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Synthesis, characterisation and dynamic behaviour of palladium complexes containing the novel terdentate nitrogen ligand 2,6-bis(pyrimidin-2-yl)pyridine

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The ionic methylpalladium complexes [Pd(Me)(bppy)]X {X = Cl **1a**, SO_3CF_3 **1b**, [3,5-$(CF_3)_2C_6H_3]_4B$ **1c**}, containing the novel flexible terdentate nitrogen ligand 2,6-bis(pyrimidin-2-yl)pyridine, have been synthesised. Complexes **1a**–**1c** reacted quantitatively with carbon monoxide, resulting in formation of the acylpalladium complexes [Pd{C(O)Me}(bppy)]X {X = Cl **2a**, SO_3CF_3 **2b**, [3,5-$(CF_3)_2C_6H_3]_4B$ **2c**}. Complexes **1a**–**1c** and **2a**–**2c** have been isolated and fully characterised. In chloroform as well as in methanol, all the complexes show dynamic behaviour due to exchange of the co-ordinated and unco-ordinated pyrimidinyl nitrogen atoms. The influence of solvent, methyl and acyl ligand, counter ion and the presence of free Cl^- and CO on the dynamic behaviour has been studied and the thermodynamic parameters have been determined. A mechanism for the observed exchange process has been proposed. This mechanism involves (*a*) dissociation of one of the pyrimidinyl nitrogen atoms, which may be initiated by chloride, solvent or CO co-ordination, (*b*) rotation about the pyrimidinyl–pyridine bond and (*c*) reformation of the nitrogen–palladium bond.

Over the past years the synthesis and reactivity of palladium(II) complexes containing bidentate nitrogen ligands have been extensively studied. For example, ionic complexes of the type [Pd(R)(solv)(N–N)]Y (R = alkyl, solv = solvent, N–N = bidentate nitrogen ligand and Y = weakly co-ordinating anion) proved to be efficient catalysts in the co- and ter-polymerisation of carbon monoxide and alkenes[1–9] and in the (co)polymerisation of alkenes.[10,11] Since insertion of unsaturated substrates into carbon–palladium bonds plays a key role in these processes, a large amount of research has been carried out on insertion reactions of CO,[12–18] alkenes,[7,12,13,17–19] allenes,[20–22] and isocyanides[23,24] in complexes containing bidentate nitrogen ligands. In contrast, relatively little research has been carried out on insertion reactions of palladium(II) complexes containing terdentate nitrogen ligands,[25,26] Recently, we reported on the remarkably high reactivity of methyl- and acyl-palladium complexes containing the terdentate ligand 2,2′:6′,2″-terpyridine (tpy) toward CO and norbornadiene (bicyclo[2.2.1]hepta-2,5-diene), respectively.[26] The mechanism of these insertion reactions, however, could not be elucidated.

To obtain more insight into the mechanism of insertion reactions in complexes containing a terdentate ligand such as tpy, we synthesised the novel nitrogen ligand 2,6-bis(pyrimidin-2-yl)pyridine (bppy). Recently, ligands containing one or more pyrimidinyl moieties have been found to be very useful in identifying the mechanism of several processes in palladium(II) complexes.[24,27,28] Here we report the synthesis, full characterisation and palladium co-ordination chemistry of 2,6-bis(pyrimidin-2-yl)pyridine. Furthermore, we present a study of the dynamic behaviour of methyl- and acyl-palladium complexes containing the bppy ligand.

Experimental

General

All manipulations were carried out in an atmosphere of purified dry nitrogen by using standard Schlenk techniques. Solvents were dried and stored under nitrogen. Carbon monoxide (99.5%) was purchased from HoekLoos and was used without further purification. The compounds 2-acetylpyrimidine,[29] Pd(Me)Cl(COD)[30] (COD = cycloocta-1,5-diene) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBR'_4$)[31] were prepared according to the literature. All other starting chemicals were used as commercially obtained. Silver trifluoromethanesulfonate was stored under nitrogen in the dark. Proton and ^{13}C NMR spectra (300.13 and 75.48 MHz, respectively) were recorded on a Bruker AMX 300 spectrometer at 20 °C, unless noted otherwise. Chemical shifts are in ppm relative to $SiMe_4$ as external standard. Variable-temperature ^1H NMR spectra were recorded on a Bruker AMX 300 or a Bruker DRX 300 spectrometer, variable-temperature units were calibrated using standard methanol (low temperature calibration) and ethylene glycol (high temperature calibration) samples. The IR spectra were obtained on a Bio-Rad FTS-7 spectrophotometer and mass spectra on a JEOL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-MP7000 data system.

