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Synthesis, characterization and reactivity of ionic palladium(II) complexes containing bidentate nitrogen ligands in a unidentate coordination mode[1,2]

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Abstract

The novel ionic complexes [Pd(Me)(*p*-An-BIAN)(L–L)]SO_3CF_3 (L–L = *p*-An-BIAN (bis(anisylimino)acenaphthene) (**1a**), phen (**2a**), dmphen (**3a**), dppe (**4a**), dppp (**5a**)) have been synthesized via the reaction of [Pd(Me)(NCMe)(*p*-An-BIAN)]SO_3CF_3 with L–L. The X-ray crystal structure of complex **1a** has been determined and shows a distorted square planar geometry in which one BIAN ligand is coordinated in a bidentate fashion (Pd–N(1) = 2.037(4) Å; Pd–N(2) = 2.189(4) Å) and, interestingly, the other BIAN ligand in a unidentate fashion (Pd–N(3) = 2.066(4) Å; Pd–N(4) = 2.714(6) Å). Spectroscopic data of the mixed ligand complexes [Pd(Me)(*p*-An-BIAN)(L–L)]SO_3CF_3 (L–L = phen (**2a**), dppe (**4a**), dppp (**5a**)) indicate that the L–L ligand is coordinated in a bidentate fashion and the *p*-An-BIAN ligand in a unidentate fashion, which is in agreement with the larger complexation strength of the phen, dppe and dppp ligands, as compared with that of the *p*-An-BIAN ligand. In contrast, complex **3a** (L–L = dmphen) contains a bidentate *p*-An-BIAN ligand and a unidentate dmphen ligand, which can be explained by the sterically demanding methyl groups of the dmphen ligand. Complexes **1a**–**4a** underwent insertion of carbon monoxide, resulting in the formation of acetylpalladium complexes [Pd(C(O)Me)(*p*-An-BIAN)(L–L)]SO_3CF_3 (**1b**–**4b**). Since mass-law retardation by excess *p*-An-BIAN has been observed for CO insertion for complexes **1a** and **4a**, it is proposed that the mechanism involves dissociation of the unidentate nitrogen ligand. Complexes **1a**–**5a** and **1b**–**4b** show fluxional behavior due to flipping of the unidentate nitrogen ligand. Complexes **1a**–**3a** and **1b**–**3b** also show fluxional behavior due to site exchange of the nitrogen atoms of the bidentate nitrogen ligand. A mechanism for this exchange process has been proposed. This mechanism involves (a) substitution of a nitrogen atom of the bidentate nitrogen ligand by the uncoordinated nitrogen atom of the unidentate nitrogen ligand, (b) flipping of the unidentate nitrogen ligand, and (c) a second nitrogen substitution reaction. Reaction of the acetylpalladium complexes **1b**–**4b** with norbornadiene led to dissociation of the unidentate nitrogen ligand and formation of the known alkylpalladium complexes [Pd(C_7H_8C(O)Me)(*p*-An-BIAN)]SO_3CF_3 (**1c**), [Pd(C_7H_8C(O)Me)(phen)]SO_3CF_3 (**2c**), **1c**, and [Pd(C_7H_8C(O)Me)(dppe)]SO_3CF_3 (**4c**), respectively.

Keywords: Bis(anisylimino)acenapthene ligand; carbon monoxide insertion; palladium(II)

1. Introduction

In the application of organopalladium complexes in homogeneous catalysis, mainly complexes containing phosphorus ligands have been employed to stabilize these complexes [1–3]. In recent years there has been a growing interest in the use of bi- and terdentate nitro-

