Reactivity of Group 10 halides toward $(Ph_2PN{=})C(Ph)[N(SiMe_3)_2]$, $(NC_5H_4)\{(Ph_2PN{=})C[N(SiMe_3)_2]\}$-4 and $C_6H_4\{C({=}NPPh_2)[N(SiMe_3)_2]\}_2$-1,4 †

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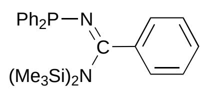
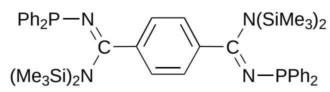
Interaction of $[NiBr_2(dme)]$ (dme = 1,2-dimethoxyethane) with 1 equivalent of $(Ph_2PN{=})C(Ph)[N(SiMe_3)_2]$ **L[1]** in tetrahydrofuran gave *cis*-$[NiBr_2\{(Ph_2PNH)C(Ph)({=}NH)\}]$ **1**, metathesis of this compound with excess NH_4BF_4 in methanol gave *cis*-$[Ni\{(Ph_2PNH)C(Ph)({=}NH)\}_2][BF_4]_2$ **2**. Reaction of $[NiBr_2(dme)]$ with 1 equivalent of $(NC_5H_4)\{Ph_2PN{=})C[N(SiMe_3)_2]\}$-4 L[3] followed by metathesis with excess NH_4BF_4 in methanol gave *cis*-$[Ni\{(NC_5H_4)[(Ph_2PNH)C({=}NH)]\text{-}4\}_2][BF_4]_2$ **3**. Reaction of $[PdCl_2(PhCN)_2]$ with 1 equivalent of L[1] in acetonitrile gave *cis*-$[PdCl_2\{(Ph_2PNH)C(Ph)({=}NH)\}]$ **4**, and with 0.5 equivalent of $C_6H_4\{C({=}NPPh_2)[N(SiMe_3)_2]\}_2$-1,4 **L[2]** in tetrahydrofuran gave *cis*-$[(PdCl_2)_2\{C_6H_4[C({=}NPPh_2)\{N(SiMe_3)_2\}]_2\text{-}1,4\}]$ **5** and *cis*-$[(PdCl_2)_2\{C_6H_4[C(NHPPh_2)({=}NH)]_2\text{-}1,4\}]$ **6**. Interaction of $[PdCl_2(PhCN)_2]$ with L[3] in 1:1 and 3:2 molar ratios gave *cis*-$[PdCl_2\{(NC_5H_4)[(Ph_2PNH)C({=}NH)]\text{-}4\}]$ **7** and *trans*-$[PdCl_2\{$*cis*-$PdCl_2[(NC_5H_4)\{(Ph_2PNH)C({=}NH)\}\text{-}4]\}_2]$ **8**, respectively. Reaction of $[MCl_2(PhCN)_2]$ (M = Pd or Pt) with 2 equivalents of L[3] followed by metathesis with excess NH_4BF_4 in methanol gave *cis*-$[M\{(NC_5H_4)[(Ph_2PNH)C({=}NH)]\text{-}4\}\{(NC_5H_4)[(Ph_2PNH)C({=}N)]\text{-}4\}][BF_4]$ (Pd **9** or Pt **10**). Crystal structures of compounds **1**, **4**, **7**, **8**, **9** and **10** have been determined.

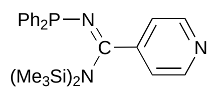
We have been interested in the preparation and the chemistry of phosphorus–nitrogen ligands as they are hemilabile ligands capable of exhibiting unusual co-ordination chemistry towards transition metals. Recently we have reported on the co-ordination chemistry of $(Ph_2PN{=})C(Ph)[N(SiMe_3)_2]$ **L[1]** and $C_6H_4\{C({=}NPPh_2)[N(SiMe_3)_2]\}_2$-1,4 **L[2]** towards $[RuCl_2(PPh_3)_3]$,[1] $[PdCl_2(PhCN)_2]$[2] and Group 6 metal carbonyl complexes.[3] Herein we report the detailed study of the reactions of Group 10 halide complexes with **L[1]**, **L[2]** and $(NC_5H_4)\{(Ph_2PN{=})C[N(SiMe_3)_2]\}$-4 **L[3]**.



L[1]



L[2]



L[3]

Results and Discussion

Preparation of $(NC_5H_4)\{(Ph_2PN{=})C[N(SiMe_3)_2]\}$-4 L[3]

The compound $(NC_5H_4)\{(Ph_2PN{=})C[N(SiMe_3)_2]\}$-4 **L[3]** was prepared in high yield (90%) as yellow crystals by reacting 4-cyanopyridine with 1 equivalent of $Li[N(SiMe_3)_2]$ followed by 1 equivalent of Ph_2PCl in tetrahydrofuran (thf). In $CDCl_3$, the ^{31}P-$\{^1H\}$ NMR spectrum of L[3] exhibited a singlet at δ 36.5 for the PPh_2 group. In addition to the phenyl and pyridinyl carbons and protons, L[3] exhibited a doublet and a singlet at δ 167.9 (J_{P-NC} = 26.7 Hz) and 2.7 for the C=N and the trimethylsilyl carbons, respectively, in the ^{13}C-$\{^1H\}$ NMR spectrum; and a singlet at δ 0.06 for the trimethylsilyl protons in the ^1H NMR spectrum. The low-resolution mass spectrum [fast atom bombardment (FAB), positive ion mode] of L[3] exhibited a peak (M + 1) at m/z 450.

Preparation of *cis*-$[NiBr_2\{(Ph_2PNH)C(Ph)({=}NH)\}]$ 1

The reaction of $[NiBr_2(dme)]$ (dme = 1,2-dimethoxyethane) with 1 equivalent of L[1] in refluxing tetrahydrofuran for 8 h gave red crystals of stoichiometry $C_{19}H_{17}Br_2N_2NiP$ **1** in good yield (76%). The IR spectrum of complex **1** exhibited an absorption at 3273 cm^{-1} indicating the presence of NH groups. The ^{31}P-$\{^1H\}$ NMR spectrum in $CDCl_3$ exhibited a singlet at δ 76.1 for the PPh_2 group. The positive increase in chemical shift from δ 36.5 for the free ligand to δ 76.1 for the co-ordinated ligand is characteristic of chelating ring formation.[4] In addition to the phenyl and pyridinyl protons, the ^1H NMR spectrum also exhibited two broad singlets of relative intensity 1:1 at δ 5.48 and 7.31 for the two non-equivalent NH protons. Based on the above data, compound **1** can be formulated as *cis*-$[NiBr_2\{(Ph_2PNH)C(Ph)({=}NH)\}]$. This was confirmed by an X-ray diffraction study.

Suitable crystals of compound **1** were grown by slow evaporation of a saturated solution of **1** in dichloromethane. A perspective drawing of **1** is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. The structure is consistent with the spectroscopic data. The nickel atom adopts a square-planar geometry with a *cis*-$NiBr_2$ configuration. The bond angles around Ni range from 84.3(2) to 94.9(1)° and sum up to approximately 360°. The Ni–Br(1) and Ni–Br(2) distances are 2.357(1) and 2.310(1) Å, respectively. The $\{(Ph_2PNH)C(Ph)({=}NH)\}$ moiety acts as a chelating ligand with the imino [N(2)] and phosphino P groups co-ordinated to the nickel forming a five-membered ring. Within the bidentate iminophosphine ligand, the P–N(1) bond length of 1.705(5) Å is in the normal range for a phosphorus–nitrogen single bond. The C(1)–N(1) and C(1)–N(2) distances of 1.357(8) and 1.288(7) Å, respectively, are intermediate between those expected for single (1.46 Å) and double (1.26 Å) bonds indicating some delocalization about the N–C–N framework. The delocalization is also reflected in the P–N(1)–C(1) bond angle

† This paper is dedicated to the late Professor Sir Geoffrey Wilkinson whom I valued very much as a good teacher as well as a good friend. I shall miss him.

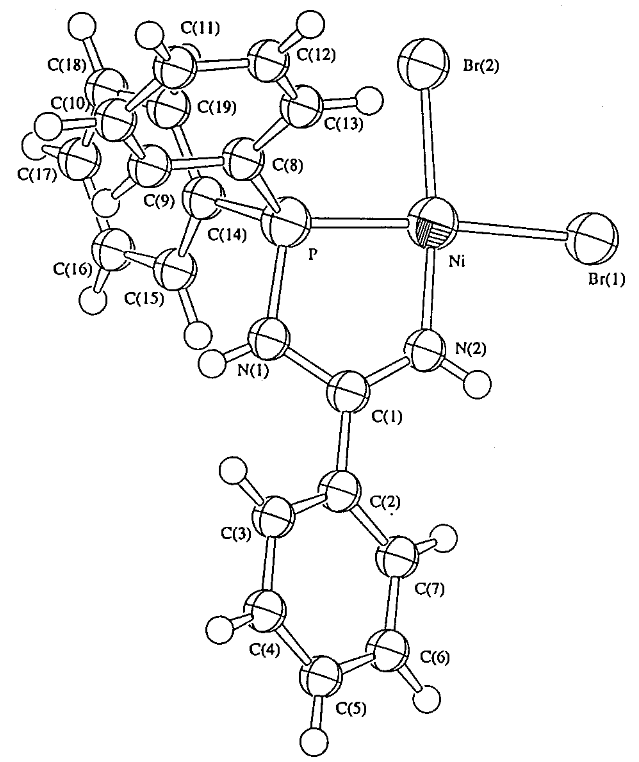


Fig. 1 Perspective view of the molecular structure of compound **1**

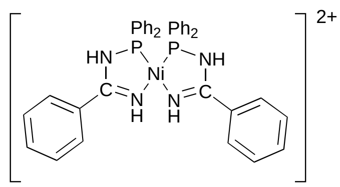
Table 1 Selected bond lengths (Å) and angles (°) for compounds **1** and **4**

