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Synthesis and co-ordination chemistry of a novel multifunctional bis-phosphine containing a P–N–Si–N–P backbone

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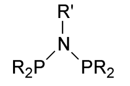
A novel multifunctionalised bidentate phosphine ligand containing the highly unusual P–N–Si–N–P backbone has been synthesized and its co-ordination chemistry studied. The ligand $Ph_2PN(C_5H_4N\text{-}2)Si(Me)_2N(C_5H_4N\text{-}2)PPh_2$, which was characterised crystallographically, forms *cis*-P,P chelate complexes with platinum or palladium. The complexes $MLCl_2$ (M = Pt or Pd) readily hydrolyse under recrystallisation conditions to give chelate complexes $[Pt(Ph_2PNHC_5H_4N\text{-}2\text{-}P,N)_2]Cl_2$. The crystal structure of the platinum complex shows both P,N ligands to chelate to the metal, in contrast to the crystal structure reported previously $[Pt(Ph_2PNHC_5H_4N\text{-}2\text{-}P,N)(Ph_2PNHC_5H_4N\text{-}2\text{-}P)Cl]Cl$. The dimethyl platinum complex $PtLMe_2$ is considerably more stable to hydrolysis, and it was therefore possible to characterise the six membered PtPNSiNP ring system by X-ray crystallography. In addition, evidence is also presented that the ligand and its complexes will react with other phosphorus electrophiles (with N–Si bond cleavage) to generate new compounds.

Introduction

Bidentate phosphine ligands are ubiquitous in co-ordination chemistry and catalysis. Whereas most consist of a carbon based backbone linking the two phosphine moieties, a smaller group of ligands consist of phosphorus atoms linked by an inorganic backbone containing main group and/or transition metals. The co-ordination chemistry of bis(phosphino)amines **1** and their oxidised derivatives has been studied extensively.[1] These ligands exhibit a variety of co-ordination modes and conformations depending on the nature of the metal and reaction conditions. They have also found applications in selective metal extraction, as NMR shift reagents, and in catalysis.[1d–f]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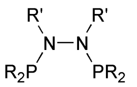
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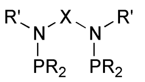
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Bis(phosphino)hydrazine ligands of type **2** can be considered the next member in the series of inorganic backboned ligands.[2,3] Reports of ligands, **3**, which contain three main group atoms linking the phosphorus atoms are very scarce.[4–7] These ligands would form six membered inorganic heterocycles on co-ordination to appropriate metal salts. We envisaged that variation of the heteroatom X could have considerable effects on their steric, electronic and co-ordination properties. As these ligands could provide new applications in both co-ordination chemistry and catalysis, we have begun an investigation into the co-ordination chemistry of this ligand class.

To the best of our knowledge, the only example of a diphosphine ligand containing a PNSiNP bridge is that reported by Verkade and co-workers which contains a hyperco-ordinate silicon atom (Fig. 1).[4] We chose to prepare this type of ligand by reaction of two equivalents of a deprotonated phosphinoamine with dichlorodimethylsilane. The secondary phosphinoamine **4**[8,9] was chosen as starting material as the presence of the pyridine moiety opens up the possibility of bidentate bridging co-ordination modes for its silicon bridged counterpart, **5**. We have recently studied the co-ordination chemistry of $Ph_2PNHC_5H_4N\text{-}2$ **4** in considerable detail;[9] it shows a very strong preference for P,N chelation. Many complexes have been isolated in which the ligand chelates a metal under conditions in which many hemilabile ligands would exhibit η^1 co-ordination. In this paper we report on the preparation and reactivity of the multifunctionalised bidentate phosphine **5** and its metal complexes.

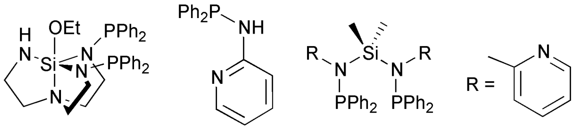
4 **5**

Fig. 1 Bidentate phosphines.

Experimental

General

All manipulations were carried out under an atmosphere of nitrogen, unless stated otherwise. All solvents were either freshly distilled from an appropriate drying agent (THF, Et_2O, DCM) or obtained as anhydrous grade. ^1H and ^{31}P NMR spectra were recorded using a "Varian 2000" 300 MHz spectrometer, IR spectra as KBr discs (prepared in air) on a Perkin-Elmer PE1720 FTIR/RAMAN spectrometer. $Pt(COD)Cl_2$, $Pt(COD)Me_2$, and $Ph_2PNHC_5H_4N\text{-}2$ **4** were prepared by literature methods.[9,10] For simplicity the ligand bis[(diphenylphosphino)(2-pyridyl)amino]dimethylsilane is referred to PNSiNP throughout this section.