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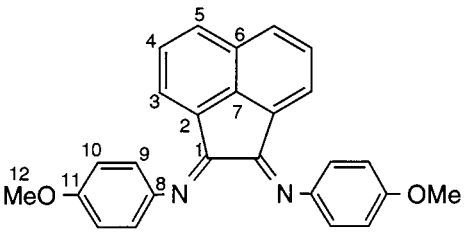
gen ligands in homogeneously catalyzed processes. For example, ionic palladium(II) complexes containing a bidentate nitrogen ligand such as bpy and phenanthroline can be used as catalyst in the copolymerization of CO and alkenes [4–12]. By using complexes containing the rigid bidentate nitrogen ligand bis(anisylimino)acenaphthene (*p*-An-BIAN), we succeeded in the synthesis and full characterization of key intermediates of the CO/alkene copolymerization [13] and more recently, of the CO/allene copolymerization [14]. Since insertion reactions into carbon–palladium bonds play a crucial role in these processes, we [13,15–20] and others [21–23] have extensively investigated the mechanistic aspects of insertion reactions in complexes containing bi- and terdentate nitrogen ligands. Brookhart et al. [23] carried out a mechanistic study of CO and ethylene insertions in ionic palladium(II) complexes of the type $[Pd(R)(solv)(N–N)]BAr_4$ and found that the insertion mechanism involves substitution of the weakly coordinating solvent molecule by the substrate. Extensive studies of CO [15], alkene [17,24], and allene [19] insertion reactions in neutral complexes Pd(R)X(N–N) (R = alkyl, acyl; X = halide, N–N = flexible or rigid bidentate nitrogen ligand) indicated that the mechanism may involve intermediates containing a bidentate nitrogen ligand coordinated as a unidentate. Interestingly, a significant retardation of both alkene and allene insertion reactions upon addition of free bidentate nitrogen ligand was explained by formation of an intermediate species of the type $Pd(R)X(N–N)_2$, which, however, could not be observed [19,24].

Here, we report the synthesis and characterization of novel complexes of the type Pd(Me)(*p*-An-BIAN)(L–L)]SO_3CF_3 (L–L = *p*-An-BIAN; 1,10-phenanthroline (phen); 2,9-dimethyl-1,10-phenanthroline (dmphen); 1,2-bis(diphenylphosphino)ethane (dppe); 1,3-bis(diphenylphosphino)propane (dppp). These complexes contain the bidentate *p*-An-BIAN ligand and a second bidentate ligand L–L, one of which is coordinated in a bidentate fashion, the other in a unidentate fashion. Furthermore, we present a study of the fluxional behavior of these complexes and of their the reactivity toward CO.

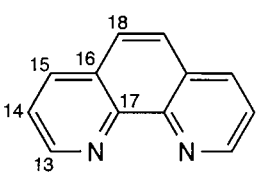
2. Experimental

2.1. General comments

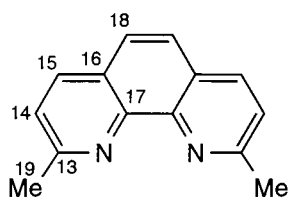
All manipulations were carried out in an atmosphere of purified dry nitrogen by using standard Schlenk techniques. Solvents were dried and stored under nitrogen. Carbon monoxide 99.5% was purchased from HoekLoos and was used without further purification. The compounds *p*-An-BIAN [25], [Pd(Me)(NCMe)(*p*-An-BIAN)]SO_3CF_3 [13], [Pd(Me)(NCMe)(dppe)]SO_3CF_3 [26] and [Pd(Me)(NCMe)(dppp)]SO_3CF_3 [26] were prepared according to the literature. All other starting chemicals were used as commercially obtained. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra (300.13, 75.48, and 121.50 MHz, respectively) were recorded on a Bruker AMX 300 spectrometer at 20°C. Chemical shifts are in ppm relative to TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P) as external standards (s = singlet, d = doublet, dd = doublet of doublets, pst = pseudotriplet, m = multiplet, br = broad). ^{15}N chemical shifts, which are in ppm relative to nitromethane as external standard, were extracted from gradient-selected (^{1}H, ^{15}N)-HMQC experiments [27–29] on a Bruker DRX 300 spectrometer. Adopted numbering schemes for *p*-An-BIAN, 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (dmphen) are as follows:



p-An-BIAN



phen



dmphen

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.

