Revealing the diastereomeric nature of pincer terdentate nitrogen ligands 2,6-bis(arylaminomethyl)pyridine through coordination to palladium †

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Palladium complexes of formula [PdLCl]X (X = Cl **1**, BF$_4$ **2**) containing the pincer terdentate ligands L [L = 2,6-(ArNHCH$_2$)$_2$C$_5$H$_3$N (Ar = 4-MeC$_6$H$_4$ **1a** and **2a**, 4-MeOC$_6$H$_4$ **1b** and **2b**); L = 2,6-(4-MeC$_6$H$_4$-NMeCH$_2$)$_2$C$_5$H$_3$N **1c** and **2c**] have been synthesised as *cis–trans* diastereomeric mixtures. The chiral nature of both amine arms of the pincer ligands accounts for the mixtures of isomers. All the complexes show dynamic behavior assigned to conversion between diastereomers. A $\Delta G^{\ddagger}_{273}$ of 68.9 kJ mol^{-1} for **2a** and a $\Delta G^{\ddagger}_{273}$ of 65.8 kJ mol^{-1} for **2c** were found through complete DNMR line-shape analysis of the –CH$_2$– signals in the ^{1}H spectra. The *cis–trans* conversion requires the inversion of the pyramidal nitrogen of one of the coordinated amine arms. Two putative pathways have been proposed for such inversion: a) dissociation of one of the amine nitrogen atoms followed by inversion of the nitrogen atom and reformation of the nitrogen–palladium bond and b) deprotonation of one of the N–H bond leading to an amido intermediate which can reprotonate on the other side. Experimental evidence is given for both mechanisms. The structural characterization of **1a** is described.

Introduction

The interest in multidentate nitrogen-donor ligands and their use in homogeneous catalysis has increased in the last few years.[1–3] There are several recent examples of processes catalyzed by complexes bearing terdentate nitrogen-donor ligands such as hydroalkoxylation,[4] Suzuki coupling,[5] polymerization of ε-caprolactam,[6] oxidation of benzylic alcohol to benzaldehyde,[7] hydrogen peroxide decomposition,[8] olefin polymerization,[9–12] or alkene epoxidations.[13] Complexes involving terdentate nitrogen-donor ligands show interesting reactivity such as CO insertion in Pd–Me[1,14] bonds and alkene insertion in acyl–palladium bonds.[14,15] In some of these processes the ligands display dynamic behavior[16–18] that could be interesting for the study of the catalytic properties of these complexes, such as better stereoselective or chemoselective control of the reactions.[19–21] Terdentate nitrogen ligands are also of interest in the synthesis of rod-like extended materials[22] and in selective complexation reactions,[23] useful for the separation of actinides and lanthanides by solvent extraction.[24]

Here we report the synthesis, full characterization and ^{1}H NMR dynamic study in solution of palladium complexes with terdentate ligands 2,6-bis(arylaminomethyl)pyridine. The pyramidal nature of the nitrogen atoms of the amine arms of these pincer ligands introduce stereochemical features onto square-planar complexes which are absent in the related terdentate pyridine-diimine ligands.[17,25]

Results and discussion

Synthesis of terdentate ligands

As shown in Scheme 1, the terdentate ligands 2,6-bis(aryl-
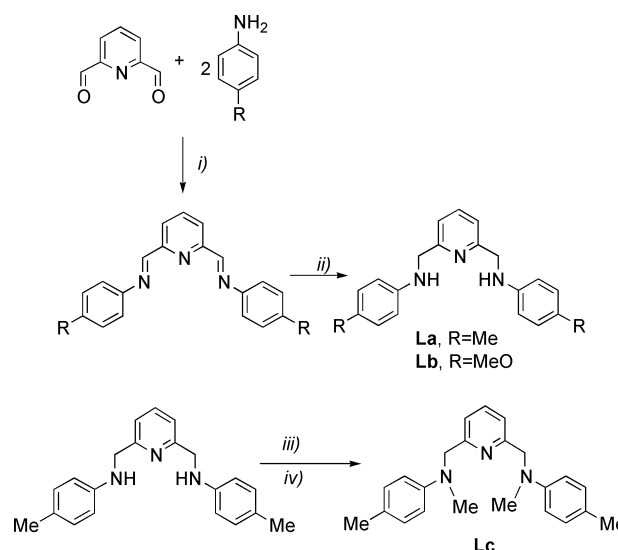
Scheme 1 Synthesis of terdentate ligands. i) toluene, reflux; ii) NaBH$_4$, methanol; iii) 2.6 equiv. n-BuLi, THF; iv) 2.6 equiv. MeI.

aminomethyl)pyridine were prepared in two steps. The condensation in toluene of ArNH$_2$ (Ar = 4-MeC$_6$H$_4$, **La**; 4-MeOC$_6$H$_4$, **Lb**) with 2,6-bis(carbaldehyde)pyridine afforded

the corresponding 2,6-bis(aryliminomethyl)pyridine. Reduction of these terdentate imines with $NaBH_4$ and further hydrolysis afforded good yields of the terdentate amine ligands.

Upon treatment with n-BuLi and then with methyl iodide the amine 2,6-bis(*p*-tolylaminomethyl)pyridine was converted into the N-methylated product, **Lc**.