Preparations

Bis[(diphenylphosphino)(2-pyridyl)amino]dimethylsilane, or PNSiNP, 5. A stirred solution of 2-(diphenylphosphinoamino)pyridine (1.542 g, 5.54 mmol) in toluene (50 mL) was cooled to −50 °C. Lithium diisopropylamide (2.8 mL of a 2 M solution in heptanes–THF–benzene) was then added dropwise over a couple of minutes. The mixture was then left for 3–4

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hours to warm to room temperature. Dichlorodimethylsilane (0.336 mL, 0.357 g, 2.77 mmol) was added in two portions 30 minutes apart, and left to stir at room temperature for 3–4 hours. The mixture was then left to settle for a short period of time, prior to the filtering off precipitated lithium chloride (using a filter stick). Removal of solvent under vacuum gave a quantitative yield of bis[(diphenylphosphino)(2-pyridyl)-amino]dimethylsilane, **5**. The compound obtained in this way is of 90% purity, and could be used in some of the complexation reactions. Analytically pure, good quality crystals of **5** can be obtained by layering a saturated toluene solution with hexane. Leaving a solution containing 2.0 g of crude ligand at room temperature in a sealed tube gave 182 mg of **5** as large colourless blocks. Found: C, 70.39; H, 5.66; N, 9.10. $C_{36}H_{34}N_4P_2Si$ requires C, 70.57; H, 5.59; N, 9.14%. ν_{max}/cm^{-1} 3052, 1587, 1566, 1480, 1463, 1427, 1294, 1265, 1182, 1155, 1091, 1050, 1027, 993, 934, 904, 815, 777, 742, 695, 515, 470 and 423. δ_P(121.4 MHz; C_6D_6) 40.9 (s). δ_H(300 MHz; C_6D_6) 0.79 (6H, t, *J* 2), 6.44 (2H, d, *J* 8.5), 6.58 (2H, dd, coupling not resolved), 6.98 (2H, m), 7.26 (12H, m), 7.58 (8H, m) and 7.96 (2H, dd, *J* 2.0, 4.9 Hz).

Se(PNSiNP)Se, 6. To a Schlenk tube containing ligand compound **5** (0.105 g, 0.171 mmol, 1 equivalent) and elemental selenium (0.027 g, 3.43 mmol, 2 equivalents) was added toluene (5 mL). The mixture was heated to 80 °C for one hour. ^{31}P NMR spectroscopy of this solution confirmed quantitative conversion into the diselenide, **6**. Removal of solvent and washing with Et_2O gave the pure compound as a white powder. Found: C, 56.11; H, 4.46; N, 7.21. $C_{36}H_{34}N_4P_2Se_2Si$ requires C, 56.24; H, 5.15; N, 6.40%. δ_P(121.4 MHz; C_6D_6) 47.6 (s + satellites, $^1J_{P\text{-}Se}$ = 778 Hz). ^{1}H NMR identical to "free" ligand.

Pt(PNSiNP)Cl$_2$, 7. To a Schlenk tube containing ligand compound **5** (0.099 g, 0.162 mmol, 1 equivalent) and Pt(COD)-Cl_2 (0.060 g, 0.162 mmol, 1 equivalent) was added DCM (5 mL). The reaction was stirred for one hour. Removal of solvent to near dryness and washing with Et_2O (2 × 10 mL) gave the pure compound as a white powder in essentially quantitative yield. Found: C, 49.28; H, 3.67; N, 6.73. $C_{36}H_{34}Cl_2$-N_4P_2SiPt requires C, 49.21; H, 3.90; N, 6.38%. ν_{max}/cm^{-1} 1596 (C=N), 1575 (aromatic C=C), 318, 305 (*cis*-Pt–Cl). δ_P(121.4 MHz; $CDCl_3$) 42.3 (s + satellites, $^1J_{P\text{-}Pt}$ = 3902 Hz). δ_H(300 MHz; C_6D_6) 0.40 (6H, s), 6.43 (2H, d, *J* 8.0), 6.81 (2H, dd, 7.3, *J* 4.8), 7.16 (2H, td, *J* 1.9, 5.8), 7.24–7.38 (12H, m), 7.88 (8H, m) and 8.11 (2H, dd, *J* 1.9, 4.9 Hz). On recrystallisation this compound hydrolysed to give good quality crystals of $Pt(Ph_2PNHC_5H_4N\text{-}2)_2Cl_2$ **9**: ν_{max}/cm^{-1} 3412, (NH), 1617 (coord. CN) and 1575 (aromatic C=C). δ_P(121.4 MHz; $CDCl_3$) 51.4 (s, br + satellites, $^1J_{P\text{-}Pt}$ = 3576 Hz).