2.2. Synthesis of [Pd(Me)(*p*-An-BIAN)(L–L)]SO_3CF_3 (L–L = *p*–An-BIAN (**1a**), phen (**2a**), dmphen (**3a**), dppe (**4a**), dppp (**5a**))

To a solution of [Pd(Me)(NCMe)(*p*-An-BIAN)]SO_3CF_3 (89.3 mg, 0.13 mmol) in dichloromethane (20 ml) *p*-An-BIAN (65.9 mg, 0.17 mmol) was added. After stirring at 20°C for 5 min, the dark brown solution was evaporated to dryness. Washing the residue with diethylether (2 × 20 ml) and hexane (2 × 20 ml) and drying in vacuo, yielded [Pd(Me)(*p*-An-

BIAN)$_2$]SO_3CF_3 (**1a**) as a brown solid compound (130.4 mg, 95%).

Complexes **2a**–**5a** could be synthesized from [Pd(Me)(NCMe)(*p*-An-BIAN)]SO_3CF_3 and L–L or from [Pd(Me)(NCMe)(L–L)]SO_3CF_3 and *p*-An-BIAN in the same way (81–93%). No correct microanalyses were obtained for **2a**–**5a** due to the presence of a small amount (5–10%) of [Pd(Me)(L–L)$_2$]SO_3CF_3 or other unidentified impurities.

1a: ^{1}H-NMR ($CDCl_3$): δ 8.08 (d, $J = 8.3$ Hz, H5), 7.50 (pst, H4), 7.0 (20H, m, H3, H9, H10), 3.89 (s, H12), 0.70 (s, Pd–Me). ^{13}C-NMR ($CDCl_3$): δ 166.9 (C1), 159.4 (C11), 143.5 (C7), 140.8 (C8), 131.6 (C5), 131.6 (C6), 128.9 (C4), 127.2 (C2), 125.2 (C3), 122.4 (C10), 115.5 (C9), 56.2 (C12), 7.1 (Pd–Me). ^{15}N-NMR ($CDCl_3$): δ −97.1. Mass found: $m/z = 905.2319$. $[C_{53}H_{43}N_4O_4Pd]^+$ calc.: $m/z = 905.2239$. Anal. Found: C, 61.23; H, 4.07; N, 5.33. $C_{54}H_{43}F_3N_4O_7PdS$ calc.: C, 61.45; H, 4.11; N, 5.31.

2a: ^{1}H-NMR ($CDCl_3$): δ 8.82 (dd, $J = 5.1$, 1.2 Hz, H13), 8.55 (dd, $J = 8.3$, 1.2 Hz, H15), 8.06 (d, $J = 8.3$ Hz, H5), 7.96 (dd, $J = 8.3$, 5.1 Hz, H14), 7.90 (s, H18), 7.51 (pst, H4), 7.13 (6H, m, H3, H10), 6.98 (d, $J = 8.9$ Hz, H9), 3.82 (s, H12), 1.06 (s, Pd–Me). ^{13}C-NMR ($CDCl_3$): δ 162.9 (C1), 158.3 (C11), 148.4 (C13), 145.5 (C17), 142.4 (C8), 141.2 (C7), 138.5 (C15), 130.9 (C6), 130.4 (C5), 130.0, 127.9, 127.9, 125.7 (C2, C14, C16, C18), 127.3 (C4), 124.5 (C3), 120.9 (C10), 115.0 (C9), 55.4 (C12), 2.1 (Pd–Me). ^{15}N-NMR ($CDCl_3$): δ −79.7 (BIAN nitrogen atoms), −138.0 (phen nitrogen atoms). Mass found: $m/z =$ 693.1443. $[C_{39}H_{31}N_4O_2Pd]^+$ calc.: $m/z = 693.1482$.