Syntheses

β-(Dimethylamino)vinyl pyrimidin-2-yl ketone.† A solution of 2-acetylpyrimidine (2.0 g, 16.3 mmol) and *N*,*N*-dimethylformamide dimethyl acetal (1,1-dimethoxytrimethylamine) (4 cm^3, 30.2 mmol) in toluene (25 cm^3) was heated to reflux and methanol was gradually removed by fractional distillation. After 3 h, the red solution was evaporated to dryness. Washing the residue with hexane (2 × 20 cm^3) and drying *in vacuo* yielded a red solid product (2.7 g, 92%). The product was sufficiently pure to be used in the next step. $\delta_H(CDCl_3)$: 8.89 (2 H, d, ^3J = 4.8, pyrimidine $H^{3,5}$), 8.00 (1 H, d, ^3J = 12.6, =CHN), 7.33 (1 H, t, ^3J = 4.8, pyrimidine H^4), 6.38 [1 H, br d, ^3J = 12.6 Hz, =CHC(O)R], 3.20 (3 H, s, NMe), 3.00 (3 H, s, NMe); $\delta_C(CDCl_3)$: 184.3 (CO), 162.9 (pyrimidine C^1), 157.0 (pyrimidine $C^{3,5}$), 155.3 (=CHN), 121.3 (pyrimidine C^4), 92.2 [br, =*C*HC(O)R], 44.9 (NMe), 37.2 (NMe). *M* [electron impact (EI)] 177. $C_9H_{11}N_3O$ requires *M* 177.

2,6-Bis(pyrimidin-2-yl)pyridine (bppy). To a solution of $KOBu^t$ (2.0 g, 17.8 mmol) in tetrahydrofuran (THF) (50 cm^3) was added 2-acetylpyrimidine (1.1 g, 8.9 mmol). After the solution

† (*E*)-3-(Dimethylamino)-1-pyrimidin-2-ylprop-2-en-1-one.

was stirred for 1 h at 20 °C, β-(dimethylamino)vinyl pyrimidin-2-yl ketone (1.6 g, 9.0 mmol) was added. The solution, which gradually turned deep red, was stirred at 20 °C for 14 h. After successive addition of NH_4OAc (OAc = O_2CMe) (7.0 g, 91 mmol) and acetic acid (25 cm^3), the THF was removed by slow distillation over a period of 2 h. The remaining solution was evaporated to dryness and water (50 cm^3) was added, Na_2CO_3 was added until effervescing ceased and the mixture was extracted with dichloromethane (3 × 50 cm^3). After drying over $MgSO_4$, the combined organic phases were evaporated. Column chromatography over silica 60 with dichloromethane–diethyl ether (1:1) as eluent resulted in bppy (0.5 g, 23%) (Found: C, 63.82; H, 4.02; N, 28.79. $C_{13}H_9N_5·0.5H_2O$ requires C, 63.92; H, 4.13; N, 28.67%). *M* (FAB) 235.0859. $C_{13}H_9N_5$ requires 235.0858.

[Pd(Me)(bppy)]Cl 1a. The compound bppy (75.5 mg, 0.32 mmol) was added to a solution of Pd(Me)Cl(COD) (67.3 mg, 0.29 mmol) in dichloromethane (20 cm^3). After stirring at 20 °C for 10 min, the solution was evaporated to dryness and the product was washed with hexane (2 × 20 cm^3) and dried *in vacuo*, yielding **1a** as a yellow solid (54.9 mg, 49%) (Found: C, 38.31; H, 3.71; N, 15.38. $C_{14}H_{12}ClN_5Pd·2.5H_2O$ requires C, 38.46; H, 3.92; N, 16.02%). *M* (FAB) 356. $[C_{14}H_{12}N_5Pd]^+$ requires 356.

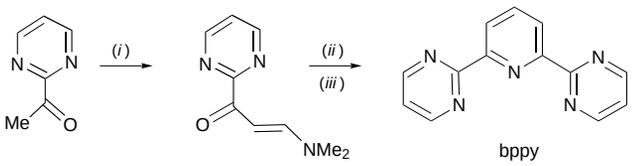
[Pd(Me)(bppy)]SO_3CF_3 1b. To a solution of [Pd(Me)-(bppy)]Cl **1a** (12.1 mg, 0.031 mmol) in a mixture of dichloromethane (20 cm^3) and acetonitrile (0.5 cm^3) was added $AgSO_3CF_3$ (16.9 mg, 0.066 mmol) and the mixture was stirred in the dark at 20 °C. After 10 min, the mixture was evaporated to dryness and methanol (20 cm^3) was added. After filtering the solution through Celite and extracting the residue with methanol (5 cm^3), the combined filtrates were evaporated to dryness. Washing the residue with diethyl ether (2 × 20 cm^3) and drying *in vacuo* yielded **1b** as a yellow solid (13.7 mg, 87%) (Found: C, 35.61; H, 2.56; N, 13.59. $C_{15}H_{12}F_3N_5O_3PdS$ requires C, 35.62; H, 2.39; N, 13.85%). *M* (FAB) 356. $[C_{14}H_{12}N_5Pd]^+$ requires 356.