Pd(PNSiNP)Cl$_2$, 8. To a Schlenk tube containing ligand **5** (0.028 g, 0.046 mmol, 1 equivalent) and Pd(COD)Cl_2 (0.060 g, 0.046 mmol, 1 equivalent) was added DCM (5 mL). Treatment as above gave the pure compound as a white powder. Found: C, 55.26; H, 4.13; N, 7.54. $C_{36}H_{34}Cl_2N_4P_2PdSi$ requires C, 54.73; H, 4.34; N, 7.09%. ν_{max}/cm^{-1} 1597 (C=N) and 1573 (aromatic C=C). δ_P(121.4 MHz; $CDCl_3$) 64.44 (s). δ_H(300 MHz; C_6D_6) 0.40 (6H, s), 6.43 (2H, d, *J* 8.0), 6.81 (2H, dd, *J* 7.3, 4.8 Hz), 7.16–7.6 (20H, m) and 8.11 (2H, m).

Pt(PNSiNP)Me$_2$, 10. To a Schlenk tube containing ligand **5** (0.289 g, 0.472 mmol, 1 equivalent) and Pt(COD)Me_2 (0.149 g, 0.472 mmol, 1 equivalent) was added DCM (5 mL). Treatment as above gave the pure compound as a white powder in near quantitative yield. This compound stubbornly refused to yield acceptable chemical analysis, probably due to traces of COD being present. Recrystallisation by layering a DCM solution of **10** with hexane gives a few crystals. It has been characterised by X-ray crystallography and spectroscopy. ν_{max}/cm^{-1} 1610, 1584 (C=N) and 1567 (aromatic C=C). δ_P(121.4 MHz; CD_2Cl_2–C_6D_6) 63.9 (s + satellites, $^1J_{P\text{-}Pt}$ = 1986 Hz). δ_H(300 MHz; C_6D_6) 0.18 (m with platinum satellites, ^2J = 72), 0.48 (6H, s), 6.55 (2H, d, *J* 8.0), 6.75 (2H, dd, *J* 7.3, 4.8), 7.15–7.70 (22H, m) and 8.11 (2H, dd, *J* 1.9, 4.9). (ES+ mass spectrum, cone voltage 90 V): *m*/*z* 860.2051 [(M + Na)$^+$ requires 860.2043] and 822.1911 [(M − CH_3)$^+$ requires 822.1906].

2-(Ph$_2$P)$_2$NC$_5$H$_4$N, 11. Chlorodiphenylphosphine (0.033 mL, 0.040 g, 0.133 mmol) was added to a DCM (2mL) solution of ligand **5** (112 mg, 0.183 mmol). After one hour the ^{31}P NMR spectrum was recorded. This confirmed that quantitative conversion into ligand **11** had taken place. δ_P(121.4 MHz; CH_2Cl_2–C_6D_6) 59.9 (s) (lit.[11] 59.9). Mass spectrum (EI): *m*/*z* 461 (M$^+$) (lit.[11] 461).

X-Ray crystallography

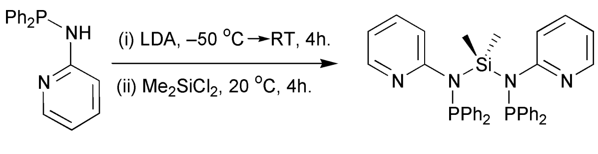
Crystal structures were obtained at 298 K using a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Intensity data were collected using 0.3 or 0.15° width ω steps accumulating area detector frames spanning a hemisphere of reciprocal space for all structures. All data were corrected for Lorentz, polarisation and long term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections. Structures were solved by direct methods and refined by full-matrix least squares against F^2 (SHELXTL)[12] for all data with $I > 2\sigma(I)$. Crystal data are summerised in Table 1.

CCDC reference numbers 154169–154171.

See http://www.rsc.org/suppdata/dt/b0/b009722p/ for crystallographic data in CIF or other electronic format.