3a: ^{1}H-NMR ($CDCl_3$): δ 8.31 (d, $J = 8.2$ Hz, H15), 8.11 (d, $J = 8.4$ Hz, H5), 7.79 (s, H18), 7.76 (d, $J =$ 8.2 Hz, H14), 7.49 (pst, H4), 7.01 (2 H, br, H3), 6.8 (8H, br, H9, H10), 3.80 (6H, br, H12), 3.35 (s, H19), 0.61 (s, Pd–Me). ^{13}C-NMR ($CDCl_3$): δ 159.0 (C13), 158.6 (C11), 144.4 (C17), 141.8 (C8), 137.7 (C15), 131.3 (C16), 131.0 (C5), 128.5 (C4), 127.7 (C2), 125.9 (C3), 124.9, 124.6 (C14, C18), 121.6 (br, C10), 114.4 (br, C9), 55.4 (C12), 28.0 (C19), 2.4 (Pd–Me), signals of C1, C6, and C7 were not observed. ^{15}N-NMR ($CDCl_3$): δ −114.0 (dmphen nitrogen atoms), signals of BIAN nitrogen atoms were not observed. Mass found: $m/z = 721.1770$. $[C_{41}H_{35}N_4O_2Pd]^+$ calc.: $m/z =$ 721.1795.

4a: ^{1}H-NMR ($CDCl_3$): δ 8.04 (d, $J = 8.4$ Hz, H5), 7.6–7.2 (22H, m, *Ph*–P, H4), 6.99 (d, $J = 7.2$ Hz, H3), 6.89 (d, $J = 8.7$ Hz, H10), 6.67 (d, $J = 8.7$ Hz, H9), 3.95 (s, H12), 2.6–2.1 (4H, m, CH_2P), 0.57 (dd, $J = 6.3$, 2.8 Hz, *Me*–Pd). ^{31}P-NMR ($CDCl_3$): δ 59.1 (d, $J = 27$ Hz, P *cis* to Me), 39.1 (d, $J = 27$ Hz, P *trans* to Me). Mass found: $m/z = 911.2171$. $[C_{53}H_{47}N_2O_2P_2Pd]^+$ calc.: $m/z = 911.2148$.

5a: ^{1}H-NMR ($CDCl_3$): δ 8.00 (d, $J = 8.3$ Hz, H5), 7.43 (pst, H4), 7.3–6.9 (30H, m, *Ph*–P, H3, H9, H10), 4.00 (s, H12), 2.6 (4H, m, CH_2P), 1.95 (2H, m, CH_2CH_2P), 0.38 (dd, $J = 6.5$, 3.2 Hz, *Me*–Pd). ^{31}P-NMR ($CDCl_3$): δ 23.6 (d, $J = 53$ Hz, P *cis* to Me), −2.0 (d, $J = 53$ Hz, P *trans* to Me). Mass found: $m/z = 925.2283$. $[C_{54}H_{49}N_2O_2P_2Pd]^+$ calc.: $m/z =$ 925.2323.

2.3. Synthesis of [Pd(C(O)Me)(p-An-BIAN)(L–L)]SO_3CF_3 (L–L = p-An-BIAN (**1b**), phen (**2b**))

A solution of [Pd(Me)(*p*-An-BIAN)$_2$]SO_3CF_3 (**1a**) (39.4 mg, 0.037 mmol) in 20 ml of dichloromethane was stirred at 20°C in a CO atmosphere. After 10 min, the solution was filtered through Celite and the residue was extracted with dichoromethane (5 ml). The combined filtrates were evaporated to dryness and the product was washed with hexane (2 × 20 ml), yielding **1b** as a dark brown solid (34.3 mg, 85%).

Complex **2b** was synthesized from **2a** in the same way (73%).

1b: ^{1}H-NMR ($CDCl_3$): δ 8.09 (d, $J = 8.3$ Hz, H5), 7.52 (pst, H4), 7.20 (d, $J = 8.9$ Hz, H10), 7.15 (d, $J = 7.3$ Hz, H3), 6.89 (d, $J = 8.9$ Hz, H9), 3.80 (s, H12), 1.89 (s, C(O)Me). ^{13}C-NMR ($CDCl_3$): δ 221.4 (CO), 165.1 (C1), 158.9 (C11), 142.8 (C7), 139.9 (C8), 131.0 (C5), 131.0 (C6), 128.2 (C4), 126.6 (C2), 124.5 (C3), 122.1 (C10), 114.9 (C9), 55.4 (C12), 30.3 (C(O)*Me*). IR (KBr): 1708 cm^{-1}, ν(CO). Mass found: $m/z = 933.2246$. $[C_{54}H_{43}N_4O_5Pd]^+$ calc.: $m/z =$ 933.2268. Anal. Found: C, 61.09; H, 3.95; N, 5.23. $C_{55}H_{43}F_3N_4O_8PdS$ calc.: C, 60.97; H, 4.00; N, 5.17.