[Pd(Me)(bppy)]BR′$_4$ 1c. To a solution of [Pd(Me)(bppy)]Cl **1a** (38.4 mg, 0.098 mmol) in dichloromethane (20 cm^3) was added NaBR′$_4$ (77.7 mg, 0.088 mmol). After stirring for 10 min at 20 °C, the solution was evaporated to dryness. After addition of diethyl ether (20 cm^3), the precipitate (NaCl and excess **1a**) was filtered off and the solvent was removed under reduced pressure. The resulting yellow solid was washed with hexane (2 × 20 cm^3) and dried *in vacuo*, yielding complex **1c** (72.0 mg, 68%) (Found: C, 45.40; H, 2.21; N, 5.85. $C_{46}H_{24}BF_{24}N_5Pd$ requires C, 45.29; H, 1.98; N, 5.74%). *M* (FAB) 356. $[C_{14}H_{12}N_5Pd]^+$ requires 356.

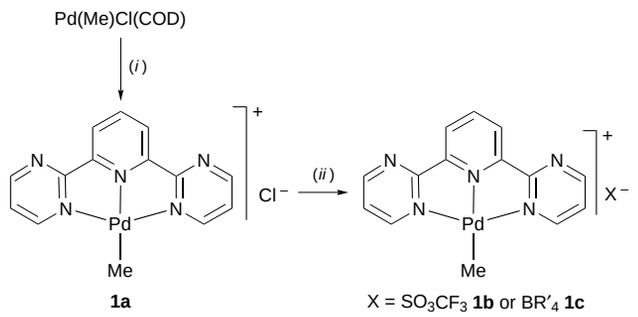
[Pd{C(O)Me}(bppy)]X (X = Cl 2a, SO_3CF_3 2b or BR′$_4$ 2c). Carbon monoxide was bubbled through a glass capillary into a solution of the methylpalladium complexes **1a**–**1c** (*ca.* 5 mg) in solvent [methanol (5 cm^3) for **1a** and **1b**; dichloromethane (5 cm^3) for **1c**] at 20 °C. After 1 min, the solution was filtered through Celite and the residue was extracted with dichloromethane (5 cm^3). The combined filtrates were evaporated to dryness and the product was washed with hexane (2 × 20 cm^3), giving the acylpalladium product as a yellow solid (82–88%). No correct analytical data nor mass spectrum could be obtained for **2a**–**2c** due to slow decarbonylation in the solid state. IR/cm^{-1} (KBr): **2a**, 1700 (ν_{CO}); **2b**, 1701 (ν_{CO}); **2c**, 1697 (ν_{CO}).

Spin-saturation transfer measurements

The spin-saturation transfer measurements were carried out on a Bruker DRX 300 spectrometer. The lattice relaxation times were obtained using standard inversion recovery methods with



Scheme 1 Synthesis of bppy. (*i*) $Me_2NCH(OMe)_2$, toluene, heat; (*ii*) $KOBu^t$, 2-acetylpyrimidine; (*iii*) NH_4OAc, acetic acid



Scheme 2 Synthesis of methylpalladium complexes **1a**–**1c**. (*i*) bppy, CH_2Cl_2, 20 °C; (*ii*) $AgSO_3CF_3$ or NaBR′$_4$, CH_2Cl_2–MeCN, 20 °C

10 data points and 90/180° pulse width. The T_1 was measured at the lowest and highest temperature for which a measurement was carried out and varied from 2.672 to 3.564 s in the temperature range from 298 to 328 K. The variable-temperature unit was calibrated using standard ethylene glycol samples. The spin-saturation experiments were carried out using the Forsén–Hoffman method[32] with a $(T_d - \pi/2)_n$ pulse sequence (presaturation time T_d = 20 s, presaturation power 70 dB, relaxation delay d_1 = 25 s, 8 scans per data point).

Results and Discussion

Synthesis of 2,6-bis(pyrimidin-2-yl)pyridine (bppy)

The novel ligand 2,6-bis(pyrimidin-2-yl)pyridine (bppy) has been prepared analogous to a previously reported method for the improved synthesis of tpy (Scheme 1).[33] The reaction proceeds *via* the compound β-(dimethylamino)vinyl pyrimidin-2-yl ketone, which could be synthesised in high yield by the reaction of 2-acetylpyrimidine with *N*,*N*-dimethylformamide dimethyl acetal. Condensation of the potassium enolate of 2-acetylpyrimidine with β-(dimethylamino)vinyl pyrimidin-2-yl ketone, followed by closure of the resulting pent-2-ene-1,5-dione with ammonium acetate resulted in bppy. The overall yield is 23%, which is lower than that reported for the synthesis of tpy (47%). The compound bbpy has been characterised by microanalysis, ^1H and ^{13}C NMR spectroscopy (Tables 1 and 2, respectively) and high-resolution mass spectroscopy.

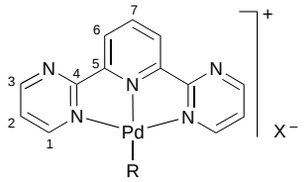
Synthesis and characterisation of complexes 1a–1c and 2a–2c

Addition of bppy to a solution of Pd(Me)Cl(COD) led to substitution of the weakly co-ordinating COD ligand by bppy and to the formation of [Pd(Me)(bppy)]Cl **1a** (Scheme 2). Upon treatment with silver trifluoromethanesulfonate and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBR′$_4$), the chloropalladium complex **1a** was converted to the trifluoromethanesulfonate and tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate analogues **1b** and **1c**, respectively.