Compound **1**		Compound **4**	
Ni–P	2.130(2)	Pd–P	2.1871(3)
Ni–N(2)	1.860(5)	Pd–N(2)	2.016(5)
Ni–Br(1)	2.357(1)	Pd–Cl(1)	2.3049(2)
Ni–Br(2)	2.310(1)	Pd–Cl(2)	2.3633(3)
P–N(1)	1.705(5)	P–N(1)	1.692(5)
N(1)–C(1)	1.357(8)	N(1)–C(1)	1.372(7)
N(2)–C(1)	1.288(7)	N(2)–C(1)	1.293(7)
P–Ni–N(2)	84.3(2)	P–Pd–N(2)	82.6(1)
P–Ni–Br(2)	88.6(1)	P–Pd–Cl(1)	90.93(1)
Br(1)–Ni–Br(2)	94.9(1)	Cl(1)–Pd–Cl(2)	94.17(1)
Br(1)–Ni–N(2)	92.3(2)	Cl(2)–Pd–N(2)	92.3(1)
P–N(1)–C(1)	115.2(4)	P–N(1)–C(1)	116.7(4)

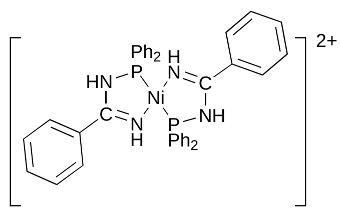
of 115.2(4)° which is intermediate between those expected of sp^2 and sp^3 nitrogen atoms. Similar observations have been reported for related chromium,[5] platinum[6] and rhodium complexes.[6]

Preparation of *cis*-[Ni{(Ph$_2$PNH)C(Ph)(=NH)}$_2$][BF$_4$]$_2$ 2

Metathesis of complex **1** with excess NH_4BF_4 in methanol gave yellow crystals of stoichiometry $C_{38}H_{34}B_2F_8N_4NiP_2$ **2** in moderate yield (47%). The IR spectrum of **2** exhibits an absorption at 3429 cm^{-1} indicating the presence of NH groups. The ^{31}P-{^{1}H} NMR spectrum in $(CD_3)_2CO$ exhibited a singlet at δ 91.6 indicating the presence of two equivalent PPh$_2$ groups. In addition to the phenyl and pyridinyl protons, the ^{1}H NMR spectrum also exhibited two broad resonances centred at δ 7.10 and 8.68 for the NH protons. The low-resolution mass spectrum (FAB, positive ion mode) exhibited a peak (M + 1 − BF$_4$) at *m*/*z* 665. The above spectroscopic data suggested that compound **2** can be formulated as either *cis*- or *trans*-[Ni{(Ph$_2$PNH)C(Ph)(=NH)}$_2$][BF$_4$]$_2$. The available spectroscopic data cannot distinguish between the two isomers. The structure of **2** was established by a preliminary X-ray diffraction study[7] to be the *cis* isomer.



cis- isomer



trans- isomer

Preparation of *cis*-[Ni{(NC$_5$H$_4$)[(Ph$_2$PNH)C(=NH)]-4}$_2$][BF$_4$]$_2$ 3

Interaction of [NiBr$_2$(dme)] with 1 equivalent of **L**^{3} in tetrahydrofuran for 1 d followed by metathesis with NH_4BF_4 gave yellow crystals of stoichiometry $C_{36}H_{32}B_2F_8N_6NiP_2$ **3** in moderate yield (55%). The spectroscopic data of compound **3** are very similar to those of **2**. In $(CD_3)_2CO$, compound **3** exhibited a singlet at δ 92.5 for the two equivalent PPh$_2$ groups in the ^{31}P-{^{1}H} spectrum; and two broad resonances centred at δ 7.80 and 8.89 for the NH protons in the ^{1}H NMR spectrum. The low-resolution mass spectrum (FAB, positive ion mode) exhibited a peak at *m*/*z* 668 for the (M − 2BF$_4$) fragment. Since the related compounds **2** and **9** (see below) adopt a *cis* configuration, compound **3** is formulated as *cis*-[Ni{(NC$_5$H$_4$)[(Ph$_2$PNH)C(=NH)]-4}$_2$][BF$_4$]$_2$.

Preparation of *cis*-[PdCl$_2${(Ph$_2$PNH)C(Ph)(=NH)}] 4

The compound [PdCl$_2$(PhCN)$_2$] was allowed to react with 1 equivalent of **L**^{1} in refluxing acetonitrile for 8 h, subsequent work-up gave yellow crystals of stoichiometry $C_{19}H_{17}Cl_2N_2PPd\cdot C_4H_8O$ (**4**·C_4H_8O) in moderate yield (60%) after recrystallization from an acetonitrile–tetrahydrofuran mixture. Compound **4** exhibited absorptions at 3449 and 3229 cm^{-1} in the IR spectrum (KBr), and a broad singlet at δ 8.14 in the ^{1}H NMR spectrum for the NH groups. The ^{31}P-{^{1}H} NMR spectrum in CD_3CN exhibited a singlet at δ 85.2 for the PPh$_2$ group indicating chelating ring formation. In addition to the phenyl and pyridinyl carbons, the ^{13}C-{^{1}H} NMR spectrum also exhibited a doublet at δ 174.1 (J_{P-NC} = 12.2 Hz) for the C=N carbon. The low-resolution mass spectrum (FAB, positive ion mode) exhibited a peak [(M + 1 − Cl) for ^{106}Pd and ^{35}Cl] at *m*/*z* 447. The spectroscopic data of compound **4** are very similar to those of **1**, thus compound **4** can be formulated as *cis*-[PdCl$_2${(Ph$_2$PNH)C(Ph)(=NH)}]. This was confirmed by an X-ray diffraction analysis.

Crystals of **4**·C_4H_8O suitable for an X-ray diffraction study were grown by diffusion of tetrahydrofuran into a solution of **4** in acetonitrile. A perspective drawing of **4** is shown in Fig. 2. Selected bond lengths and angles are given in Table 1. Compound **4** is isostructural to **1**, the geometry of the palladium atom is approximately square planar with a *cis*-PdCl$_2$ configuration. The bond angles around Pd range from 82.6(1) to 94.17(1)° and sum to approximately 360°. The Pd–Cl(1) and Pd–Cl(2) distances are 2.3049(2) and 2.3633(3) Å, respectively. The {(Ph$_2$PNH)C(Ph)(=NH)} moiety acts as a chelating ligand with the imino [N(2)] and phosphino (P) groups co-ordinated to the palladium forming a five-membered ring. Within the five-membered chelating ring, the P–N(1), C(1)–N(1) and C(1)–N(2) distances are 1.692(5), 1.372(7) and 1.293(7) Å,

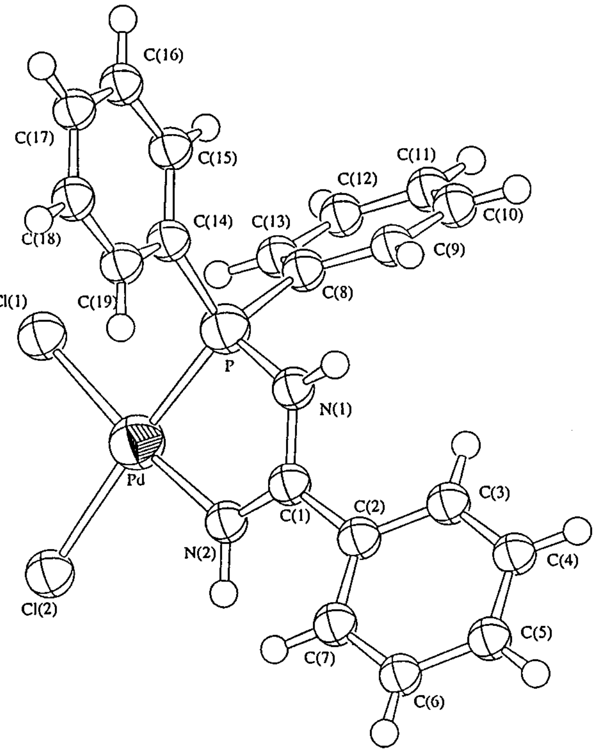
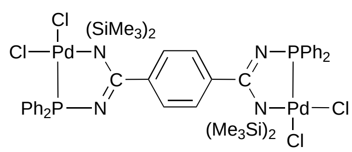


Fig. 2 Perspective view of the molecular structure of compound **4**



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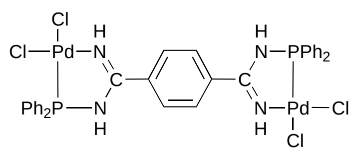


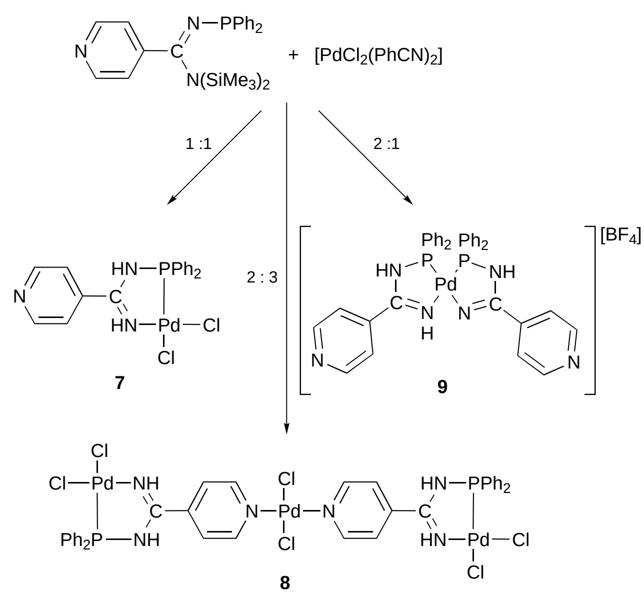
6

respectively; and the P–N(1)–C(1) bond angle is 116.7(4)° indicating delocalization about the N–C–N framework.

