation of the new complexes and to further confirm our conclusions about the binding modes we determined the crystal structures of three representative examples (Figs. 2–4). The X-ray structures of **5** and **10** reveal the expected monodentate N–PPh₂ coordination mode while that of **9** confirms bidentate coordination. The M–P bond lengths are in the expected range; interestingly upon chelation M–P(1) appears somewhat shorter than in the monodentate complexes. In **5** and **10** the P(1)–N(1)–C(1)–C(2)–P(2) chains are approximately planar and P(2) adopts a ‘syn’ geometry with respect to P(1)—though this does not appear to be a consequence of any intramolecular interactions. The monodentate systems are quite well preorganised for chelation. Apart from the effect already mentioned and the obvious changes in conformation, chelation has little effect on the bond lengths within the ligand. In **9** the N–H group is hydrogen bonded to the $[\text{BF}_4]^-$ anion [H(1)... F(3) 2.28 Å, N(1)–H(1)...F(3) 156°] (Table 3).

This work clearly illustrates a simple route to unsymmetrical phosphines which have potentially interesting hemilabile behaviour. Further work is in progress.

4. Supplementary material

Crystallographic data for the structural analyses has been deposited with the Cambridge Crystallographic data centre, CCDC No. 103142 for **5**, 103143 for **9** and 103144 for **10**. Copies of this information may be

obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK. (Fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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