The methylpalladium complexes **1a**–**1c** reacted rapidly with carbon monoxide to give the corresponding acylpalladium complexes **2a**–**2c** (Scheme 3). The reactions were carried out by bubbling CO through a glass capillary into a solution of complexes **1a**–**1c** and were completed within 1 min.

Complexes **1a**–**1c** and **2a**–**2c** were obtained as yellow solids which are soluble in methanol and, except for **1b** and **2b**, in dichloromethane and chloroform. All methyl- and acyl-

Table 1 The ^{1}H NMR data for bppy and complexes **1a**–**1c** and **2a**–**2c**[a]



	δ				
Compound	$H^{1,3}$	H^2	H^6	H^7	Other signals
bppy	8.96 (d, ^3J = 4.9)	7.33 (t, ^3J = 4.9)	8.59 (d, ^3J = 7.8)	8.07 (t, ^3J = 7.8)	—
1a[b]	9.06 (br)	7.83 (pst)	8.57 (s.o. m, ^3J = 8.0)	8.46 (s.o. m, ^3J = 8.0)	0.93 (s, Pd–Me)
1b[c]	8.98 (br, H^1) 9.19 (br, H^3)	7.83 (pst)	8.63 (s.o. m, ^3J = 7.9)	8.50 (s.o. m, ^3J = 7.9)	1.01 (s, Pd–Me)
1c	8.71 (dd, ^3J = 5.0, ^4J = 2.1, H^1), 8.99 (dd, ^3J = 5.6, ^4J = 2.1, H^3)	7.59 (pst)	8.44 (d, ^3J = 8.1)	8.24 (t, ^3J = 8.1)	7.71 (s, *o*-H of R′), 7.49 (s, *p*-H of R′), 0.94 (s, Pd–Me)
2a[b]	9.05 (d, ^3J = 5.2)	7.84 (t, ^3J = 5.2)	8.64 (d, ^3J = 7.9)	8.46 (t, ^3J = 7.9)	2.67 [s, C(O)Me]
2b[c]	9.07 (d, ^3J = 5.1)	7.96 (t, ^3J = 5.1)	8.57 (s.o. m, ^3J = 7.9)	8.49 (s.o. m, ^3J = 7.9)	2.69 [s, C(O)Me]
2c	8.86 (br)	7.64 (t, ^3J = 5.1)	8.49 (d, ^3J = 7.8)	8.22 (t, ^3J = 7.8)	7.69 (s, *o*-H of R′), 7.49 (s, *p*-H of R′), 2.60 [s, C(O)Me]

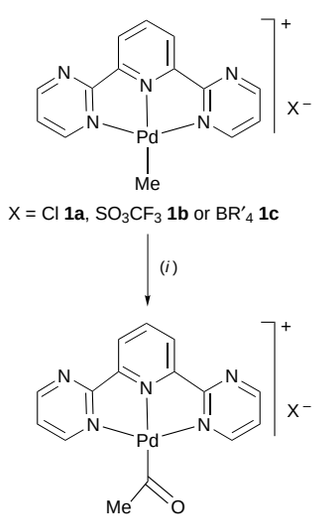
[a] Recorded at 300.13 MHz in $CDCl_3$ at 20 °C, unless noted otherwise (s = singlet, d = doublet, t = triplet, pst = pseudo triplet, m = multiplet, br = broad, s.o. = second order; *J* in Hz). [b] Recorded in CD_3OD. [c] Recorded in $(CD_3)_2SO$.

Table 2 The ^{13}C NMR data for bppy and complexes **1a**–**1c** and **2a**–**2c**[a]

	δ					
Compound	$C^{1,3}$	$C^{2,6}$	C^4	C^5	C^7	Other signals
bppy	158.5	125.4, 121.1	164.5	156.0	138.7	—
1a[b]	161.7 (br)	128.3, 125.2	167.4	151.7	143.7	5.1 (Pd–Me)
1b[c]	164.4	131.8, 129.0	170.0	154.6	147.7	9.3 (Pd–Me)
1c[d]	159.4, 157.5	127.1, 123.1	165.1	149.3	141.7	6.4 (Pd–Me)
2a[e]	157.5	126.7, 121.7	162.9	155.2	139.9	224.5 [*C*(O)Me], 35.6 [C(O)*Me*]
2b[c]	163.8	130.4, 128.1	166.5	153.9	147.3	233.8 [*C*(O)Me], 34.6 [C(O)*Me*]
2c[f]	159.1 (br)	126.9, 123.2	162.6	149.8	142.6	223.7 [*C*(O)Me], 28.4 [C(O)*Me*]