Results and discussion

Ligand **5** can be prepared by deprotonation of **4** using ^{n}BuLi as base, followed by dropwise addition of Me_2SiCl_2. However, the use of lithium diisopropylamide (LDA) as base results in product of greater purity (Scheme 1). It is also important to allow sufficient reaction time after addition of Me_2SiCl_2, as after 1–3 hours the product is contaminated with two other phosphorus containing impurities which we assume to be $2\text{-}Ph_2PN(Li)C_5H_4N\text{-}2$ and $Ph_2P(C_5H_4N)NSi(Me)_2Cl$. Analytically pure crystals of **5** were obtained by recrystallisation (toluene–hexane) under strictly anaerobic conditions.



4 **5**

Scheme 1

The molecular structure of ligand **5** is shown in Fig. 2. The structure confirms the exact identity and gives us information regarding the P–N–Si–N–P chain, in which the pyridine moieties adopt a staggered conformation with respect to each other. The P–N bond lengths (1.724(2) and 1.7224(14) Å) are fairly typical of a P–N single bond, although they are longer than those found in $Ph_2PNHC_5H_4N\text{-}2$ (1.705(3) Å). The nitrogen atoms, N(1) and N(2), are entirely planar (sum of angles about N(1) and N(2) = 359.75 and 359.98° respectively) as is commonplace in diphenylphosphinoamines. The C–N bonds between the aromatic carbons of the pyridine group and phosphorus bound nitrogen atoms are 1.420(2) and 1.423(2) Å, and are longer than those in $Ph_2PNHC_5H_4N\text{-}2$ (1.329(4) Å). The longer P–N and C–N bond lengths found in ligand **5** may reflect the presence of the Me_2Si group as the nitrogen lone pair will be

Table 1 Crystal data for compounds **5**, **9** and **10**

	5	**9**	**10**
Empirical formula	$C_{36}H_{34}N_4P_2Si$	$C_{35}H_{31}Cl_5N_4P_2Pt$	$C_{28}H_{40}N_4P_2PtSi$
M	612.70	941.92	837.86
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1$	$P\bar{1}$	$P2_1/n$
a/Å	10.39310(10)	10.0529(2)	12.5811(2)
b/Å	13.8309(2)	15.5961(6)	18.3389(3)
c/Å	11.72530(10)	16.3639(3)	15.4399(3)
α/°		101.805(2)	
β/°	105.9710(10)	105.754(2)	90.8350(10)
γ/°		95.934(2)	
U/Å	1620.41(3)	2385.37(11)	3561.97(11)
Z	2	2	4
μ/mm^{-1}	0.203	3.313	4.096
Reflections measured	10133	14884	15304
Independent reflections	4629	6838	5072
Final *R*1, *wR*2[$I > 2\sigma(I)$]	0.0237, 0.0582	0.0928, 0.2508	0.0259, 0.0517

Table 2 Selected bond lengths (Å) and angles (°) for compound **5**

P(1)–N(1)	1.724(2)	P(1)–N(2)	1.7224(14)
Si(1)–N(1)	1.7754(14)	Si(1)–N(2)	1.769(2)
Si(1)–C(37)	1.862(2)	Si(1)–C(38)	1.865(2)
N(1)–C(13)	1.420(2)	N(2)–C(31)	1.423(2)
C(13)–N(14)	1.330(2)	C(31)–N(32)	1.330(2)
N(2)–Si(1)–N(2)	116.88(8)	C(37)–Si(1)–C(38)	105.06(12)
P(1)–N(1)–Si(1)	117.48(8)	P(2)–N(2)–Si(1)	119.48(9)
C(13)–N(1)–P(1)	124.15(12)	C(31)–N(2)–P(2)	123.79(13)

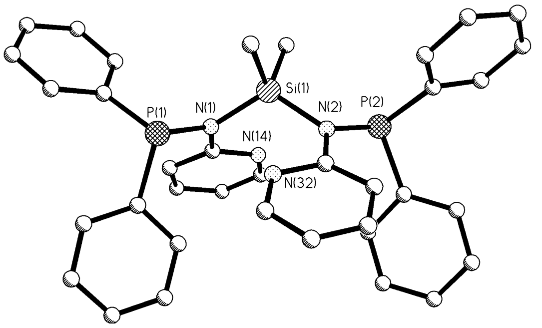
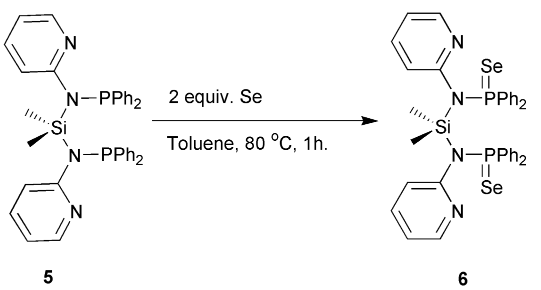


Fig. 2 The crystal structure of compound **5**.