Synthesis of complexes [PdLCl]X {X = Cl 1, BF$_4$ 2; L = 2,6-(ArNHCH$_2$)$_2$C$_5$H$_3$N (Ar = 4-MeC$_6$H$_4$ 1a and 2a, 4-MeOC$_6$H$_4$ 1b and 2b); L = 2,6-(4-MeC$_6$H$_4$NMeCH$_2$)$_2$C$_5$H$_3$N 1c and 2c}

As shown in Scheme 2, addition of a solution of the amine in
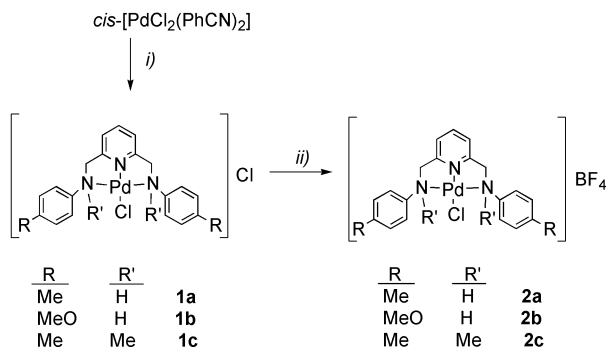
Scheme 2 Synthesis of complexes. i) terdentate ligand, CH$_2$Cl$_2$; ii) TlBF$_4$, methanol.

dichloromethane to a solution of *cis*-[PdCl$_2$(PhCN)$_2$] in dichloromethane led to substitution of the weakly coordinating benzonitrile ligand by the chelating amine ligand in an almost quantitative yield. Treatment of complexes **1a–c** in methanol with TlBF$_4$ afforded the corresponding salts of tetrafluoroborate **2a–c**. Complexes **1a** and **1b** were obtained as yellow solids which are poorly soluble in acetone, dichloromethane and chloroform, slightly soluble in methanol and ethanol and soluble in dimethylsulfoxide. Replacement of N–H by N–Me groups led to higher solubility of complex **1c** when compared with that of **1a** and **1b**. Replacement of the chloride counterion by tetrafluoroborate led also to higher solubility of complexes **2a–c** in common solvents when compared with that of complexes **1a–c**.

Structural characterization of [Pd{2,6-(4-MeC$_6$H$_4$NHCH$_2$)$_2$-C$_5$H$_3$N}Cl]Cl 1a and stereochemistry of ligands and complexes

A single crystal of **1a** suitable for X-ray diffraction was obtained by layering a solution of the compound in ethanol with n-hexane. The corresponding ORTEP diagram is shown in Fig. 1. Selected bond lengths and angles are collected in Table 1.

The palladium atom has a distorted square-planar geometry. The chelating ligand is acting as an N,N,N-chelate and this
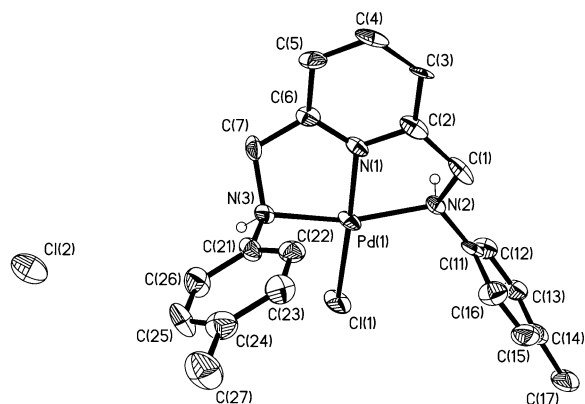
Fig. 1 ORTEP[34] drawing of [Pd{2,6-(4-MeC$_6$H$_4$NHCH$_2$)$_2$C$_5$H$_3$N}-Cl]Cl **1a**. Only hydrogen atoms attached to N(2) and N(3) are shown for clarity.

Table 1 Selected bond distances (Å) and angles (°) for complex **1a**

Pd(1)–N(1)	1.952(8)	Pd(1)–N(3)	2.059(9)
Pd(1)–N(2)	2.068(9)	Pd(1)–Cl(1)	2.295(2)
N(1)–Pd(1)–N(3)	80.8(4)	N(1)–Pd(1)–N(2)	81.2(4)
N(3)–Pd(1)–N(2)	162.0(3)	N(1)–Pd(1)–Cl(1)	177.7(3)
N(3)–Pd(1)–Cl(1)	97.2(2)	N(2)–Pd(1)–Cl(1)	100.9(2)

closes the angles N(3)–Pd(1)–N(1) and N(1)–Pd(1)–N(2) at about 81.0°, opening the angles N(3)–Pd(1)–Cl(1) and N(2)–Pd(1)–Cl(1) at about 99.0°. In this structure, the *p*-tolyl groups are oriented *cis* with regard to the coordination plane. There are two hydrogen bonds between the Cl(2) and N(2) and N(3) atoms, through the H(2) and H(3) hydrogen atoms, respectively. Simple molecular models show that this arrangement is sterically more constrained than *trans*, leading to close contact between the aryl groups. In order to avoid this contact both aminic nitrogen atoms undergo a distortion in the hybridization leading to an intermediate situation between sp^3 and sp^2 with more sp^3 character. This geometric distortion, that is stronger in the solid state for N(2), can be calculated by addition of the values of the bonding angles around the nitrogen atoms. These values are 342.0° for N(2) and 332.6° for N(3) both of them between the theoretical 360° for sp^2 hybridization and 328.2° for sp^3.

In spite of the square-planar geometry of the complexes here described, the geometrical requirements of the terdentate ligands and their symmetry (C_s or C_2) supply interesting stereochemical features. The molecular structure shown in Fig. 1 corresponds to a chiral complex with C_1 symmetry. The lack of a plane of symmetry perpendicular to the coordination plane is due to the non-planarity of the chelate rings. From molecular models it is clear that both chelating rings have to adopt the same conformation (*i.e.* δδ or λλ) to keep the planarity of the pyridine ring. As a consequence of such a requirement C(1) and C(7) lie on opposite sides of the coordination plane. The *cis* disposition of the aryl groups implies that N(2) and N(3) must to have different R,S configurations. The complex shown in Fig. 1 has Rδ,Sδ configuration and since the space group P2$_1$/n is centric, both enantiomers Rδ,Sδ and Rλ,Sλ are present in equal numbers in the unit cell.