[a] Recorded at 75.48 MHz in $CDCl_3$ at 20 °C, unless noted otherwise. See Table 1 for the adopted numbering scheme (q = quartet, qq = quartet of quartets). [b] Recorded in CD_3OD. [c] Recorded in $(CD_3)_2SO$. [d] Signals of BR′$_4$: δ 161.5 (q, $^1J_{CB}$ = 49, *ipso*-C), 134.5 (*o*-C), 128.7 (qq, $^2J_{CF}$ = 32, $^4J_{CF}$ = 3, *m*-C), 124.2 (q, $^1J_{CF}$ = 272 Hz, CF_3), 117.2 (*p*-C). [e] Recorded at −20 °C. [f] Signals of BR′$_4$: δ 161.5 (q, $^1J_{CB}$ = 50, *ipso*-C), 134.5 (*o*-C), 128.7 (qq, $^2J_{CF}$ = 32, $^4J_{CF}$ = 3, *m*-C), 124.2 (q, $^1J_{CF}$ = 272 Hz, CF_3), 117.3 (*p*-C).

palladium complexes were isolated and characterised by ^{1}H and ^{13}C NMR spectroscopy (Tables 1 and 2, respectively). The stable methylpalladium complexes **1** were further characterised by mass spectroscopy and microanalysis. Similar to acylpalladium complexes containing tpy or rigid analogues of tpy,[34] complexes **2** show slow decarbonylation in solution as well as in the solid state. For this reason no correct mass spectra or microanalyses were obtained. Complexes **1a**–**1c** show characteristic methyl–palladium resonances at about δ 0.9 in the ^{1}H NMR spectra and in the range δ 5 to 10 in the ^{13}C NMR spectra.[12,14–17,26] Formation of the acylpalladium complexes **2** is evident from the CO stretching frequency at *ca.* 1700 cm^{-1} in the IR spectra and the C(O)Me resonances in the ^{1}H NMR (at *ca.* δ 2.6) and the ^{13}C NMR spectra {at δ 224–234[*C*(O)Me] and δ 36–28[C(O)*Me*]}.[12–17,19,26]



Scheme 3 Synthesis of acylpalladium complexes **2a**–**2c**. (*i*) CO, CH_3OH (**1a** or **1b**) or CH_2Cl_2 (**1c**), 20 °C

Dynamic behaviour of complexes 1a–1c and 2a–2c

In the temperature range 213 to 323 K the ^{1}H NMR spectra of complexes **1a**–**1c** and **2a**–**2c** show one set of signals for H^1/$H^{1'}$, H^2/$H^{2'}$, H^3/$H^{3'}$ and H^6/$H^{6'}$, indicating that the bppy ligand is co-ordinated to the palladium centre in the expected symmetric terdentate fashion, as usually observed for terdentate nitrogen ligands in complexes of the type [Pd(R)(N–N–N)]X.[26,34,35] In the same temperature range the ^{1}H NMR spectra of the chloropalladium complex **1a** in $CDCl_3$ reveal one sharp averaged signal for H^1 and H^3, indicating an exchange process that is fast on the NMR time-scale. In contrast, the ^{1}H NMR spectra of the corresponding tetrakis[3,5-bis(trifluoromethyl)-

Table 3 Parameters of activation of nitrogen exchange processes in complexes **1a**–**1c** (standard deviations in parentheses)

Compound	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}
1a[a]	43.2(11)	−59(4)	60.8(16)
1b[a]	47.6(6)	−55(2)	64.0(8)
1c[a]	47.6(16)	−53(5)	63.4(22)
1c[b]	73.0(33)	−40(11)	84.9(47)
1c[c]	35.3(26)	−49(11)	49.9(42)
1c[d]	47.5(20)	−51(7)	62.7(29)

[a] CD_3OD as solvent. [b] $CDCl_3$ as solvent. [c] In the presence of 0.25 equivalent of free chloride; $CDCl_3$ as solvent. [d] In the presence of 0.25 equivalent of free chloride; CD_3OD as solvent.

phenyl]borate complex **1c** in $CDCl_3$ (213–323 K) show two sharp doublets of doublets at δ 8.71 and 8.99 for the protons H^1 and H^3, respectively. Assignment of these signals was inferred from a ^1H nuclear Overhauser effect (NOE) difference experiment, which revealed a large NOE effect of the signal for protons of the methyl ligand to the resonance at δ 8.71. Irradiation of proton H^3 in the ^1H NMR spectrum of **1c** in $CDCl_3$ caused a spin-saturated transfer to proton H^1 and *vice versa*, indicating that protons H^1 and H^3 are exchanging with one another. The rates of exchange for complex **1c** in $CDCl_3$ have been determined at different temperatures by spin-saturation transfer measurements using the Forsén-Hoffman method.[32] The thermodynamic parameters of activation for the exchange process in **1c**, which have been derived from Eyring plots, have been collected in Table 3.