Preparation of *cis*-[$(PdCl_2)_2\{C_6H_4[C(=NPPh_2)\{N(SiMe_3)_2\}]_2$-1,4}] 5 and *cis*-[$(PdCl_2)_2\{C_6H_4[C(NHPPh_2)(=NH)]_2$-1,4}] 6

Interaction of [$PdCl_2(PhCN)_2$] with 0.5 equivalent of $\mathbf{L}^2$ in tetrahydrofuran at room temperature gave a tetrahydrofuran-soluble orange-red product and a tetrahydrofuran-insoluble yellow product. Recrystallization of the orange-red product in tetrahydrofuran gave orange-red crystals of stoichiometry $C_{44}H_{60}Cl_4N_4P_2Pd_2Si_4$ **5** in moderate yield (30%). The ^{31}P-{^{1}H} NMR spectrum of **5** CD_3CN exhibited a singlet at δ 57.6 indicating the presence of two equivalent PPh_2 groups. Compound **5** also exhibited a singlet at δ 0.32 in the ^{1}H NMR spectrum and a singlet at δ 3.2 in the ^{13}C-{^{1}H} NMR spectrum for the trimethylsilyl groups. The low-resolution mass spectrum (FAB, positive ion mode) exhibited a peak [$(M - Cl)$ for ^{106}Pd and ^{35}Cl] at *m/z* 1137. On the basis of the above data, compound **5** can be formulated as *cis*-[$(PdCl_2)_2\{C_6H_4[C(=NPPh_2)\{N(SiMe_3)_2\}]_2$-1,4}].

Recrystallization of the tetrahydrofuran-insoluble yellow product in dimethylformamide–tetrahydrofuran gave yellow crystals of stoichiometry $C_{32}H_{28}Cl_4N_4P_2Pd_2\cdot6C_3H_7NO$ (**6**·$6C_3H_7NO$) in moderate yield (50%). Compound **6** exhibited an absorption at 3524 cm^{-1} in the IR spectrum (KBr), and two broad singlets of intensity 2:2 at δ 9.16 and 10.43 in the ^{1}H NMR spectrum for the NH groups. The ^{31}P-{^{1}H} NMR spectrum in $(CD_3)_2SO$ exhibited a singlet at δ 85.3 indicating the presence of two equivalent PPh_2 groups and the formation of two equivalent chelating five-membered rings. The structure of compound **6** was established by X-ray diffraction analysis[2] to be a dinuclear species with C_2 symmetry.



Scheme 1 Results of the interaction of [$PdCl_2(PhCN)_2$] with $\mathbf{L}^3$

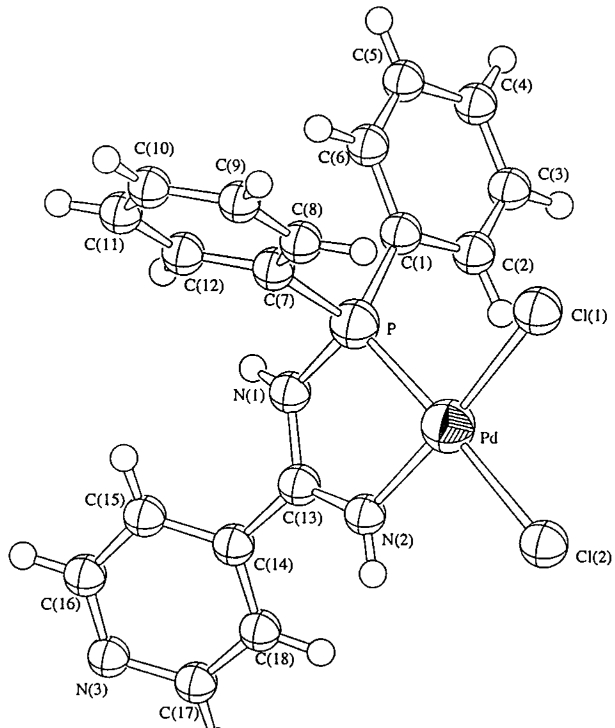


Fig. 3 Perspective view of the molecular structure of compound **7**

Preparation of *cis*-[$PdCl_2\{(NC_5H_4)[(Ph_2PNH)C(=NH)]$-4}] 7

The results of the interaction of [$PdCl_2(PhCN)_2$] with L^3 are summarised in Scheme 1. When [$PdCl_2(PhCN)_2$] was treated with $\mathbf{L}^3$ in a 1:1 molar ratio in tetrahydrofuran for 16 h at ambient temperature, subsequent work-up gave yellow crystals of stoichiometry $C_{18}H_{16}Cl_2N_3PPd\cdot C_4H_8O$ (**7**·C_4H_8O) in moderate yield (65%) after recrystallization from a tetrahydrofuran solution. The ^{31}P-{^{1}H} NMR spectrum in $(CD_3)_2SO$ exhibited a singlet at δ 85.1 for the PPh_2 group. Compound **7** also exhibited absorptions at 3214 and 3448 cm^{-1} in the IR spectrum (KBr)

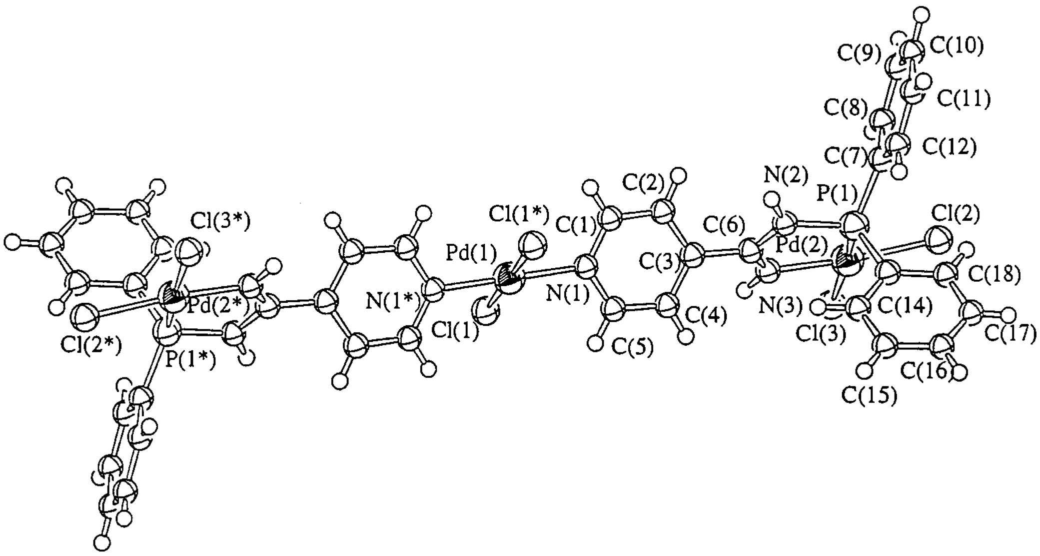


Fig. 4 Perspective view of the molecular structure of compound **8**

Table 2 Selected bond lengths (Å) and angles (°) for compounds **7** and **8**

Compound **7**		Compound **8**	
Pd–Cl(1)	2.293(2)	Pd(1)–Cl(1)	2.293(2)
Pd–Cl(2)	2.365(2)	Pd(1)–N(1)	2.207(7)
Pd–P	2.187(2)	Pd(2)–Cl(2)	2.300(3)
Pd–N(2)	2.018(7)	Pd(2)–Cl(3)	2.364(3)
P–N(1)	1.699(7)	P(2)–P(1)	2.182(3)
N(1)–C(13)	1.366(10)	Pd(2)–N(3)	2.004(9)
N(2)–C(13)	1.296(10)	P(1)–N(2)	1.722(9)
		N(2)–C(6)	1.36(1)
		N(3)–C(6)	1.27(1)
Cl(1)–Pd–Cl(2)	95.65(9)	Cl(1)–Pd(1)–N(1)	89.9(2)
P–Pd–Cl(1)	90.56(9)	Cl(1*)–Pd(1)–N(1)	90.1(2)
Cl(2)–Pd–N(2)	93.0(2)	Cl(2)–Pd(2)–Cl(3)	94.8(1)
P–Pd–N(2)	82.9(2)	Cl(2)–Pd(2)–P(1)	91.6(1)
P–N(1)–C(13)	117.3(5)	Cl(3)–Pd(2)–N(3)	91.7(3)
N(1)–C(13)–N(2)	117.9(7)	P(1)–Pd(2)–N(3)	80.0(3)
		Pd(2)–N(3)–C(6)	120.6(7)
		P(1)–N(2)–C(6)	113.8(7)
		N(2)–C(6)–N(3)	120.8(10)

and two broad singlets at δ 9.35 and 10.52 in the ^{1}H NMR spectrum for the NH groups. The low-resolution mass spectrum (FAB, positive ion mode) exhibited a peak [(M + 1) for ^{106}Pd and ^{35}Cl] at m/z 482. Based on the spectroscopic data, compound **7** can be formulated as *cis*-[$PdCl_2${(NC_5H_4)[(Ph_2PNH)-C(=NH)]-4}]. This was confirmed by an X-ray diffraction study.