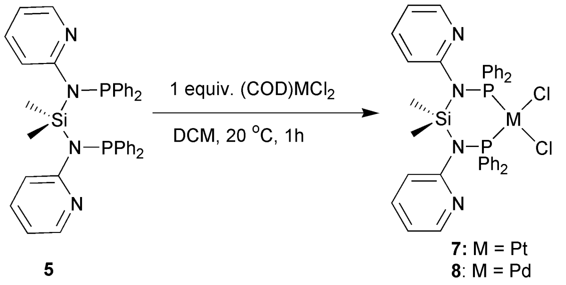
less available to strengthen the P–N and C–N bonds. It is thought that silylated amines have much lower basicity than their parent amines. Other selected bond lengths and angles are found in Table 2.

Heating a toluene solution of ligand **5** with two equivalents of elemental selenium gave the diselenide, **6** (Scheme 2). The ^{31}P NMR spectrum shows the expected singlet with selenium satellites. The magnitude of $^1J\{^{31}P–^{77}Se\}$(778 Hz) is typical of a diphenylphosphinoamine selenide ($^1J\{^{31}P–^{77}Se\}$ for $Ph_2P(Se)$-$NHP(Se)Ph_2$ = 793 Hz).[13]



Scheme 2

Ligand **5** reacts with the well known precursor $Pt(COD)Cl_2$ to generate the dichloroplatinum(II) complex **7**, which contains an unusual PNSiNPPt heterocycle (Scheme 3). The phosphorus NMR spectrum shows a single line with platinum satellites (*δ* 42.3, $^1J\{^{31}P–^{195}Pt\}$ = 3902 Hz). This coupling constant is fully consistent with a bidentate phosphine bound *trans* to chloride ligands, although somewhat larger than that found for $Pt(dppe)Cl_2$ ($^1J\{^{31}P–^{195}Pt\}$ = 3620 Hz)[14] or $Pt(dppp)Cl_2$ ($^1J\{^{31}P–^{195}Pt\}$ = 3406 Hz).[15] Addition of two equivalents $Pt(COD)Cl_2$ to the ligand does not generate the bimetallic compound $Cl_2Pt(\mathbf{5})PtCl_2$ as we might have expected given the strong preference that **4** shows for P,N chelation. Reaction with $Pd(COD)Cl_2$ gave the analogous palladium complex **8**.



Scheme 3

The position of *ν*(C=N) in the IR spectrum has been found to be diagnostic in assigning bidentate or monodentate co-ordination for ligand **4**. We have previously found that on pyridine co-ordination the position of *ν*(C=N) moves to higher wavenumber by about 20–35 cm^{-1}. The fact that the position of *ν*(C=N) for **7** and **8** is in a fairly similar position to that of the "free" ligand (1596 *vs.* 1597 cm^{-1}) suggests that the pyridine moieties are not co-ordinated. It is also well known that Pt–Cl stretching frequencies can be observed at around 300 cm^{-1} in the infrared spectrum of *cis*-dichloroplatinum complexes. Complex **7** shows two sharp bands at 318 and 305 cm^{-1} in its IR spectrum, which is also consistent with its structure (IR of *cis*-$Pt(dppp)Cl_2$ 309, 288 cm^{-1}).[15]

Attempts to obtain crystals of complex **7** suitable for X-ray diffraction by recrystallisation (CH_2Cl_2–Et_2O, slow diffusion) yielded the hydrolysed product, $Pt(Ph_2PNHC_5H_4N\text{-}2)_2Cl_2$, **9** (Scheme 4). Interestingly, the crystal structure of **9** shows both P,N ligands chelating to the platinum centre, with the two chloride ions located outside the co-ordination sphere. We have previously prepared $Pt(Ph_2PNHC_5H_4N\text{-}2)_2Cl_2$ by more conventional means. The compound gave a single broadened resonance in its phosphorus NMR spectrum (*δ* 51.4, $^1J\{^{31}P\text{-}^{195}Pt\}$ = 3576 Hz). The structure we previously obtained revealed one monodentate ligand and one chelating ligand to