The exchange processes in complexes **1a**–**1c** show a strong dependence on the solvent. In the temperature range 213 to 253 K the ^1H NMR spectra of **1a**–**1c** in CD_3OD show separate sharp signals for H^1 and H^3 (see Fig. 1 for variable-temperature ^1H NMR spectra of **1a** in CD_3OD). Coalescence of the H^1 and H^3 protons is reached at 298 K for **1a** and at 318 K for **1b** and **1c**. The rates of exchange for complexes **1a**–**1c** in CD_3OD at different temperatures have been determined by a full lineshape analysis. The thermodynamic parameters of activation for the exchange process in the mentioned complexes, which have been derived from Eyring plots, have been collected in Table 3.

Analogous to the corresponding methylpalladium complexes **1a**–**1c**, the acylpalladium complexes **2a**–**2c** show dynamic behaviour. In the temperature range 203 to 293 K the ^1H NMR spectra of **2a** in $CDCl_3$ or CD_3OD show one sharp averaged signal for protons H^1 and H^3. At 203 K the ^1H NMR spectra of **2b** in CD_3OD and **2c** in $CDCl_3$ or CD_3OD show a broad averaged signal for H^1 and H^3, which sharpens upon raising the temperature.

The influence of free chloride ions on the exchange process has been studied for complex **1c** in $CDCl_3$ or CD_3OD. Addition of a small amount of free chloride (0.25 equivalent) to a solution of **1c** in $CDCl_3$ leads to an enormous increase of the exchange rate [$\Delta G^{\ddagger}_{298} = 84.9(47)$ in the absence of added Cl^-; $\Delta G^{\ddagger}_{298} = 49.9(42)$ kJ mol^{-1} in the presence of 0.25 equivalent of free Cl^-]. In CD_3OD, addition of free chloride also accelerates the exchange processes in **1c**, although to a much lesser extent [$\Delta G^{\ddagger}_{298} = 63.4(22)$ in the absence of added Cl^-; $\Delta G^{\ddagger}_{298} = 62.7(29)$ kJ mol^{-1} in the presence of 0.25 equivalent of free Cl^-]. Interestingly, the presence of CO also influences the exchange process. Bubbling CO through a solution of **2c** in CD_3OD leads in the ^1H NMR spectrum at 203 K to a sharp averaged doublet for protons H^1 and H^3. Unfortunately, the influence of CO on the exchange process in the methylpalladium complexes **1a**–**1c** could not be studied due to fast insertion of CO into the methyl–palladium bond. The exchange rates are neither influenced by addition of free bppy (1–2.5 equivalents) nor by the concentration of the cationic complex, which indicates that intermolecular nitrogen ligand exchange can be excluded as a source of the observed exchange process.

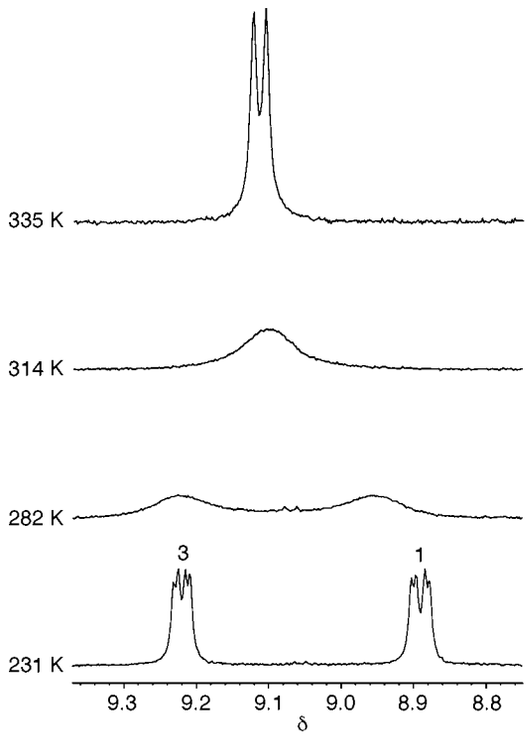
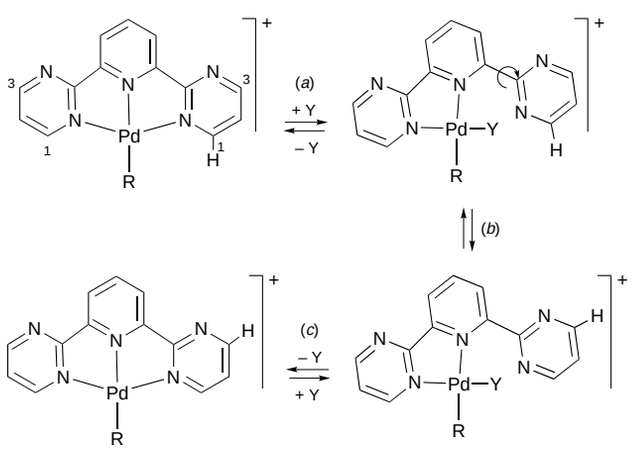