Crystals of **7** suitable for X-ray diffraction study were grown from tetrahydrofuran–diethyl ether as a tetrahydrofuran solvate, **7**·C_4H_8O. A perspective drawing of **7** is shown in Fig. 3. Selected bond lengths and angles are given in Table 2. The palladium adopts a square-planar geometry with a *cis*-$PdCl_2$ configuration. The bond angles around Pd range from 82.9(2) to 95.65(9)°. The [(NC_5H_4){(Ph_2PNH)C(=NH)}-4] moiety acts as a chelating ligand with the imino [N(2)] and phosphino (P) groups co-ordinated to the palladium forming a five-membered ring. Delocalization about the N–C–N framework is also observed and reflected by the P–N(1), C(13)–N(1) and C(13)–N(2) distances of 1.699(7), 1.366(10) and 1.296(10) Å, respectively; and the P–N(1)–C(13) angle of 117.3(5)°.

Preparation of *trans*-[$PdCl_2${*cis*-$PdCl_2$[(NC_5H_4){(Ph_2PNH)-C(=NH)}-4}]$_2$] 8

When [$PdCl_2(PhCN)_2$] was treated with $\mathbf{L^3}$ in a 3:2 molar ratio in tetrahydrofuran for 2 d at ambient temperature, subsequent work-up gave yellow crystals of stoichiometry $C_{36}H_{32}Cl_6$-$N_6P_2Pd_3$·$4C_3H_7NO$ (**8**·$4C_3H_7NO$) in moderate yield (55%) after recrystallisation from dimethylformamide–tetrahydrofuran. Compound **8** can be formulated as *trans*-[$PdCl_2${*cis*-$PdCl_2$[(NC_5H_4){(Ph_2PNH)C(=NH)}-4]}$_2$]. The structure was established by X-ray diffraction analysis to be a trinuclear species with C_i symmetry.

Crystals of **8** suitable for X-ray diffraction study were grown from a solution of dimethylformamide–tetrahydrofuran as a dimethylformamide (dmf) solvate, **8**·4dmf. A perspective drawing of **8** is shown in Fig. 4. Selected bond lengths and angles are given in Table 2. The trinuclear species is centrosymmetric with the three palladium centres linked together *via* two [(NC_5H_4){(Ph_2PNH)C(=NH)}-4] moieties in a linear conformation. All three palladium centres adopt a square planar geometry with the central metal [Pd(1)] having a *trans*- and the terminal metals [Pd(2) and Pd(2*)] a *cis*-$PdCl_2$ configuration. The bond angles around the palladium centres range from 89.9(2) and 90.1(2) for the central palladium Pd(1); and 80.0(3) to 94.8(1)° for the terminal palladium atoms. The [(NC_5H_4){(Ph_2PNH)C(=NH)}-4] moieties behave as tridentate bridges with the imino [N(3)] and phosphino [P(1)] groups co-ordinated to the terminal *cis*-$PdCl_2$ moieties forming five-membered rings and the pyridino [N(1) and N(1*)] groups co-ordinated to the central *trans*-$PdCl_2$ moiety. Delocalization about the N–C–N framework is also observed and reflected by the C(6)–N(2) and C(6)–N(3) distances of 1.36(1) and 1.27(1) Å, respectively, and P(1)–N(2)–C(6) bond angles of 113.8(7)°.

The spectroscopic data of compound **8** are consistent with its solid-state structure. The ^{31}P-{^{1}H} NMR spectrum in $(CD_3)_2SO$ exhibited a singlet at δ 85.6 for the PPh_2 group, it also exhibited a broad absorption at 3448 cm^{-1} in the IR spectrum (KBr) and four broad singlets at δ 9.36, 9.60, 10.52 and 10.63 in the ^{1}H NMR spectrum for the NH groups.

Preparation of [Pd{(NC_5H_4)[(Ph_2PNH)C(=NH)]-4}{(NC_5H_4)-[(Ph_2PNH)C(=N)]-4}][BF_4] 9

When [$PdCl_2(PhCN)_2$] was treated with $\mathbf{L^3}$ in a 1:2 molar ratio in tetrahydrofuran for 1 d at 55 °C followed by metathesis with excess NH_4BF_4 in methanol, subsequent work-up gave white crystals of stoichiometry $C_{36}H_{31}BF_4N_6P_2Pd$·C_3H_7NO (**9**·C_3H_7NO) in high yield (80%) after recrystallization from dimethylformamide–tetrahydrofuran. The ^{31}P-{^{1}H} NMR spectrum of **9** in $(CD_3)_2SO$ exhibited two singlets at δ 86.4 and 91.5 indicating the presence of two non-equivalent PPh_2 groups. The lack of observable coupling between the two phosphorus atoms in a square-planar complex is characteristic of a

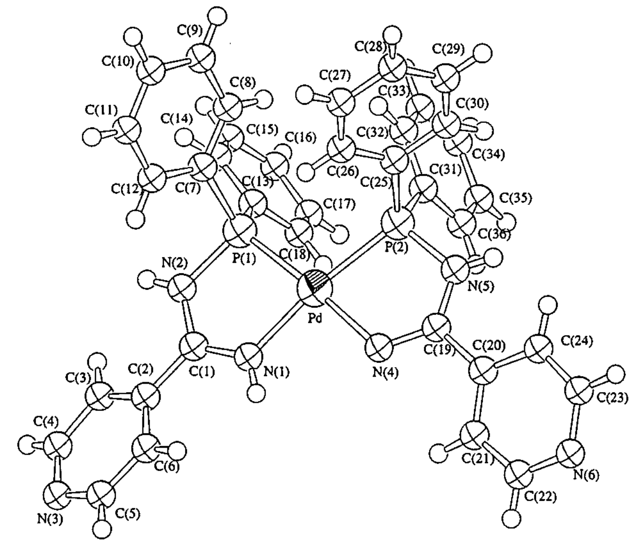


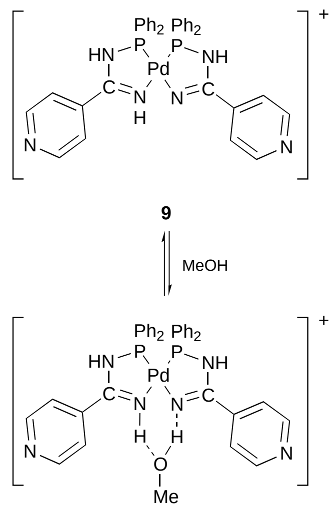
Fig. 5 Perspective view of the molecular structure of the cation of compound **9**

Table 3 Selected bond lengths (Å) and angles (°) for compounds **9** and **10**

Compound **9**		Compound **10**	
Pd–P(1)	2.248(1)	Pt–P(1)	2.218(6)
Pd–P(2)	2.263(1)	Pt–P(2)	2.246(6)
Pd–N(1)	2.058(4)	Pt–N(1)	2.07(2)
Pd–N(4)	2.046(4)	Pt–N(4)	2.03(2)
P(1)–N(2)	1.714(4)	P(1)–N(2)	1.73(2)
P(2)–N(5)	1.664(4)	P(2)–N(5)	1.67(2)
N(1)–C(1)	1.283(6)	N(1)–C(1)	1.26(2)
N(2)–C(1)	1.340(6)	N(2)–C(1)	1.30(2)
N(4)–C(19)	1.319(6)	N(4)–C(19)	1.27(2)
N(5)–C(19)	1.324(6)	N(5)–C(19)	1.34(2)
P(1)–Pd–P(2)	106.05(4)	P(1)–Pt–P(2)	106.3(2)
P(1)–Pd–N(1)	81.3(1)	P(1)–Pt–N(1)	80.1(5)
P(2)–Pd–N(4)	79.1(1)	P(2)–Pt–N(4)	79.2(5)
N(1)–Pd–N(4)	93.5(2)	N(1)–Pt–N(4)	94.3(7)
P(1)–N(2)–C(1)	119.2(3)	P(1)–N(2)–C(1)	116(1)
P(2)–N(5)–C(19)	113.1(3)	P(2)–N(5)–C(19)	112(1)

cis configuration for the PPh_2 groups.[6] Compound **9** exhibited absorptions at 3243, 3381 and 3442 cm^{-1} in the IR spectrum (KBr) and three broad singlets of relative intensity 1 : 1 : 1 at δ 8.19, 9.91 and 10.58 for the NH groups in the ^1H NMR spectrum. The low-resolution mass spectrum (FAB, positive ion mode) exhibited a peak $[(M - BF_4)$ for $^{106}Pd]$ at *m/z* 715. Based on the above data, the monocation of **9** should have an anionic imidophosphine ligand $[4\text{-}(NC_5H_4)(Ph_2PNH)C{=}N]^-$ as well as a neutral iminophosphine ligand $[4\text{-}(NC_5H_4)(Ph_2PNH)C{=}NH]$ co-ordinated to the Pd^{II} metal centre forming two non-equivalent chelating five-membered rings. Thus, compound **9** can be formulated as *cis*-$[Pd\{(NC_5H_4)[(Ph_2PNH)C(=NH)]\text{-}4\}\{(NC_5H_4)[(Ph_2PNH)C(=N)]\text{-}4\}][BF_4]$. This was confirmed by a single crystal X-ray diffraction study.