The simple structural behavior in the solid state contrasts with the behavior in solution. Whereas only one conformer (Rδ,Sδ) is expected for *cis*-**1** in solution (the conformer Rδ,Sλ is sterically forbidden as mentioned above), for *trans*-**1** two conformers can be expected (Rδ,Rδ and Rλ,Rλ) although the barriers for their exchange should be very small and the unobserved transformation very fast even at low temperatures.[26,27] However, the *cis–trans* exchange can be followed by dynamic NMR line-shape analysis as discussed below.

Structure and dynamic behavior in solution of complexes 1 and 2

The ^{1}H NMR spectra of complexes **1a** and **1b** in deuterated dimethylsulfoxide show broad and complicated signals in the methylene region between 4.5 and 5.5 ppm (the –CH$_2$– region) suggesting that we have two species in solution and that probably these species are in equilibrium. The highly coordinating ability of the solvent can be responsible, at least in part, for such less informative spectra. The chloride counterion has coordinating ability and it can also account for the origin of the uncertainty in interpreting the spectra. In order to gain more information about the structure of the complexes in solution we decided upon the substitution of the chloride counterion by tetrafluoroborate and this met with success.

On one hand, the higher solubility of complexes **2a** and **2b** allows the use of the less coordinating solvent acetone but on the other, the BF$_4^-$ counterion is not prone to participate in substitution processes whereas chloride can participate, as has been reported in related cases.[17] ^{1}H NMR spectra were recorded

for **2a** and **2b** using both deuterated dimethylsulfoxide and deuterated acetone. The ^{1}H NMR spectra of the methylene region for complex **2a** in deuterated dimethylsulfoxide and acetone are shown in Fig. 2.
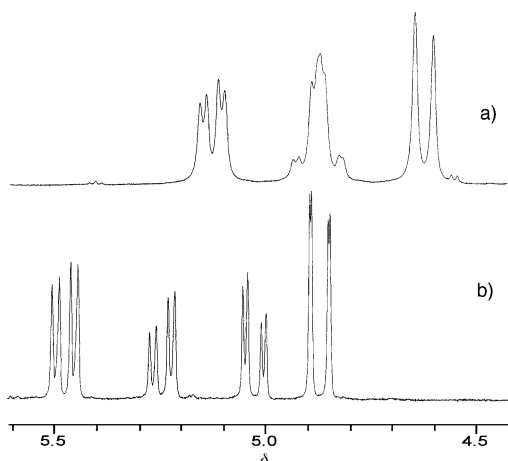
Fig. 2 Methylene region of the ^{1}H NMR spectra (400 MHz) of [Pd{2,6-(4-MeC$_6$H$_4$NHCH$_2$)$_2$C$_5$H$_3$N}Cl](BF$_4$) (**2a**) at room temperature in a) DMSO-d$_6$ and b) CD$_3$COCD$_3$.

The spectra recorded in DMSO-d$_6$ show a better resolution for **2a** and **2b** than for **1a** and **1b** indicating that the chloride counterion in complexes **1a** and **1b** is likely to be involved in substitution reactions. The spectrum of **2a** in deuterated acetone displays a pattern of four double doublets (sixteen signals) assigned to two ABX(–CH$_2$–NH–) systems. A COSY experiment confirms that the external set of two double doublets belong to one compound, and the internal set of two double doublets belong to the other compound. The ^{1}H NMR spectra corresponds to a mixture of *cis* and *trans* isomers of **2a** where *cis* and *trans* refers to the disposition of the aryl groups with regard to the coordination plane. Analysis of the integral values gives an isomeric ratio of 1.5 : 1 but, with the NMR information, it is not possible to distinguish which is the major isomer (*cis* or *trans*).

Variable temperature ^{1}H NMR spectra of complex **2a** in a mixture of deuterated acetone–dimethylsulfoxide are collected in Fig. 3. The change of the signal shape can be explained as a
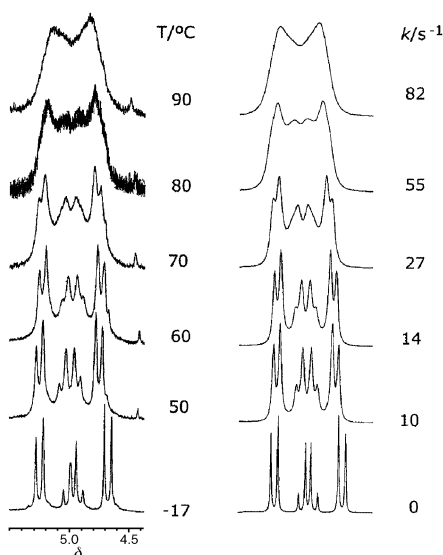
consequence of a *cis–trans* transformation that is faster at higher temperatures. Spectral simulation afforded the values of the kinetic constants (major to minor isomer) at different temperatures.[28] The correlation between the temperature and the kinetic constants $k_{\text{major–minor}}$ gave the activation parameters from the Eyring representation as $\Delta H^{\ddagger} = 46.5(2.5)$ kJ mol^{-1}, $\Delta S^{\ddagger} = -82(7)$ J mol^{-1} K^{-1} and $\Delta G^{\ddagger}_{273} = 68.9(4.4)$ kJ mol^{-1}.

The influence of DMSO-d$_6$ on the exchange process has been studied for complex **2a** in CD$_3$COCD$_3$ at 20 °C. Addition of a small amount of DMSO-d$_6$ (5%) leads to an increase of the exchange rate ($k = 6$ s^{-1}). Further addition of DMSO-d$_6$ does not increase this value.