Fig. 1 Variable-temperature ^1H NMR spectra of [Pd(Me)(bppy)]Cl **1a** in CD_3OD



Scheme 4 Mechanism for nitrogen exchange process in complexes **1a**–**1c** and **2a**–**2c** with Y = Cl^-, solvent or CO

A mechanism which explains the exchange of protons H^1 and H^3 involves the following steps: (*a*) dissociation of one of the co-ordinated pyrimidinyl nitrogen atoms, which may be initiated by co-ordination of chloride; (*b*) an internal rotation about the pyrimidinyl–pyridine C–C bond and (*c*) reformation of the nitrogen–palladium bond (Scheme 4). The associative nature of this process is supported by the negative value of the entropy of activation for complex **1a** [$\Delta S^{\ddagger} = -59(4)$ J mol^{-1} K^{-1}] and the recent observations that chloride ion may substitute one of the distal nitrogen atoms of a nitrogen ligand that is co-ordinated in a terdentate fashion to a metal.[26,34,36] Furthermore, it explains the fast nitrogen exchange process in the chloro complex **1a** compared to those in complexes **1b** and **1c**, which both contain a weakly co-ordinating anion and the observed increase of the exchange rate in **1c** upon addition of free chloride ions. The slow exchange rate for **1a** in CD_3OD as compared to that in the less polar $CDCl_3$ is understandable as in CD_3OD co-ordination of the chloride, which is fully dissociated and efficiently solvated, is energetically highly unfavourable.

The higher exchange rate for **1c** in CD_3OD [$\Delta G^{\ddagger}_{298}$ = 63.4(22) kJ mol^{-1}] than that in $CDCl_3$ [$\Delta G^{\ddagger}_{298}$ = 84.9(47) kJ mol^{-1}] and the faster exchange process in **2c** in the presence of CO indicate that both methanol and CO may take on the role of the chloride ion initiating dissociation of a nitrogen atom of the bppy ligand from the palladium.

The much higher exchange rates for the acyl complexes than those for the corresponding methyl complexes can be explained by the larger *cis* influence [37,38] of an acetyl group. This indicates that the initial state of acyl complexes is more destabilised than that of the corresponding methyl complexes, which is in agreement with the relatively high instability of the acylpalladium complexes **2a**–**2c** as compared to that of the corresponding methyl complexes **1a**–**1c** (see above).

A very interesting observation is that nitrogen dissociation may be initiated by co-ordination of CO. A similar process may well be a part of the mechanism of the CO insertion in complexes **1a**–**1c** and of insertion reactions in methyl- and acylpalladium complexes containing other flexible terdentate nitrogen ligands, *e.g.* tpy. It should be noted here that the basicity of pyridine (pK_a = 5.25) is much larger than that of pyrimidine (pK_a = 1.23),[39] which suggests a better σ-donor capability of the former group. This may result in a higher activation energy for nitrogen dissociation in complexes containing a tpy ligand.

Conclusion

Methyl- and acyl-palladium complexes containing the novel terdentate nitrogen ligand bppy show dynamic behaviour due to exchange of the pyrimidinyl nitrogen atoms. The mechanism of this process involves nitrogen dissociation, which may be initiated by chloride, solvent or CO co-ordination, subsequent rotation about the C–C bond and reformation of the nitrogen–palladium bond. Hereby, we have demonstrated that nitrogen dissociation in palladium complexes containing flexible terdentate nitrogen ligands, *e.g.* tpy and bppy, is a low-energy process, which should certainly not be excluded from being part of the process of insertion reactions in these types of complexes.