Table 3 Selected bond lengths (Å) and angles (°) for complex **9**

Pt(1)–N(14)	2.126(11)	Pt(1)–N(32)	2.143(12)
Pt(1)–P(1)	2.231(3)	Pt(1)–P(2)	2.233(4)
P(1)–N(1)	1.690(8)	P(2)–N(2)	1.667(9)
N(14)–Pt(1)–N(32)	99.5(4)	P(1)–Pt(1)–P(2)	101.50(12)
N(14)–Pt(1)–P(1)	79.6(3)	N(32)–Pt(1)–P(2)	79.6(3)

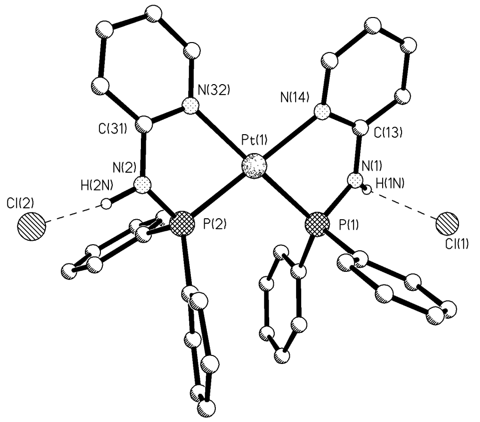
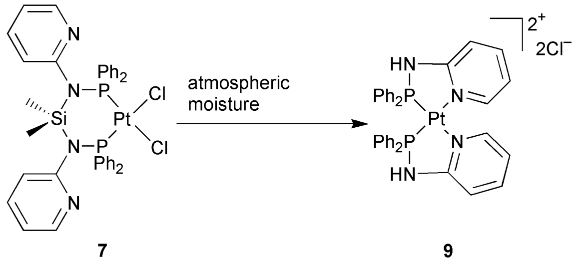


Fig. 3 The crystal structure of complex **9**.



Scheme 4

be present. This did not tie up with the single phosphorus environment indicated by NMR. The crystal structure we have now obtained explains the broadened resonance in the NMR spectra, as both bis(chelate) and mono(chelate) forms presumably interconvert in solution. The IR spectrum of each of the two sets of crystals is also consistent with the structures obtained (mono-chelate, ν(C=N) 1620 and 1600; bis-chelate, ν(C=N) 1617 cm^{-1}). The platinum–chloride stretching vibrations, which we observed in the IR spectrum of complex **7**, are not present for the crystals of **9**, although they are replaced by a weak, broad band at 329 cm^{-1}.

The molecular structure of complex **9** (shown in Fig. 3) shows the platinum centre to be square planar and confirms that a bis-chelate species is formed. As has been found in other crystal structures of $Ph_2PNHC_5H_4N$-2, the chloride counter ions form a hydrogen bond with the ligand NH functionality (H1N–Cl(1) 2.39(3) Å, N(1)–Cl(1) 3.082(9) and H2N–Cl(2) 2.181(12), N(2)–Cl(2) 3.103(9) Å). As the refinement of this structure was hampered by the presence of disordered solvent molecules, and the possibility of the presence of small amounts of a neutral deprotonated species,[9] we have not drawn accurate quantitative information from the bond lengths and angles (Table 3). However, there are some general features worth noting. The crystallographic bite angle of this ligand is around 80°, and the P–N bond lengths (1.690(8), 1.667(9) Å) may be shorter than those observed in the "free" ligand (1.705(3) Å). This has been observed in other chelate structures of this ligand.

The palladium complex also decomposed to $Pd(Ph_2PNHC_5H_4N\text{-}2)_2Cl_2$ under recrystallisation conditions. Hence both ligand **5** and its dichloroplatinum and palladium complexes are very susceptible to hydrolysis by atmospheric moisture. We considered that the strong preference for P,N chelation found in ligand **4** may be assisting the hydrolysis of complexes of **5**. It was hoped that if we removed the possibility for P,N chelation a metal complex with considerably greater stability might result. This would enable us structurally to characterise a MPNSiNP ring system. We therefore decided to prepare the dimethylplatinum complex of ligand **5**. Addition of **5** to $Pt(COD)Me_2$ results in the expected complex **10** (Scheme 5).