In light of the results obtained for **2** we suggest that the ^{1}H NMR spectra of **1** correspond to the same behavior, but their low solubility in non-freezing solvents prevented us performing similar dynamics studies for **1**.

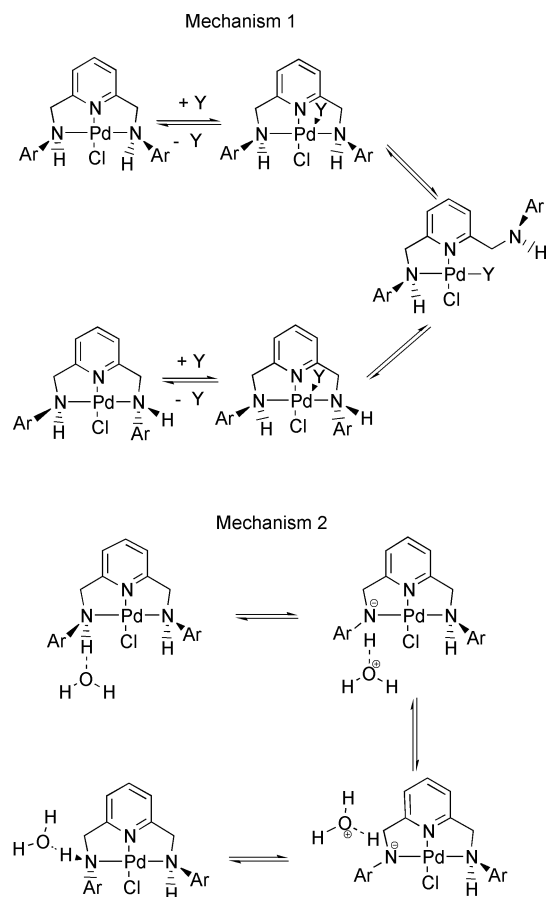Attempts to grow crystals of **2** for X-ray diffraction studies were unsuccessful.

When N-methylated complexes **1c** and **2c** were studied we could see a similar behavior to that reported above for **1a** and **1b** and **2a** and **2b**. The higher solubility of complex **1c**, compared to **1a** and **1b**, allows the use of mixtures of deuterated acetone with deuterated dimethylsulfoxide whereas for complexes **1a** and **1b** pure DMSO-d$_6$ had to be used in order to dissolve the solids. Fig. 4 shows the variation of the resonances of the methylenic protons with temperature for complex **2c**.
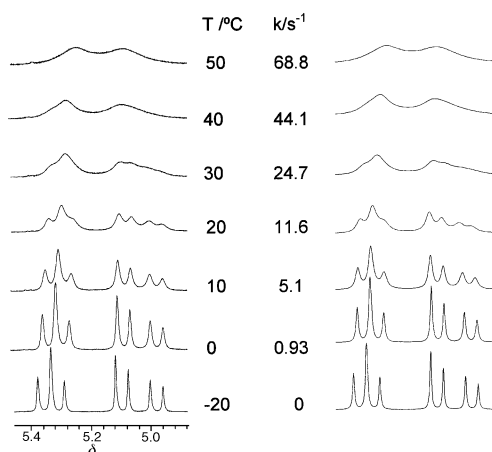
Fig. 4 Methylene region of the variable-temperature ^{1}H NMR spectra (400 MHz) of [Pd{2,6-(4-MeC$_6$H$_4$NMeCH$_2$)$_2$C$_5$H$_3$N}Cl](BF$_4$) (**2c**) in CD$_3$COCD$_3$ in the temperature range −20 to 50 °C.

Complex **1c** also shows broadening of the signals at high temperatures (likely due to dynamic behavior), but the signals were too broad to develop an accurate calculation. Again, the substitution of the chloride counterion with BF$_4^-$ led to more informative spectra for **2c**. At 253 K it is possible to see two doublets at 4.98 and 5.10 ppm and an apparent triplet at 5.35 ppm. This triplet is actually two doublets with two signals overlapped. Upon heating the sample to 323 K the signals broaden and finally resolve into two broad signals centered at 5.18 ppm. The lineshape analysis carried out, under the same conditions as for **2a**, gave the activation parameters from the Eyring representation as $\Delta H^{\ddagger} = 59.8(3.8)$ kJ mol^{-1}, $\Delta S^{\ddagger} = -22(12)$ J mol^{-1} K^{-1} and $\Delta G^{\ddagger}_{273} = 65.8(7.1)$ kJ mol^{-1}, (standard deviations in parentheses).

In complexes with an N–H bond (**1a** and **1b** and **2a** and **2b**) two mechanisms, which are shown in Scheme 3, can be invoked to explain the *cis–trans* isomerization. The first mechanism involves dissociation of one of the amine nitrogens which may be initiated by associative coordination of chloride or solvent in complexes **1** or by solvent alone in complexes **2**.[29] The next steps are the inversion of the nitrogen atom and the reformation of the nitrogen–palladium bond. The second mechanism starts with a *cis* isomer that loses a proton from a coordinated amine

Fig. 3 Methylene region of the ^{1}H NMR spectra (300 MHz) of [Pd{2,6-(4-MeC$_6$H$_4$NHCH$_2$)$_2$C$_5$H$_3$N}Cl](BF$_4$) (**2a**) in DMSO-d$_6$–CD$_3$COCD$_3$ (0.7 : 0.3) in the temperature range −17 to 90 °C. The N–H signal was irradiated.