White crystals of $\mathbf{9}{\cdot}C_3H_7NO$ suitable for an X-ray diffraction study were grown by slow diffusion of tetrahydrofuran into a solution of compound **9** in dimethylformamide. A perspective drawing of the cation of compound **9** is shown in Fig. 5. Selected bond lengths and angles are given in Table 3. The geometry of the palladium atom is approximately square planar with the two phosphino ligands in a *cis* configuration and the bond angles around Pd ranging from 78.7(1) to 106.05(4)° and summing to about 360°. Steric repulsion between the two bulky *cis*-PPh_2 groups causes a significant deviation of the P(1)–Pd–P(2) angle [106.05(4)°] from the ideal angle (90°). The Pd–N(4) distance [2.046(4) Å] is slightly shorter than the Pd–N(1) distance [2.058(4) Å]. This would be expected if N(4) is the anionic imide $(C{=}N)^-$ forming a σ bond with Pd, and N(1) is the neutral imine (C=NH) forming a dative bond with Pd. Furthermore, it is anticipated that π back donation from Pd to P(1) will be stronger than from Pd to P(2) if N(4) which is *trans* to P(1) is the electron-rich anionic imide and N(1) which is *trans* to P(2) is the neutral imine. The degree of π back donation can be reflected by the Pd–P distances which would be shorter for stronger π back donation. The Pd–P(1) distance [2.248(1) Å] is slightly shorter than the Pd–P(2) distance [2.263(1) Å]. Thus, N(4) can be assigned as the anionic imide nitrogen and N(1) as the neutral imine nitrogen. Both the anionic imidophosphine moiety $[(NC_5H_4)\{(Ph_2PNH)C(=N)\}\text{-}4]^-$ and the neutral iminophosphine moiety $[(NC_5H_4)\{(Ph_2PNH)C{=}(NH)\}\text{-}4]$ behave as chelating ligands with the imido [N(4)] and phosphino [P(2)] groups of the anionic imidophosphine ligand, and the imino [N(1)] and phosphino [P(1)] groups of the neutral iminophosphine ligand co-ordinated to the palladium forming two five-membered rings. The P(1)–N(2), C(1)–N(1) and C(1)–N(2) distances are 1.714(4), 1.283(6) and 1.340(6) Å, respectively; and the P(1)–N(2)–C(1) angle is 119.2(3)° for the neutral iminophosphine ligand. The P(2)–N(5), C(19)–N(4) and C(19)–N(5) distances are 1.664(4), 1.319(6) and 1.324(6) Å, respectively; and the P(2)–N(5)–C(19) angle is 113.1(3)° for the anionic iminophosphine ligand. The structural data indicate delocalization about the N–C–N framework for both ligands.



Scheme 2 Hydrogen-bond formation between methanol and compound **9**

When **9** was dissolved in CD_3OD, the $^{31}P\text{-}\{^1H\}$NMR spectrum only exhibited a singlet at δ 90.4 indicating that the two PPh_2 groups had become equivalent. This is probably due to the formation of hydrogen-bonding between the methanol and the imino and imido groups as shown in Scheme 2.

Preparation of $[Pt\{(NC_5H_4)[(Ph_2PNH)C(=NH)]\text{-}4\}\{(NC_5H_4)\text{-}[(Ph_2PNH)C(=N)]\text{-}4\}][BF_4]$ 10

The result of the interaction of $[PtCl_2(PhCN)_2]$ with 2 equivalents of $\mathbf{L^3}$ is similar to that of the Pd analogue **9**. Metathesis of the Pt complex with NH_4BF_4 in methanol gave white crystals of stoichiometry $C_{36}H_{31}BF_4N_6P_2Pt{\cdot}C_3H_7NO$ ($\mathbf{10}{\cdot}C_3H_7NO$) in high yield (76%) after recrystallization from dimethylformamide–tetrahydrofuran. The spectroscopic data of compound **10** are very similar to those of **9**. The $^{31}P\text{-}\{^1H\}$ NMR spectrum in $(CD_3)_2SO$ exhibited two singlets at δ 68.1 ($J_{Pt-P} = 3036$ Hz) and 71.0 ($J_{Pt-P} = 3223$ Hz) indicative of a *cis* configuration for the two non-equivalent PPh_2 groups. Compound **10** also exhibited absorptions at 3243, 3381 and 3442 cm^{-1} in the IR spectrum (KBr) and two broad singlets of relative intensity 1 : 2 at δ 10.58 and 11.06 in the ^1H NMR spectrum for the NH groups. The low-resolution mass spectrum (FAB,

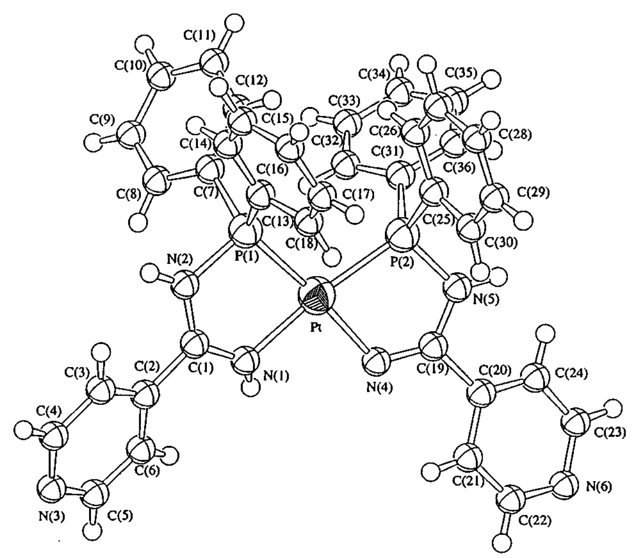
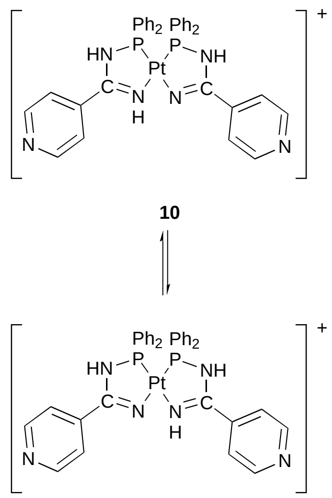


Fig. 6 Perspective view of the molecular structure of the cation of compound **10**



Scheme 3 Solution dynamic behaviour of compound **10**

positive ion mode) exhibited a peak [(M − BF_4) for ^{195}Pt] at *m/z* 804. Thus compound **10** can be formulated as *cis*-[Pt{(NC_5H_4)[(Ph_2PNH)C(=NH)]-4}{(NC_5H_4)[(Ph_2PNH)C(=N)]-4}][BF_4] confirmed by an X-ray diffraction analysis.

Crystals of **10**·C_3H_7NO suitable for an X-ray diffraction study were grown by slow diffusion of tetrahydrofuran into a solution of **10** in dimethylformamide. A perspective drawing of the cation of compound **10** is shown in Fig. 6. Selected bond lengths and angles are given in Table 3. Compounds **9** and **10** are isomorphous. The geometry of the platinum atom is approximately square planar with the two phosphino ligands in a *cis* configuration and the bond angles around Pt ranging from 79.2(5) to 106.3(2)°.

Compound **10** exhibited temperature-dependent ^{31}P-{^{1}H} NMR spectra. The variable-temperature ^{31}P-{^{1}H} NMR spectra of **10** in $(CD_3)_2SO$ revealed that at 100 °C the two singlets coalesced to a broad singlet at δ 69.5. The observed solution dynamic behaviour is probably due to the intramolecular hydrogen exchange process shown in Scheme 3. Similar to **9**, the ^{31}P-{^{1}H} NMR spectra of **10** in CD_3OD exhibited only a singlet at δ 71.8 (J_{Pt-P} = 3129 Hz) for the two PPh_2 groups indicating formation of hydrogen bonding between the methanol and the imino and imido groups.

The formation of (NC_5H_4){(Ph_2PNH)C(=NH)}-4 from (NC_5H_4){(Ph_2PN=)C[N($SiMe_3$)$_2$]}-4 is probably *via* a 1,3-silyl shift followed by hydrolysis. A similar mechanism has been proposed for related complexes.[6] The NH protons of the imido- and imino-phosphine ligands are very labile and undergo facile deuterium exchange with D_2O at ambient temperature indicating significant delocalization about the N−C−N framework.[3,5,6] This is supported by the structural data of compounds **1**, **4**, **7**, **8**, **9** and **10** which show that the two C−N distances of the N−C−N framework are intermediate between those expected for single and double bonds.

Experimental

Procedures

All operations were carried out in an atmosphere of dry nitrogen or *in vacuo*. Solvents were dried by standard procedures, distilled and deaerated prior to use. All chemicals used were of reagent grade, obtained from the Aldrich Chemical Company and, where appropriate, degassed before use. The compounds (Ph_2PN=)C(Ph)[N($SiMe_3$)$_2$],[6] C_6H_4{C(=NPPh_2)[N($SiMe_3$)$_2$]}$_2$-1,4[6] and [MCl_2(PhCN)$_2$][8] (M = Pd or Pt) were prepared according to literature methods. The compound [$NiBr_2$(dme)] was prepared by reacting a suspension of nickel powder in dme with stoichiometric amounts of bromine in dme. Microanalyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China. Infrared spectra were recorded on a Nicolet Nagna-IR 550 spectrometer, NMR spectra on a JEOL EX270 spectrometer. Chemical shifts of ^{1}H and ^{13}C-{^{1}H} NMR spectra were referenced to internal deuteriated solvents and then recalculated to $SiMe_4$ (δ 0.00), those of ^{31}P-{^{1}H} NMR spectra were referenced to external 85% H_3PO_4. Low-resolution mass spectra were obtained on a Finnigan MAT SSQ-710 spectrometer in FAB (positive ion) mode.