Table 4 Selected bond lengths (Å) and angles (°) for complex **10**

Pt(1)–C(40)	2.089(5)	Pt(1)–C(39)	2.101(5)
Pt(1)–P(2)	2.2892(12)	Pt(1)–P(1)	2.2961(12)
P(1)–N(1)	1.709(4)	P(2)–N(2)	1.713(4)
N(1)–Si(1)	1.773(4)	N(2)–Si(1)	1.785(4)
N(2)–C(31)	1.422(6)	N(1)–C(13)	1.435(6)
C(40)–Pt(1)–C(39)	83.7(2)	P(1)–Pt(1)–P(2)	95.24(4)
C(39)–Pt(1)–P(1)	91.2(2)	C(40)–Pt(1)–P(2)	90.0(2)
P(1)–N(1)–Si(1)	119.3(2)	P(2)–N(2)–Si(1)	118.6(2)
C(13)–N(1)–P(1)	122.0(3)	C(31)–N(2)–P(2)	121.7(3)
C(13)–N(1)–Si(1)	118.5(3)	C(31)–N(2)–Si(1)	118.0(3)
N(1)–Si(1)–N(2)	107.7(2)	C(37)–Si(1)–C(38)	110.1(2)

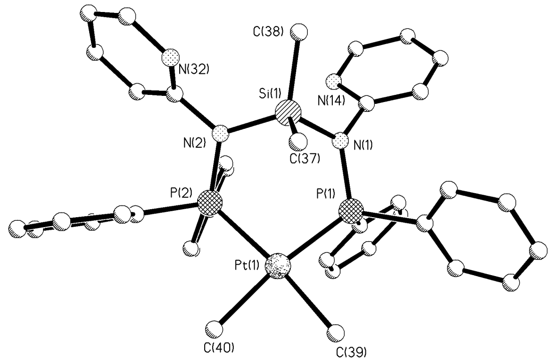
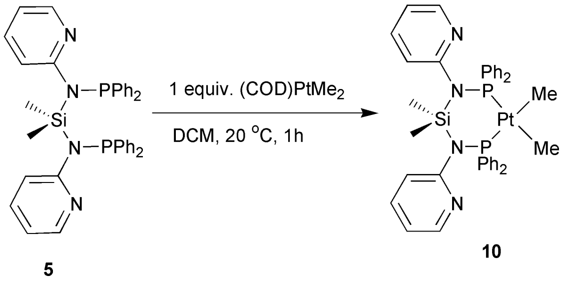


Fig. 4 The crystal structure of complex **10**.



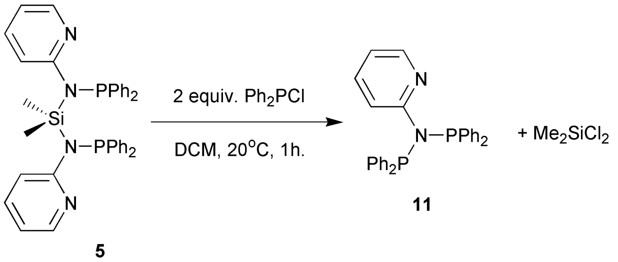
Scheme 5

The size of $^1J_{P\text{-}Pt}$ in the phosphorus NMR spectrum (δ 63.9 ppm, $^1J\{^{31}P–^{195}Pt\}$ = 1986 Hz) is typical of a bidentate phosphine bound *trans* to methyl ligands, and reflects the high *trans* influence of the σ-bonded carbon ligands. This complex is significantly less susceptible to hydrolysis compared to the compounds described above. In fact, addition of 50% aqueous THF to a DCM solution of **10** results in no decomposition even after 24 hours. This suggests that chloride and/or the potential for P,N chelation do play a part in the decomposition of complexes **8** and **9**.

Recrystallisation of complex **10** from CH_2Cl_2–Et_2O gave crystals suitable for X-ray diffraction. The structure (Fig. 4 and Table 4) clearly shows the Pt–P–N–Si–N–P ring system which adopts a puckered 'boat' conformation with the silane moiety located 1.96(1) Å from the Pt(1)–P(1)–P(2)–C(39)–C(40) plane. The metal centre is essentially square planar, but with some deviations from idealised geometry. The angle between the two methyl ligands (C(40)–Pt(1)–C(39) 83.7(2)°) is contracted from the ideal 90°. This is also observed in the related complex (also a six membered platinacycle containing methyl ligands) *cis*-[(η^6-