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References

1 E. Drent, *Eur. Pat. Appl.*, 1986, 0229408; *Chem. Abstr.*, 1988, **108**, 6617b.
2 E. Drent, *Neth. Pat. Appl.*, 1986, 86/1199; *Chem. Abstr.*, 1988, **108**, 168148b.
3 E. Drent, *Neth. Pat. Appl.*, 1986, 86/2595; *Chem. Abstr.*, 1988, **109**, 171100f.
4 E. Drent, *Eur. Pat. Appl.*, 1989, 315279; *Chem. Abstr.*, 1989, **111**, 233894v.
5 E. Drent, *Neth. Pat. Appl.*, 1989, 89/1928; *Chem. Abstr.*, 1991, **115**, 30163r.
6 M. Barsacchi, G. Consiglio, L. Medici, G. Petrucci and U. W. Sutter, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 989.
7 M. Brookhart, F. C. Rix, J. M. DeSimone and J. C. Barborak, *J. Am. Chem. Soc.*, 1992, **114**, 5894.
8 A. Sen and Z. Jiang, *Macromolecules*, 1993, **26**, 911.
9 S. Bartolini, C. Carfagna and A. Musco, *Macromol. Rapid Commun.*, 1995, **16**, 9.
10 L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414.
11 L. K. Johnson, S. Mecking and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 267.
12 R. van Asselt, E. E. C. G. Gielens, R. E. Rülke, K. Vrieze and C. J. Elsevier, *J. Am. Chem. Soc.*, 1994, **116**, 977.
13 B. A. Markies, D. Kruis, M. H. P. Rietveld, K. A. N. Verkerk, J. Boersma, H. Kooijman, M. T. Lakin, A. L. Spek and G. van Koten, *J. Am. Chem. Soc.*, 1995, **117**, 5263.
14 R. E. Rülke, J. G. P. Delis, A. M. Groot, C. J. Elsevier, P. W. N. M. van Leeuwen, K. Vrieze, K. Goubitz and H. Schenk, *J. Organomet. Chem.*, 1996, **508**, 109.
15 J. G. P. Delis, P. W. N. M. van Leeuwen, K. Vrieze, N. Veldman, A. L. Spek, J. Fraanje and K. Goubitz, *J. Organomet. Chem.*, 1996, **514**, 125.
16 J. G. P. Delis, M. Rep, R. E. Rülke, P. W. N. M. van Leeuwen, K. Vrieze, J. Fraanje and K. Goubitz, *Inorg. Chim. Acta*, 1996, **250**, 87.
17 J. H. Groen, M. J. M. Vlaar, P. W. N. M. van Leeuwen, K. Vrieze, H. Kooijman and A. L. Spek, *J. Organomet. Chem.*, in the press.
18 F. C. Rix, M. Brookhart and P. S. White, *J. Am. Chem. Soc.*, 1996, **118**, 4746.
19 J. H. Groen, J. G. P. Delis, P. W. N. M. van Leeuwen and K. Vrieze, *Organometallics*, 1997, **16**, 68.
20 R. E. Rülke, D. Kliphuis, C. J. Elsevier, J. Fraanje, K. Goubitz, P. W. N. M. van Leeuwen and K. Vrieze, *J. Chem. Soc., Chem. Commun.*, 1994, 1817.
21 J. H. Groen, C. J. Elsevier, K. Vrieze, W. J. J. Smeets and A. L. Spek, *Organometallics*, 1996, **15**, 3445.
22 J. G. P. Delis, J. H. Groen, K. Vrieze, P. W. N. M. van Leeuwen, N. Veldman and A. L. Spek, *Organometallics*, 1997, **16**, 551.
23 J. G. P. Delis, P. G. Aubel, P. W. N. M. van Leeuwen, K. Vrieze, N. Veldman and A. L. Spek, *J. Chem. Soc., Chem. Commun.*, 1995, 2233.
24 J. G. P. Delis, P. G. Aubel, K. Vrieze, P. W. N. M. van Leeuwen, N. Veldman, A. L. Spek and F. J. R. van Neer, *Organometallics*, 1997, **16**, 2948.
25 B. A. Markies, P. Wijkens, A. Dedieu, J. Boersma, A. L. Spek and G. van Koten, *Organometallics*, 1995, **14**, 5628.
26 R. E. Rülke, V. E. Kaasjager, D. Kliphuis, C. J. Elsevier, P. W. N. M. van Leeuwen and K. Goubitz, *Organometallics*, 1996, **15**, 668.
27 A. Gogoll, J. Örnebro, H. Grennberg and J.-E. Bäckvall, *J. Am. Chem. Soc.*, 1994, **116**, 3631.
28 J. Elguero, A. Fruchier, A. de la Hoz, F. A. Jalón, B. R. Manzano, A. Otero and F. Gómez-de la Torre, *Chem. Ber.*, 1996, **129**, 589.
29 I. I. Naumenko, M. A. Mikhaleva and V. P. Mamaev, *Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1981, **7**, 958.
30 R. E. Rülke, J. M. Ernsting, C. J. Elsevier, A. L. Spek, P. W. N. M. van Leeuwen and K. Vrieze, *Inorg. Chem.*, 1993, **32**, 5769.
31 M. Brookhart, B. Grant and A. F. Volpe, jun., *Organometallics*, 1992, **11**, 3920.
32 B. E. Mann, *J. Magn. Reson.*, 1976, **21**, 17.
33 D. L. Jameson and L. E. Guise, *Tetrahedron Lett.*, 1991, **32**, 1999.
34 J. H. Groen, A. de Zwart, M. J. M. Vlaar, J.-M. Ernsting, P. W. N. M. van Leeuwen, K. Vrieze, H. Kooijman, W. J. J. Smeets, A. L. Spek, P. H. M. Budzelaar, Q. Xiang and R. P. Thummel, unpublished work.
35 B. A. Markies, P. Wijkens, J. Boersma, H. Kooijman, N. Veldman, A. L. Spek and G. van Koten, *Organometallics*, 1994, **13**, 3244.
36 H. F. Haarman, F. R. Bregman, J.-M. Ernsting, N. Veldman, A. L. Spek and K. Vrieze, *Organometallics*, 1997, **16**, 54.
37 S. S. Zumdahl and R. S. Drago, *J. Am. Chem. Soc.*, 1968, **90**, 6669.
38 T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev.*, 1973, **10**, 335.
39 Z. Rappoport, *Handbook of Tables for Organic Compound Identification*, CRC Press, Cleveland, OH, 3rd edn., 1967.

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