Mechanism 1

Mechanism 2

Scheme 3

to form an amido complex. This spontaneous deprotonation can be helped by the presence of water as the deuterated solvents used always showed small amounts of water in the spectra. After this deprotonation the nitrogen atom can be reprotonated and, depending on the side of reprotonation, it generates the *cis* or the *trans* isomer. It has been observed that the addition of 0.6 equivalents of proton sponge to a solution of **2a** in DMSO-d_6–CD$_3$COCD$_3$ (0.7 : 0.3) led to a seven-fold increase of the exchange rate which supports the second mechanism.

An interesting observation is that the chloride counterion broadens the signals of the methylene groups compared to the BF$_4^-$ counterion. This fact can be related to a faster process in complexes with chloride as counterion supporting the associative mechanism 1. The calculated values of the entropy of activation (they are negative) support the first mechanism as well, but mechanism 2 can not be ruled out for those complexes containing N–H bonds. In the presence of base, mechanism 2 dominates over mechanism 1 but both pathways are involved in these processes. Obviously, only mechanism 1 is possible for complexes **1c** and **2c**.

Conclusion

Chloro-palladium square-planar complexes containing pincer terdentate pyridine-diamine ligands 2,6-bis(arylaminomethyl)-pyridine have been synthesised and characterized as *cis–trans* diastereomeric mixtures. The geometry depends on the arrangement of the aryl groups with regard to the coordination plane. Both diastereomers are chiral. The chirality in the *cis* isomers arises from the non-planarity of the chelate rings. The mixtures of isomers show dynamic behavior due to *cis–trans* conversion. Two mechanisms are possible for such conversion. The first involves nitrogen dissociation, which may be initiated by chloride or solvent, subsequent inversion of the uncoordinated nitrogen and reformation of the nitrogen–palladium bond. The

second involves deprotonation of one of the N–H bonds and reprotonation on the other side with inversion of the nitrogen atom.

Experimental

General

All manipulations were carried out using standard Schlenk techniques. Solvents were dried and stored under nitrogen. The starting compounds 2,6-pyridinedicarbaldehyde[30] and *cis*-[PdCl$_2$(PhCN)$_2$][31] were prepared according to the literature. All other starting chemicals were used as commercially obtained.

^{1}H NMR spectra were recorded on either Bruker ARX 300, Bruker AC 80 or Varian Unity Inova-400 spectrometers. Chemical shifts are reported in ppm relative to SiMe$_4$ (TMS) as external standard. Variable-temperature ^{1}H NMR spectra were obtained on Bruker ARX 300 and Varian Unity Inova-400 instruments, the variable-temperature units were calibrated using methanol in methanol-d_4 for low temperatures and ethylene glycol in DMSO-d_6 for high temperatures. Kinetic data were derived from band shape analysis of ^{1}H NMR spectra using a version of the standard DNMR program[28] for [Pd{2,6-(4-MeC$_6$H$_4$NHCH$_2$)$_2$C$_5$H$_3$N}Cl](BF$_4$) **2a** and a version of the gNMR program[32] for [Pd{2,6-(4-MeC$_6$H$_4$NMeCH$_2$)$_2$C$_5$H$_3$N}-Cl](BF$_4$) **2c**.† Activation parameters were calculated from a least-squares fit of the Arrhenius and Eyring plots. Quoted errors are statistical errors on scattering of the rate constants around the straight line only. IR spectra were recorded as KBr disks on a Nicolet Impact 410 instrument, elemental analyses were made on a Leco CHNS 932, GC analysis was on a Hewlett-Packard serie II chromatograph and mass spectra were obtained on a Hewlett-Packard 5791A with a mass selective detector.

Synthesis

2,6-Bis[{*N*-(4-methylphenyl)imino}methyl]pyridine, 2,6-(4-MeC$_6$H$_4$NCH)$_2$C$_5$H$_3$N. A 250 ml flask equipped with a stir bar and a Dean–Stark glassware was charged with 2,6-pyridine-dicarbaldehyde (2 g, 14.8 mmol), *p*-toluidine (*p*-methylaniline) (3.19 g, 29.6 mmol) and a catalytic amount of *p*-toluenesulfonic acid in toluene (50 cm^3). It was refluxed for 2 h.[33] The solution was evaporated to dryness. The precipitate was recrystallized in hexane and dried *in vacuo* yielding a white solid product. (3.66 g, 79%). ^{1}H NMR (80 MHz, CDCl$_3$): δ 8.68 (s, 2H, N= CH), 8.26 (2H, m, py H$^{3–5}$), 7.88 (1H, m, py H^4), 7.23 (8H, m, Ar), 2.37 (6H, s, Me); IR (KBr): $v_{C=N}$ = 1624 cm^{-1}; Found: C, 80.12; H, 6.05; N, 13.09. C$_{21}$H$_{19}$N$_3$ requires C, 80.48; H, 6.11; N, 13.41%.

2,6-Bis[{*N*-(4-methoxyphenyl)imino}methyl]pyridine, 2,6-(4-MeOC$_6$H$_4$NCH)$_2$C$_5$H$_3$N. The synthesis was carried out according to the procedure followed above for 2,6-(4-MeC$_6$H$_4$NCH)$_2$-C$_5$H$_3$N. ^{1}H NMR (80 MHz, CDCl$_3$): δ 8.70 (s, 2H, N=CH), 8.25 (2H, m, py H$^{3–5}$), 7.89 (1H, m, py H^4), 7.16 (8H, m, Ar), 3.64 (6H, s, MeO); IR (KBr): $v_{C=N}$ = 1625 cm^{-1}; Found: C, 72.79; H, 5.85; N, 11.88. C$_{21}$H$_{19}$N$_3$O$_2$ requires C, 73.03; H, 5.54; N, 12.17%.