Preparations

(NC_5H_4){(Ph_2PN=)C[N($SiMe_3$)$_2$]}-4 L^3. A solution of Li[N($SiMe_3$)$_2$], generated *in situ* by reacting NH($SiMe_3$)$_2$ (16.5 g, 102 mmol) in diethyl ether (60 cm^3) with LiBu^n (63 cm^3 of 1.6 M, 101 mmol) in hexane, was slowly added to a solution of 4-cyanopyridine (10.4 g, 100 mmol) in tetrahydrofuran (20 cm^3) at 0 °C. The resultant dark red solution was warmed to room temperature and stirred for an additional 2 h before cooling to −78 °C. A solution of chlorodiphenylphosphine (22.0 g, 100 mmol) in tetrahydrofuran (50 cm^3) was then slowly added to the reaction mixture which was stirred at −78 °C for an hour before warming to room temperature and allowed to react overnight. The solvent was then removed *in vacuo*. The residue was dissolved in dichloromethane (40 cm^3) and the solution was filtered through Celite to afford a clear red filtrate which was concentrated to *ca.* 20 cm^3. Hexane (15 cm^3) was added to the dichloromethane solution slowly until it just turned cloudy. The resultant solution was then cooled to −20 °C to give yellow crystals which were filtered off and dried *in vacuo*. Yield: 40.1 g, 90%, yellow crystals, m.p. 96–97 °C (Found: C, 64.1; H, 7.1; N, 9.5. Calc. for $C_{24}H_{32}N_3PSi_2$: C, 64.1; H, 7.1; N, 9.4%). IR (cm^{-1}, in KBr): 3039w, 2958w, 2898w, 1588s, 1548w, 1480w, 1433m, 1404m, 1326w, 1260s, 1246s, 1209w, 1092s, 1079m, 1060m, 930s, 888s, 833vs, 761m, 740s, 695s, 681m, 637w, 557w, 512m, 463m and 418w. NMR ($CDCl_3$): ^{31}P-{^{1}H}, δ 36.5 (s); ^{13}C-{^{1}H}, C=N carbons, δ 167.9 (d, J_{P-NC} = 26.7); pyridinyl and phenyl carbons, 127.6, 129.0 (d, J_{P-C} = 9.8), 130.7 (d, J_{P-C} = 13.4), 130.9, 137.5 (d, J_{P-C} = 39.0) and 139.4 (d, J_{P-C} = 6.1 Hz); trimethylsilyl carbons, 2.7; ^{1}H, phenyl and pyridinyl protons, 7.24 (8 H, m), 7.49 (4 H, m) and 8.57 (2 H, m); trimethylsilyl protons, 0.06 (18 H, s). Positive-ion FAB mass spectrum: *m/z* 450 (M + 1).

***cis*-[$NiBr_2${(Ph_2PNH)C(Ph)(=NH)}] 1.** A solution of **L^1** (1.0 g, 2.2 mmol) in tetrahydrofuran (20 cm^3) was added to a stirring solution of [$NiBr_2$(dme)] (0.7 g, 2.3 mmol) in tetrahydrofuran (10 cm^3) at ambient temperature. The reaction mixture was then refluxed for 8 h. A brick-red precipitate was formed upon cooling to ambient temperature, it was filtered off, washed with tetrahydrofuran (4 cm^3), and dried *in vacuo*. Yield: 0.87 g, 76%, red crystals, m.p. 234–236 °C (decomp.) (Found: C, 43.5; H, 3.1; N, 5.4. Calc. for $C_{19}H_{17}Br_2N_2NiP$: C, 43.7; H, 3.3; N, 5.4%). IR (cm^{-1}, in KBr): 3273s, 3051w, 2980w, 2874w, 1636w, 1588w, 1561m, 1460s, 1437s, 1316w, 1099s, 1040m, 885w, 825m, 775m, 747m, 694s, 533m and 492s. NMR ($CDCl_3$): $^{31}P-\{^1H\}$, δ 76.1 (s); $^{13}C-\{^1H\}$, 127.4, 127.9, 129.0, 129.5, 132.8 and 133.6; ^1H, phenyl and pyridinyl protons, 7.38–7.61 (11 H, m) and 8.05 (4 H, br, s); NH proton, 5.48 (1 H, br, s) and 7.31 (1 H, br, s).

***cis*-[Ni{(Ph$_2$PNH)C(Ph)(=NH)}$_2$][BF$_4$]$_2$ 2.** An aqueous solution of NH_4BF_4 (0.5 g, 4.8 mmol) was added to a solution of **1** (0.5 g, 1.0 mmol) in methanol and the resultant solution was stirred overnight at room temperature to give a yellow precipitate which was filtered off, washed with water (2 × 5 cm^3) and dried *in vacuo*. The yellow solid was dissolved in acetone and filtered. Diethyl ether was then slowly diffused into the filtrate to give yellow crystals which were filtered off and dried *in vacuo*. Yield: 0.35 g, 47%, yellow crystals, m.p. 210–214 °C (decomp.) (Found: C, 54.5; H, 3.8; N, 7.0. Calc. for $C_{38}H_{34}B_2F_8N_4NiP_2$: C, 54.2; H, 4.1; N, 6.7%). IR (cm^{-1}, in KBr): 3429m, 3127s, 2926m, 2858w, 1596w, 1564w, 1463m, 1429m, 1401s, 1314w, 1106vs, 1071vs, 1035vs, 828w, 788w, 744w, 690m, 534m, 521m, 498w and 474w. NMR [$(CD_3)_2CO$]: $^{31}P-\{^1H\}$, δ 91.6 (s); $^{13}C-\{^1H\}$, C=N carbons, 175.5 (br, s); phenyl carbons, 124.9, 125.3, 125.7, 129.2, 130.5 (t, J_{P-C} = 6.1), 134.1 (t, J_{P-C} = 6.1), 134.9 (d, J_{P-C} = 14.2 Hz) and 135.3; ^1H, NH protons, 7.10 (2 H, br, s), 8.68 (2 H, br, s); phenyl protons, 7.40–7.83 (26 H, m), 8.03 (4 H, m). Positive-ion FAB mass spectrum: *m/z* 665 (M + 1 − BF_4).

***cis*-[Ni{(NC$_5$H$_4$)[(Ph$_2$PNH)C(=NH)]-4}][BF$_4$]$_2$ 3.** A solution of [$NiBr_2$(dme)] (0.69 g, 2.2 mmol) in tetrahydrofuran (10 cm^3) was added to a stirring solution of L^3 (1.0 g, 2.2 mmol) in tetrahydrofuran (15 cm^3) at ambient temperature. The mixture after reacting for 1 d gave a yellow precipitate which was filtered off, washed with tetrahydrofuran (2 × 10 cm^3), dissolved in methanol and filtered. Then an aqueous solution (5 cm^3) of NH_4BF_4 (0.5 g, 4.8 mmol) was added to the filtrate to give a yellow precipitate which was filtered off, washed with water (2 × 5 cm^3), dissolved in acetone and filtered. Diethyl ether slowly diffused into the filtrate to give yellow crystals. Yield: 0.51 g, 55%, yellow crystals, m.p. 240–242 °C (decomp.) (Found: C, 51.0, H, 3.7; N, 10.3. Calc. for $C_{36}H_{32}B_2F_8N_6NiP_2$: C, 51.3; H, 3.8; N, 10.0%). IR (cm^{-1}, in KBr): 3385m, 3332m, 3237s, 3112m, 3056m, 2791w, 1695w, 1650w, 1589m, 1549w, 1470vs, 1434s, 1357w, 1280m, 1226w, 1130m, 1102s, 1070w, 1006m, 880w, 835vs, 809m, 748s, 703s, 689vs, 670m, 618w, 560w, 537m, 522m, 499m, 488m, 470m and 418w. NMR [$(CD_3)_2CO$]: $^{31}P-\{^1H\}$, δ 92.5 (s); $^{13}C-\{^1H\}$, pyridinyl and phenyl carbons, 122.4, 124.7, 125.2, 125.6, 130.5 (t, J = 6.1), 134.2 (t, J = 6.1 Hz), 134.9, 151.8 and 174.2; ^1H, NH protons, 7.80 (2 H, br, s), 8.89 (2 H, br, s); pyridinyl and phenyl protons, 7.35 (8 H, m), 7.62 (12 H, m), 7.88 (4 H, m) and 8.77 (4 H, m). Positive-ion FAB mass spectrum: *m/z* 668 (M − 2BF_4).

***cis*-[PdCl$_2${(Ph$_2$PNH)C(Ph)(=NH)}] 4.** This compound was prepared as described for **1**: [$PdCl_2$(PhCN)$_2$] (0.34 g, 0.9 mmol), L^1 (0.40 g, 0.9 mmol) and acetonitrile (30 cm^3) were used. Yellow crystals of **4**·C_4H_8O were obtained from acetonitrile–tetrahydrofuran. Yield: 0.30 g, 60%, yellow crystals, m.p. 198–201 °C (decomp.) (Found: C, 49.6; H, 4.6; N, 5.6. Calc. for $C_{23}H_{25}Cl_2N_2OPPd$: C, 49.9; H, 4.5; N, 5.1%). IR (cm^{-1}, in KBr): 3449m, 3229s, 3054m, 2977w, 2878w, 2763w, 1677w, 1640w, 1594s, 1570s, 1505w, 1462vs, 1436vs, 1332w, 1236w, 1111s, 1049m, 997w, 889m, 831m, 782m, 748m, 720m, 705s, 695vs, 588m, 537m, 487s, 471m and 442w. NMR (CD_3CN): $^{31}P-\{^1H\}$, δ 85.2 (s); $^{13}C-\{^1H\}$, C=N carbons, 174.1 (d, J_{P-NC} = 12.2); phenyl carbons, 129.1, 129.9, 130.1 (d, J_{P-C} = 12.2), 133.9 (d, J_{P-C} = 12.2), 134.1 and 134.2 (d, J_{P-C} = 2.4 Hz); thf carbons, 26.2 and 68.2; ^1H, NH protons, 8.14 (2 H, br, s); phenyl protons, 7.48–7.75 (11 H, m) and 7.95 (4 H, m); thf protons, 1.79 (4 H, m) and 3.63 (4 H, m). Positive-ion FAB mass spectrum: *m/z* 447 [(M + 1 − Cl) for ^{106}Pd and ^{35}Cl].