$Ph_2P(CH_2)_3P(Ph)CH_2Ph)Cr(CO)_3)]PtMe_2$, in which the angle between methyl ligands is 83.7°.[16] This angle reflects the steric demands of the diphosphine ligands. The angle between phosphine groups is larger than 90° (P(2)–Pt(1)–P(2) 95.24(4)°), but similar to that found in the chromium complex (95.94(4)°). The Pt–P bond lengths (2.2892(12) and 2.2961(12) Å) are typical of a dimethylplatinum complex, and are longer than those found in dichloroplatinum complexes (in *cis*-$[PtCl(Ph_2PNHC_5H_4N$-2-*P*,*N*)$(Ph_2PNHC_5H_4N$-2-*P*)]Cl the Pt–P bond *trans* to chloride is 2.219(2) Å). This reflects the stronger *trans* influence of the methyl ligands. The methyl ligands found in complex **10** (Pt(1)–C(39) 2.101(5), Pt(1)–C(40) 2.089(5)) are shorter than in the related structures *cis*-$[(\eta^6\text{-}Ph_2P(CH_2)_3P(Ph)CH_2Ph)Cr(CO)_3]$-$PtMe_2$ (2.130(5) and 2.162(6) Å) and *cis*-$[Pt(Ph_2MeP)_2Me_2]$ (2.122(6) and 2.119(5) Å),[17] which may reflect that ligand **5** does not exert a very strong *trans* influence. There is a slight contraction in P–N bond length on complexation [P(1)–N(1) 1.709(4), P(2)–N(2) 1.713(4) compared to 1.724(2) and 1.7224(14) Å in the "free" ligand], which suggests that some donation of charge from the nitrogen lone pair through phosphorus may in fact be occurring. The P–N bond lengths are shorter still in complexes of $Ph_2PNHC_5H_4N$-2 (1.686(6) and 1.689(7) Å in *cis*-[PtCl-$(Ph_2PNHC_5H_4N$-2-*P*,*N*)$(Ph_2PNHC_5H_4N$-2-*P*)]Cl). The Si–N bond lengths are very similar in both the co-ordinated and free PNSiNP backbone. The angles about silicon have changed on metallocycle formation. N(1)–Si(1)–N(2) has contracted from 116.88(8) to 107.7(2)° due to the constraints imposed by the six membered ring.

We also made attempts at preparing metal complexes of compound **5** from other well known starting materials such as $[RhCp^*Cl_2]_2$, $[Rh(COD)Cl]_2$, $Mo(c\text{-}C_5H_{11}N)_2(CO)_4$, and $Pt(dppe)Cl_2$–$AgClO_4$. In each case at least some (or complete) hydrolysis of the N–Si bonds was found to occur. These reactions are not described here for reasons of brevity. It was hoped that we could use the labile nature of the Si–N bonds to our advantage by treating complexes of **5** with electrophiles to generate new and unusual complexes. To demonstrate the viability of this approach we treated ligand **5** with Ph_2PCl, and found that the ligand reacts quantitatively at room temperature to give the diphosphine **11** (Scheme 6).



Scheme 6

Reaction of complex **10** with *cis*-$Pt(Ph_2PCl)_2Cl_2$ did not occur cleanly, but there is evidence that the desired bridged product was detected in about 40% conversion. We suggest that structure, *cis*-$[Me_2Pt\{\mu\text{-}Ph_2PN(C_5H_4N\text{-}2)PPh_2\}_2PtCl_2]$, which contains an eight membered PtPNPPtPNP ring, is the most likely compound that fits the ^{31}P NMR data observed (δ_P 65.2, $^2J\{^{31}P–^{31}P\} = 17.8$, $^1J\{^{195}Pt–^{31}P\} = 1893$; 50.9, $^2J\{^{31}P–^{31}P\} = 17.8$, $^1J\{^{195}Pt–^{31}P\} = 4645$ Hz). We have made several further unsuccessful attempts at this type of reaction, and reaction conditions are clearly critical to the success of this type of transformation. Further studies are in progress.

Conclusion

We have prepared a novel PNSiNP backboned diphosphine ligand and shown it to act as a bidentate ligand for platinum and palladium complexes. If the complexes contain chloride ligands hydrolysis of the M–P–N–Si–N–P ring is facile with resulting formation of a strong P, N five membered chelate ring. It remains to be seen whether unfunctionalised P–N–Si–N–P backboned ligands would exhibit greater stability. The M–P–N–Si–N–P ring is considerably more stable in Pt(PNSiNP)-Me_2, and could be characterised crystallographically. This structure suggests that this type of ligand may ideally chelate to a metal with a larger valence angle than 90°, and that the ligand may exert a slightly smaller *trans* labilising effect than those of carbon backbone ligands. The reactivity of this type of backbone suggests that these types of ligand are not suitable stabilising ligands for catalysis and organometallic chemistry, although the easily cleaved N–Si–N linkage may well be exploitable in the synthesis of multimetallics and co-ordination chemistry.

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