2,6-Bis[{*N*-(4-methylphenyl)amino}methyl]pyridine, 2,6-(4-MeC$_6$H$_4$NHCH$_2$)$_2$C$_5$H$_3$N, La. To a stirred solution of 2,6-(4-MeC$_6$H$_4$NCH)$_2$C$_5$H$_3$N (2.44 g, 9.86 mmol) in methanol (60 cm^3) at 40–50 °C was slowly added NaBH$_4$ (0.93 g, 24.6 mmol).[33] The solution was then refluxed for 1.5 h and, after cooling, water (50 cm^3) was added. The methanol was removed in a rota-vapor. The organic product was extracted with diethyl ether (3 × 30 cm^3) and dried over anhydrous MgSO$_4$. The filtered solution was evaporated to dryness. The residue was recrystallized from dichloromethane–hexane (1 : 1) and dried *in vacuo* yielding a pale yellow solid product (2.65 g, 84.76%). ^{1}H NMR (80 MHz, CDCl$_3$): δ 7.57 (m, 1H, py H^4), 7.19 (m, 2H, py

H$^{3-5}$), 6.79 (m, 8H, Ar), 4.43 (br, 6H, –CH$_2$ + NH), 2.24 (s, 6H, Me); ^{13}C{^{1}H} NMR (52.3 MHz, CDCl$_3$): δ 158.4, 145.8, 136.9, 129.6, 126.7, 119.7, 113.2, 49.6, 20.2; IR (KBr): $\nu_{(N-H)}$: 3351 cm^{-1}; Found: C, 79.21; H, 7.16; N, 13.24. C$_{21}$H$_{23}$N$_3$ requires C, 79.46; H, 7.30; N, 13.27%.

2,6-Bis[{*N*-(4-methoxyphenyl)amino}methyl]pyridine, 2,6-(4-MeOC$_6$H$_4$NHCH$_2$)$_2$C$_5$H$_3$N, Lb. The synthesis was carried out according to the procedure followed above for 2,6-(4-MeC$_6$H$_4$NHCH$_2$)$_2$C$_5$H$_3$N. Yield 84% of a pale yellow solid. ^{1}H NMR (80 MHz, CDCl$_3$): δ 7.58 (m, 1H, py H^4), 7.19 (m, 2H, py H$^{3-5}$), 6.70 (m, 8H, Ar), 4.41 (a, 6H, –CH$_2$), 3.97 (br, 2H, NH), 2.24 (s, 6H, Me); ^{13}C{^{1}H} NMR (52.3 MHz, CDCl$_3$,): δ 158.5, 152.4, 142.3, 137.0, 119.9, 115.0, 114.4, 55.8, 50.3; IR (KBr): $\nu_{(N-H)}$: 3388 cm^{-1}; Found: C, 71.90; H, 6.37; N, 11.01. C$_{21}$H$_{23}$N$_3$O$_2$ requires C, 72.18; H, 6.63; N, 12.03%.

2,6-Bis[{*N*-(4-methylphenyl)-*N*-methylamino}methyl]pyridine, 2,6-(4-MeC$_6$H$_4$NMeCH$_2$)$_2$C$_5$H$_3$N, Lc. To a stirred solution of 2,6-(4-MeC$_6$H$_4$NHCH$_2$)$_2$C$_5$H$_3$N (3.6 g, 11.3 mmol) at −25 °C in dry THF (40 cm^3) were added 29.33 mmol of n-BuLi. The solution was allowed to warm to room temperature and stirred for an additional hour. On cooling the solution to 0 °C 4.0 g (28.25 mmol) of MeI was added and the solution was allowed to warm to room temperature again. The solution was evaporated to dryness and the crude product was purified by flash column chromatography (AcOEt–hexane, 1 : 5) to give 2.6 g of pale brown solid (68%). ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.49 (t, 1H, py H^4), 7.02 (m, 2H, py H$^{3-5}$), 6.85 (m, 8H, Ar), 4.63 (s, 4H, –CH$_2$), 3.10 (s, 6H, N–Me), 2.26 (s, 6H, Me); ^{13}C NMR (52.3 MHz, CDCl$_3$): δ 159.6, 147.4, 137.6, 129.9, 126.0, 119.1, 112.6, 59.3, 39.4, 20.5; *m/z* 345 (M$^+$, 11.6), 226 (100), 134 (14.1), 121 (22.5), 120 (19.7) 107 (11); Found: C, 79.61; H, 7.86; N, 11.94. C$_{23}$H$_{27}$N$_3$ requires C, 79.96; H, 7.88; N, 12.16 %.

[Pd{2,6-(4-MeC$_6$H$_4$NHCH$_2$)$_2$C$_5$H$_3$N}Cl]Cl 1a. To a solution of *cis*-[PdCl$_2$(PhCN)$_2$] (180 mg, 0.47 mmol) in dichloromethane (20 cm^3) was slowly added the terdentate ligand 2,6-(4-MeC$_6$H$_4$NHCH$_2$)$_2$C$_5$H$_3$N (148 mg, 0.47 mmol). The mixture was stirred at 20 °C for 2 h and then hexane was added to induce precipitation. Washing the residue with hexane (2 × 10 cm^3) and diethyl ether (2 × 15 cm^3) and drying *in vacuo* yielded **1a** as a yellow solid (198 mg, 85%). ^{1}H NMR (300.13 MHz, DMSO-d$_6$, rt):‡ δ 9.02 (br, 2H′, NH), 8.94 (d, 2H, $J_{CH_AH_B-NH}$ 6.05 Hz, NH), 8.25 (m, 1H + 1H′, py H^4), 7.68 (m, 2H + 2H′, py H$^{3-5}$), 7.13 (m, 8H + 8H′, Ar), 5.13 (dd, 2H, $J_{H_A-H_B}$ 17.37 Hz, $J_{CH_AH_B-NH}$ 6.05 Hz, CH$_A$$H_B$), 4.83 (br, 4H′, C$H_AH_B$), 4.62 (d, 2H, $J_{H_A-H_B}$ 17.37 Hz, CH_AH$_B$), 2.22 (s, 6H + 6H′, Me); IR (KBr): $\nu_{(NH)}$ = 3436 cm^{-1}; Found: C, 50.71; H, 4.75; N, 8.60. PdC$_{21}$H$_{23}$N$_3$Cl$_2$ requires C, 50.98; H, 4.69; N, 8.49%.