***cis*-[(PdCl$_2$)$_2${C$_6$H$_4$[C(=NPPh$_2$){N(SiMe$_3$)$_2$}]$_2$-1,4}] 5 and *cis*-[(PdCl$_2$)$_2${C$_6$H$_4$[C(NHPPh$_2$)(=NH)]$_2$-1,4}] 6.** A solution of L^2 (0.33 g, 0.4 mmol) and [$PdCl_2$(PhCN)$_2$] (0.31 g, 0.8 mmol) in tetrahydrofuran (10 cm^3) was stirred overnight at ambient temperature to give an orange-red solution and a yellow precipitate. The solution was filtered, concentrated to *ca.* 5 cm^3 and cooled to −20 °C to give orange-red crystals of **5** which were filtered off and dried *in vacuo*. Yield: 0.14 g, 30%, orange-red crystals, m.p. 198–201 °C (decomp.) (Found: C, 45.2; H, 5.2; N, 4.7. Calc. for $C_{44}H_{60}Cl_4N_4P_2Pd_2Si_4$: C, 45.0; H, 5.2; N, 4.8%). IR (cm^{-1}, in KBr): 3063w, 2979w, 2952w, 2915w, 1577m, 1561m, 1536s, 1436m, 1397w, 1313s, 1278m, 1258m, 1161w, 1099m, 999w, 982m, 867s, 845vs, 817m, 778w, 743m, 707m, 689m, 676w, 643w, 625w, 578m, 524s, 501m, 471w, 452w and 431w. NMR (CD_3CN): $^{31}P-\{^1H\}$, δ 57.6 (s); $^{13}C-\{^1H\}$, 128.5, 128.6, 128.7, 128.8, 128.9, 131.1, 131.3, 132.5, 132.6, 132.8, 134.0, 135.1 and 135.2; trimethylsilyl carbons, 3.2; ^1H, phenyl and phenylene protons, 7.37–7.60 (18 H, m), 7.75 (2 H, m) and 8.14–8.26 (4 H, m); trimethylsilyl protons, 0.32 (36 H, s). Positive-ion FAB mass spectrum: *m/z* 1137 [(M − Cl) for ^{106}Pd and ^{35}Cl].

The yellow precipitate was dissolved in dimethylformamide and filtered. Tetrahydrofuran slowly diffused into the yellow filtrate to give yellow crystals of **6**·6C_3H_7NO which were filtered off and dried *in vacuo*. Yield: 0.26 g, 50%, yellow crystals, m.p. 302–305 °C (decomp.) (Found: C, 45.5; H, 5.4; Cl, 10.5; N, 10.7. Calc. for $C_{50}H_{70}Cl_4N_{10}O_6P_2Pd_2$: C, 45.4; H, 5.3; Cl, 10.7; N, 10.6%). IR (cm^{-1}, in KBr): 3524w, 3060w, 1640vs, 1582s, 1524m, 1460s, 1432s, 1412m, 1386s, 1354s, 1254m, 1156w, 1100s, 1014w, 878w, 852w, 804s, 746m, 714w, 684s, 664m, 536m and 470m. NMR [$(CD_3)_2SO$]: $^{31}P-\{^1H\}$, δ 85.3 (s); $^{13}C-\{^1H\}$, phenyl and phenylene carbons, 128.8, 129.0, 129.2, 132.6, 132.8 and 133.0; dmf carbons, 30.7, 35.7 and 162.3; ^1H, Pd–NH protons, 10.43 (2 H, br s); P–NH protons, 9.16 (2 H, br s); phenyl and phenylene protons, 7.60–7.97 (24 H, m); methyl protons of dmf 2.69 (18 H, s) and 2.72 (18 H, s); CHO protons of dmf, 7.94 (6 H, s).

***cis*-[PdCl$_2${(NC$_5$H$_4$)[(Ph$_2$PNH)C(=NH)]-4}] 7.** A solution of [$PdCl_2$(PhCN)$_2$] (0.38 g, 1.0 mmol) in tetrahydrofuran (10 cm^3) was added to a stirring solution of L^3 (0.45 g, 1.0 mmol) in tetrahydrofuran (15 cm^3) at ambient temperature. Upon stirring for 16 h, the resulting yellow solution was filtered, concentrated to *ca.* 15 cm^3 and cooled at −20 °C to give yellow crystals of **7**·C_4H_8O which were filtered off and dried *in vacuo*. Yield: 0.36 g, 65%, yellow crystals, m.p. 228–230 °C (decomp.) (Found: C, 47.6; H, 4.4; N, 7.5. Calc. for $C_{22}H_{24}Cl_2N_3OPPd$: C, 47.7; H, 4.4; N, 7.6%). IR (cm^{-1}, in KBr): 3448m, 3214s, 3052m, 2969m, 2874m, 2772m, 2676w, 1583m, 1548m, 1496m, 1460vs, 1434vs, 1405m, 1340w, 1232w, 1104vs, 1070w, 1042s, 997w, 889m, 843s, 812s, 756m, 744s, 719m, 707m, 689s, 661w, 578m, 538m, 490s, 476s and 442w. NMR [$(CD_3)_2SO$]: $^{31}P-\{^1H\}$, δ 85.1 (s); $^{13}C-\{^1H\}$, C=N carbon, 171.0 (d, J_{P-NC} = 12.2); pyridinyl carbons, 122.6, 133.0 and 150.0; phenyl carbons of PPh_2, 128.3, 129.1 (d, 12.2), 132.7 (d, 13.4) and 135.7 (d, 12.2); thf carbons, 25.1 and 67.0; ^1H, NH protons, 9.35 (1 H, br, s) and 10.52 (1 H, br, s); pyridinyl protons, 7.76 (2 H, d, J = 5.7) and 8.76 (2 H, d, J = 5.7 Hz); phenyl protons, 7.64 (4 H, m), 7.72 (2 H, m) and 7.92 (4 H, m); thf protons, 1.74 (4 H, m) and 3.59 (4 H, m). Positive-ion FAB mass spectrum: *m/z* 482 [(M + 1) for ^{106}Pd and ^{35}Cl] and 446 [(M − Cl)].

***trans*-[PdCl$_2${*cis*-PdCl$_2$[(NC$_5$H$_4$){(Ph$_2$PNH)C(=NH)}-4]}$_2$] 8.** A solution of [$PdCl_2$(PhCN)$_2$] (0.38 g, 1.01 mmol) in tetrahydrofuran (10 cm^3) was added to a stirring solution of L^3

Table 4 Data collection and processing parameters for compounds **1**, **4**, **7**, **8**, **9** and **10***

	1	**4**	**7**	**8**	**9**	**10**
Empirical formula	$C_{19}H_{17}Br_2N_2NiP$	$C_{23}H_{25}Cl_2N_2OPPd$	$C_{22}H_{24}Cl_2N_3OPPd$	$C_{48}H_{60}Cl_6N_{10}O_4P_2Pd_3$	$C_{39}H_{38}BF_4N_7OP_2Pd$	$C_{39}H_{38}BF_4N_7OP_2Pt$
M	522.8	1234.1	554.7	1434.9	875.9	964.6
Colour; habit	Red prism	Yellow prism	Yellow block	Yellow block	Yellow block	Colourless plate
Crystal size/mm	0.22 × 0.22 × 0.4524	0.27 × 0.29 × 0.32	0.21 × 0.22 × 0.26	0.22 × 0.23 × 0.26	0.12 × 0.19 × 0.21	0.27 × 0.23 × 0.21
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	12.911(2)	9.540(2)	9.386(1)	7.840(1)	9.047(1)	10.439(5)
b/Å	11.880(3)	22.503(2)	22.657(2)	19.026(2)	10.543(1)	22.06(1)
c/Å	13.868(2)	11.802(2)	11.854(1)	21.450)1)	22.089(2)	9.081(6)
α/°					98.52(2)	101.16(7)
β/°	110.28(1)	111.28(1)	112.38(10)	97.85(2)	100.90(2)	100.65(5)
γ/°					100.58(2)	98.10(4)
U/Å^3	1995.2(7)	2360.9(6)	2331.0(5)	3169.6(5)	1996.9(5)	1982(2)
Z	4	4	4	2	2	2
D_c/g cm^{-3}	1.740	1.558	1.581	1.503	1.457	1.616
μ/cm^{-1}	50.74	10.98	11.13	11.92	6.05	36.66
F(000)	1032	1120	1120	1440	892	956
2θ Range	3.0–48.0°	6.0–45.0°	2.0–45.0°	2.0–51.3°	2.8–51.0°	3.0–45.0°
Scan type	ω–2θ	ω–2θ	ω–2θ	ω	ω	ω–2θ
Scan rate (deg min^{-1} in ω)	16.0 (up to 6 scans)	16.0 (up to 6 scans)	Variable, 1.2 to 16.5	—	—	16.0 (up to 6 scans)
Scan range (ω)	(0.89 + 0.35 tan θ)°	(0.84 + 0.35 tan θ)°	(0.65 + 0.35 tan θ)°	—	—	(1.10 + 0.35 tan θ)°
Reflections collected	3471	3405	4480	23414	32141	5536
Independent reflections (R_{int})	3313 (0.044)	3191 (0.018)	4248 (0.073)	5844 (0.023)	6691 (0.031)	5190 (0.092)
Observed reflections [$I_o > 3.0\sigma(I_o)$]	1743	2458	2420	3248	5640	2605
No. variables	226	210	246	331	462	232
P Factor	0.007	0.011	0.001	0.001	0.021	0.012
R	0.030	0.040	0.049	0.056	0.053	0.060
R′	0.028	0.046	0.054	0.081	0.068	0.063
Goodness of fit	1.16	2.42	1.85	2.68	3.18	1.77
Largest Δ/σ	0.02	0.04	0.01	0.01	0.06	0.08
Residual extrema/e Å^{-3}	0.15, −0.16	0.86, −0.91	0.84, −0.79	1.78, −0.49	0.93, −0.85	0.95, −0.79

* Details in common: Mo-Kα radiation (λ = 0.71073 Å); solution methods, direct methods (SIR 92); refinement method, full-matrix least squares; quantity minimized, $\Sigma w(|F_o| - |F_c|)^2$; weighting scheme, $w^{-1} = \sigma^2(F_o) + [(P/2)F_o]^2$; refinement program, TEXSAN.