[Pd{2,6-(4-MeOC$_6$H$_4$NHCH$_2$)$_2$C$_5$H$_3$N}Cl]Cl 1b. The synthesis was carried out according to the procedure followed above for **1a**. Yield 88% of a yellow solid. ^{1}H NMR (300.13 MHz, DMSO-d$_6$, rt):‡ δ 9.18 (br, 2H′, NH), 9.04 (d, 2H, $J_{CH_AH_B-NH}$ 6.31 Hz, NH), 8.22 (m, 1H + 1H′, py H^4), 7.66 (m, 2H + 2H′, py H$^{3-5}$), 7.06 (m, 8H′, Ar), 7.03 (m, 8H, Ar), 5.08 (dd, 2H, $J_{H_A-H_B}$ 17.56 Hz, $J_{CH_AH_B-NH}$ 6.31 Hz, CH$_A$$H_B$), 4.83 (br, 4H′, C$H_AH_B$), 4.60 (d, 2H, $J_{H_A-H_B}$ 17.56 Hz, CH_AH$_B$), 3.69 (s, 6H + 6H′, MeO); IR (KBr): $\nu_{(N-H)}$ 3456 cm^{-1}; Found: C, 47.49; H, 4.77; N, 7.96. C$_{21}$H$_{23}$Cl$_2$N$_3$O$_2$Pd requires C, 47.88; H, 4.40; N, 7.98%.

[Pd{2,6-(4-MeC$_6$H$_4$NHCH$_2$)$_2$C$_5$H$_3$N}Cl](BF$_4$) 2a. To a solution of **1a** (72 mg, 0.145 mmol) in methanol (50 cm^3) was added TlBF$_4$ (42.4 mg, 0.145 mmol). A white precipitate (TlCl) was

‡ The ^{1}H NMR spectra of complexes **1** and **2** correspond to the presence of two species as discussed in the text. Protons are reported as H (major isomer) and H′(minor isomer).

formed instantaneously. After filtering the solution through Celite the methanol was evaporated to dryness. The precipitate was recrystallized from dichloromethane–hexane (1 : 1). The resulting precipitate was filtered off, washed with hexane (2 × 10 cm^3) and diethyl ether (2 × 15 cm^3) and dried *in vacuo* yielding **2a** as a yellow solid (77.6 mg, 98%). ^{1}H NMR (399.9 MHz, CD$_3$COCD$_3$, rt):‡ δ 8.35 (t, 1H, $J_{H^4-H^{3-5}}$ 7.9 Hz, py H^4), 8.29 (t, 1H′, $J_{H^4-H^{3-5}}$ 7.9 Hz, py H^4), 7.98 (br, 2H + 2H′, NH), 7.84 (d, 2H, $J_{H^4-H^{3-5}}$ 7.9 Hz, py H$^{3-5}$), 7.77 (d, 2H′, $J_{H^4-H^{3-5}}$ 7.9 Hz, py H$^{3-5}$), 7.37–7.10 (m, 8H + 8H′, Ar), 5.46 (dd, 2H, $J_{H_A-H_B}$ 17.73 Hz, $J_{CH_AH_B-NH}$ 6.93 Hz, CH$_A$$H_B$), 5.23 (dd, 2H′, $J_{H_A-H_B}$ 17.60 Hz, $J_{CH_AH_B-NH}$ 6.45 Hz, CH$_A$$H_B$), 5.01 (dd, 2H′, $J_{H_A-H_B}$ 17.60 Hz, $J_{CH_AH_B-NH}$ 4.71 Hz, CH_AH$_B$), 4.85 (dd, 2H, $J_{H_A-H_B}$ 17.73 Hz, $J_{CH_AH_B-NH}$ 1.72 Hz, CH_AH$_B$), 2.28 (s, 6H, Me), 2.26 (s, 6H′, Me); IR (KBr): $\nu_{(N-H)}$ 3426, $\nu_{(B-F)}$ 1084 cm^{-1}; Found: C, 45.55; H, 4.36; N, 7.62. PdC$_{21}$H$_{23}$N$_3$ClBF$_4$ requires C, 46.19; H, 4.25; N, 7.69%.

[Pd{2,6-(4-MeOC$_6$H$_4$NHCH$_2$)$_2$C$_5$H$_3$N}Cl](BF$_4$) 2b. The synthesis was carried out according to the procedure followed above for **2a**. Yield 79% of a yellow solid. ^{1}H NMR (399.9 MHz, CD$_3$COCD$_3$, rt):‡ δ 8.35 (t, 1H, $J_{H^4-H^{3-5}}$ 7.9 Hz, py H^4), 8.28 (t, 1H′, $J_{H^4-H^{3-5}}$ 7.9 Hz, py H^4), 8.02 (br, 2H′, NH), 7.96 (br, 2H, NH), 7.83 (d, 2H, $J_{H^4-H^{3-5}}$ 7.9 Hz, py H$^{3-5}$), 7.76 (d, 2H′, $J_{H^4-H^{3-5}}$ 7.9 Hz, py H$^{3-5}$), 7.46–6.83 (m, 8H + 8H′, Ar), 5.47 (dd, 2H, $J_{H_A-H_B}$ 17.8 Hz, $J_{CH_AH_B-NH}$ 6.6 Hz, CH$_A$$H_B$), 5.23 (dd, 2H′, $J_{H_A-H_B}$ 17.70 Hz, $J_{CH_AH_B-NH}$ 5.5 Hz, CH$_A$$H_B$), 4.99 (dd, 2H′, $J_{H_A-H_B}$ 17.70 Hz, $J_{CH_AH_B-NH}$ 4.00 Hz, CH_AH$_B$), 4.85 (d, 2H, $J_{H_A-H_B}$ 17.80 Hz, CH_AH$_B$), 3.78 (s, 6H, MeO), 3.76 (s, 6H′, MeO); IR (KBr): $\nu_{(N-H)}$ 3426, $\nu_{(B-F)}$ 1083 cm^{-1}; Found: C, 43.47; H, 4.26; N, 7.31. PdC$_{21}$H$_{23}$N$_3$O$_2$ClBF$_4$ requires C, 43.63; H, 4.01; N, 7.27%.