(0.30 g, 0.67 mmol) in tetrahydrofuran (15 cm^3) at ambient temperature. The reaction mixture, upon stirring for 2 d, gave a brownish-yellow precipitate which was filtered off, washed with tetrahydrofuran (2 × 10 cm^3) and dried *in vacuo*. The brownish-yellow solid was dissolved in a minimum amount of dimethylformamide and filtered. Tetrahydrofuran diffused slowly into the yellow filtrate to give yellow crystals of **8**·$4C_3H_7NO$ which were filtered off and dried *in vacuo*. Yield: 0.21 g, 55%, yellow crystals, m.p. 240–242 °C (decomp.) (Found: C, 40.0; H, 4.5; N, 10.1. Calc. for $C_{48}H_{60}Cl_6N_{10}O_4P_2Pd_3$: C, 40.2; H, 4.2; N, 9.8%). IR (cm^{-1}, KBr): 3448s (br), 3100w, 2964w, 2804w, 1651vs, 1600m, 1508w, 1477m, 1435s, 1387m, 1338w, 1252w, 1106s, 1063w, 1000w, 853m, 817m, 747m, 719m, 690m, 664m, 600w, 541m, 523w and 487m. NMR [$(CD_3)_2SO$]: ^{31}P-{^1H}, δ 85.6 (s); ^{13}C-{^1H}, pyridinyl carbons, 122.6, 132.9 and 153.0; phenyl carbons of PPh_2, 129.0 (d, $J = 12.2$) and 132.6 (d, 12.2); dmf carbons, 30.7, 35.7 and 162.2; ^1H, NH protons, δ 9.36 (1 H, br, s), 9.60 (1 H, br, s), 10.52 (1 H, br, s) and 10.63 (1 H, br, s); pyridinyl and phenyl protons, 7.20–7.60 (14 H, br, m), 7.90 (8 H, m), 8.77 (4 H, br, s) and 8.94 (2 H, d, $J = 6.2$ Hz); dmf protons, 2.71 (12 H, s), 2.88 (12 H, s) and 7.94 (4 H, s).

***cis*-[Pd{(NC_5H_4)[(Ph_2PNH)C(=NH)]-4}{(NC_5H_4)[(Ph_2PNH)-C(=N)]-4}][BF_4] 9.** A solution of [$PdCl_2(PhCN)_2$] (0.46 g, 1.2 mmol) in tetrahydrofuran (10 cm^3) was added to a stirring solution of $\mathbf{L}^3$ (1.26 g, 2.8 mmol) in tetrahydrofuran (15 cm^3) at ambient temperature. The mixture after heating at 55 °C for 1 d gave a white precipitate which was filtered off, washed with tetrahydrofuran (2 × 10 cm^3), dissolved in methanol and filtered. Then an aqueous solution of NH_4BF_4 (0.50 g, 4.8 mmol) was added to the filtrate to give a white precipitate which was filtered off, washed with water (2 × 5 cm^3), dissolved in dimethylformamide and filtered. Tetrahydrofuran slowly diffused into the filtrate to give white crystals of **9**·C_3H_7NO which were filtered off and dried *in vacuo*. Yield: 0.84 g, 80%, white crystals, m.p. 240–242 °C (decomp.) (Found: C, 53.2; H, 4.4; N, 11.2. Calc. for $C_{39}H_{38}BF_4N_7OP_2Pd$: C, 53.5; H, 4.3; N, 11.2%). IR (cm^{-1}, in KBr): 3442s, 3381s, 3243m, 3052m, 2928w, 1649vs, 1588m, 1550w, 1506m, 1481s, 1435s, 1385m, 1349w, 1277w, 1123m, 1107vs, 1084vs, 1065m, 1024m, 997m, 849w, 826s, 806m, 743m, 719w, 707m, 693m, 660m, 553m, 533m, 506m, 495s and 474m. NMR [$(CD_3)_2SO$]: ^{31}P-{^1H}, δ 86.4 (s) and 91.5 (s); ^{13}C-{^1H}, pyridinyl and phenyl carbons, 121.7, 122.2, 128.3, 129.2 (br, s), 131.7 (br, s), 132.5 (br, s) and 150.8 (br, s); dmf carbons, 30.7, 35.7 and 162.3; ^1H, NH protons, 8.19 (1 H, br, s), 9.91 (1 H, br, s) and 10.58 (1 H, br, s); pyridinyl and phenyl protons, 7.35 (20 H, br, m), 7.86 (4 H, br, s), 8.77 (2 H, br, s) and 8.88 (2 H, br, s); dmf protons, 2.72 (3 H, s), 2.88 (3 H, s) and 7.94 (1 H, s). Positive-ion FAB mass spectrum: m/z 715 [$(M - BF_4)$ for ^{106}Pd].

***cis*-[Pt{(NC_5H_4)[(Ph_2PNH)C(=NH)]-4}{(NC_5H_4)[(Ph_2PNH)-C(=N)]-4}][BF_4] 10.** This compound was prepared in the same manner as described for compound **9**: [$PtCl_2(PhCN)_2$] (0.15 g, 0.3 mmol) and $\mathbf{L}^3$ (0.32 g, 0.7 mmol) were used. White crystals of **10**·C_3H_7NO were obtained. Yield: 0.22 g, 76%, white crystals, m.p. 240–242 °C (decomp.) (Found: C, 48.8; H, 3.9; N, 10.6. Calc. for $C_{39}H_{38}BF_4N_7OP_2Pt$: C, 48.6; H, 3.9; N, 10.2%). IR (cm^{-1}, in KBr): 3442s, 3381s, 3243m, 3052w, 2927w, 1649vs, 1588w, 1550w, 1506w, 1481s, 1435s, 1385w, 1349w, 1277w, 1107vs, 1084vs, 1065m, 1024m, 997w, 849w, 826s, 806m, 743m, 719w, 707w, 693m, 660w, 553w, 533m, 506m, 494s and 474m. NMR [$(CD_3)_2SO$]: ^{31}P-{^1H}, δ 68.1 ($J_{Pt-P} = 3036$) and 71.0 ($J_{Pt-P} = 3223$ Hz); ^{13}C-{^1H}, pyridinyl and phenyl carbons, 122.1 (br, s), 128.8 (br, s), 131.9 (br, m) and 150.6; dmf carbons, 30.7, 35.7 and 162.3; ^1H, NH protons, 10.58 (1 H, br, s), 11.06 (2 H, br, s); pyridinyl and phenyl protons, 7.32 (20 H, br, s), 7.91 (4 H, br, s) and 8.85 (4 H, br, s); dmf protons, 2.72 (3 H, s), 2.88 (3 H, s) and 7.94 (1 H, s). Positive-ion FAB mass spectrum: m/z 804 [$(M - BF_4)$ for ^{195}Pt].

X-Ray crystallography

All pertinent crystallographic data and other experimental details are summarised in Table 4. Intensity data of **1**,**4** and **10** were collected on a Rigaku AFC7R diffractometer, **7** on a Enraf-Nonius CAD4 diffractometer, **8** and **9** on a MAR research image plate scanner using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at room temperature. Data of **1**, **4**, **7** and **10** were corrected for Lorentz and polarization factors and absorption using the ψ-scan method. For **8** and **9**, 65 3° frames with an exposure time of 5 min per frame were used. Intensity data were corrected for Lorentz and polarization effects but not absorption. The structures were solved by a combination of direct methods (SIR 92)[9] and Fourier-difference techniques. The solutions were refined by full-matrix least-squares analysis on F until convergence was reached. For compounds **1**, **4**, **7**, **8** and **9**, all non-hydrogen atoms except atoms of the solvate molecule were refined anisotropically. For compound **10**, only the Pt and P atoms were refined anisotropically and the rest of the non-hydrogen atoms were refined isotropically. Hydrogen atoms on the nitrogen were located from Fourier-difference synthesis using low angle data (2θ < 30°) while other hydrogen atoms on the organic moieties were generated at their ideal positions (C−H 0.95 Å) and allowed to ride on their respective parent carbon atoms. These hydrogen atoms were assigned appropriate isotropic thermal parameters and included in the structure factor calculations but not in the refinement. All calculations were performed on a Silicon-Graphics computer using the program package TEXSAN.[10]

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