[Pd{2,6-(4-MeC$_6$H$_4$NMeCH$_2$)$_2$C$_5$H$_3$N}Cl]Cl 1c. To a solution of *cis*-[PdCl$_2$(PhCN)$_2$] (333 mg, 0.87 mmol) in dichloromethane (20 cm^3) was slowly added 2,6-(4-MeC$_6$H$_4$NMeCH$_2$)$_2$C$_5$H$_3$N (300 mg, 0.87 mmol). The mixture was stirred at 20 °C for 4 h at which point hexane was added to induce precipitation. Washing the residue with hexane (2 × 10 cm^3) and diethyl ether (2 × 15 cm^3) and drying *in vacuo* yielded **1c** as a yellow solid (310 mg, 71%). ^{1}H NMR (399.9 MHz, CDCl$_3$, rt):‡ δ 8.20–6.05 (broad and unresolved, 11H + 11H′, H^4, H$^{3-5}$, Ar), 5.04 (br, 4H + 4H′, –CH$_2$), 3.22 (s, 6H, NMe), 3.16 (s, 6H′, NMe). 2.25 (s, 6H′, Me), 2.18 (s, 6H, Me); Found: C, 52.64; H, 5.23; N, 8.08. C$_{23}$H$_{27}$Cl$_2$N$_3$Pd requires C, 52.84; H, 5.21; N, 8.04%.

[Pd{2,6-(4-MeC$_6$H$_4$NMeCH$_2$)$_2$C$_5$H$_3$N}Cl](BF$_4$) 2c. To a solution of **1c** (150 mg, 0.28 mmol) in acetone (75 cm^3) was added TlBF$_4$ (83.5 mg, 0.28 mmol). A white precipitate (TlCl) was formed instantaneously. After filtering the solution though Celite and concentration of the filtrate hexane was added to induce precipitation. The resulting precipitate was filtered off, washed with hexane and dried *in vacuo* yielding **2c** as a yellow solid (99 mg, 62%). ^{1}H NMR (399.9 MHz, CD$_3$COCD$_3$, 253 K):‡ δ 8.34 (t, 1H, $J_{H^4-H^{3-5}}$ 8.0 Hz, py H^4), 8.31 (t, 1H′, $J_{H^4-H^{3-5}}$ 8.1 Hz, py H^4), 7.87 (d, 2H, $J_{H^4-H^{3-5}}$ 8.0 Hz, py H$^{3-5}$), 7.79 (d, 2H′, $J_{H^4-H^{3-5}}$ 8.1 Hz, py H$^{3-5}$), 7.77–7.22 (m, 8H + 8H′, Ar), 5.36 (d, 2H, $J_{H_A-H_B}$ 17.52 Hz, CH$_A$$H_B$), 5.31 (d, 2H′, $J_{H_A-H_B}$ 17.40 Hz, CH$_A$$H_B$), 5.10 (d, 2H, $J_{H_A-H_B}$ 17.52 Hz, CH_AH$_B$), 4.98 (d, 2H′, $J_{H_A-H_B}$ 17.40 Hz, CH_AH$_B$), 3.38 (s, 6H, NMe), 3.29 (s, 6H′, NMe), 2.30 (s, 6H, Me), 2.29 (s, 6H′, Me); IR (KBr): $\nu_{(B-F)}$ 1056 cm^{-1}; Found: C, 48.04; H, 4.83; N, 7.22. PdC$_{23}$H$_{27}$N$_3$ClBF$_4$ requires C, 48.11; H, 4.74; N, 7.32%.

Crystal structure of [Pd{2,6-(4-MeC$_6$H$_4$NHCH$_2$)$_2$C$_5$H$_3$N}Cl]Cl 1a

The molecular structure of **1a** was determined by a single-crystal X-ray diffraction study. Structural and refinement details are given in Table 2.

Table 2 Crystal data and structure refinement for **1a**

Empirical formula	$C_{21}H_{23}Cl_2N_3Pd$
FW	494.73
T/K	143
$\lambda/\text{Å}$	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
$a/\text{Å}$	13.731(2)
$b/\text{Å}$	9.709 (1)
$c/\text{Å}$	17.230(2)
$\beta/°$	110.188(2)
$V/\text{Å}^3$	2156.0(5)
Z	4
$\rho_{calc}/\text{g cm}^{-3}$	1.524
μ/cm^{-1}	11.19
Reflections collected	5914
Independent reflections	3279 (R_{int} = 0.0747)
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0747, wR2 = 0.1487$
R indices (all data)	$R1 = 0.1421, wR2 = 0.1773$

CCDC reference number 179002.

See http://www.rsc.org/suppdata/dt/b2/b201319c/ for crystallographic data in CIF or other electronic format.

Acknowledgements

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