2b: ^{1}H-NMR ($CDCl_3$): δ 8.70 (d, $J = 5.0$ Hz, H13), 8.60 (d, $J = 8.2$ Hz, H15), 8.10 (d, $J = 8.3$ Hz, H5), 7.98 (s, H18), 7.94 (dd, $J = 8.2$, 5.0 Hz, H14), 7.54 (pst, H4), 7.15 (d, $J = 7.4$ Hz, H3), 7.01 (d, $J = 8.9$ Hz, H10), 6.94 (d, $J = 8.9$ Hz, H9), 3.83 (s, H12), 2.57 (s, C(O)Me). ^{13}C-NMR ($CDCl_3$): δ 229.8 (CO), 163.4 (C1), 158.5 (C11), 149.6 (C13), 144.2 (C7), 141.5 (C8), 139.9 (C17), 138.9 (C15), 131.0 (C6), 130.9 (C5), 129.9, 128.1, 127.5, 127.4, 125.8, 124.9 (C2, C3, C4, C14, C16, C18), 120.9 (C10), 115.1 (C9), 55.4 (C12), 34.6 (C(O)*Me*). IR (KBr): 1693 cm^{-1}, ν(CO). Mass found: $m/z = 721.1408$. $[C_{40}H_{31}N_4O_3Pd]^+$ calc.: $m/z =$ 721.1431. No correct microanalysis was obtained due to the presence of a small amount (5–10%) of [Pd(C(O)Me)(phen)$_2$]SO_3CF_3.

2.4. Synthesis of [Pd(C(O)Me)(p-An-BIAN)(L–L)]SO_3CF_3 (L–L = dmphen (**3b**), dppe (**4b**))

A solution of [Pd(Me)(*p*-An-BIAN)(dmphen)]SO_3CF_3 (**3a**) (30.2 mg, 0.035 mmol) in dichloromethane (20 ml) was placed in a 100 ml stainless-steel autoclave, and CO was introduced up to 15

bar. After stirring at 20°C for 30 min, the pressure was released and the solution was filtered through Celite. The residue was extracted with dichloromethane (5 ml) and the combined filtrates were evaporated to dryness. The product was washed with hexane (2 × 20 ml) and dried in vacuo, yielding a dark brown product (0.025 mmol, 71%).

Complex **4b** was obtained from **4a** in the same way by using 25 bar of CO (86%).

3b: ^{1}H-NMR ($CDCl_3$): δ 8.36 (d, $J = 8.3$ Hz, H15), 8.10 (d, $J = 8.3$ Hz, H5), 7.86 d ($J = 8.3$ Hz, H14), 7.81 (s, H18), 7.49 (pst, H4), 7.03 (d, $J = 7.3$ Hz, H3), 6.7 (8H, br, H9, H10), 3.76 (s, H12), 3.61 (s, H19), 1.74 (s, C(O)Me). ^{13}C-NMR ($CDCl_3$): δ 166.8 (C1), 159.6, 158.6 (C11, C13), 144.1 (C7), 141.4 (C8), 139.2 (C17), 138.2 (C15), 131.2 (C6), 131.1 (C5), 128.4 (C4), 127.4 (C16), 126.1 (C2), 125.9, 125.5, 124.8 (C3, C14, C18), 121.2 (C10), 114.4 (C9), 55.4 (C12), 31.0 (C(O)*Me*), 28.0 (C19), signal of *C*(O)Me was not observed. IR (KBr): 1704 cm^{-1}, ν(CO). Mass found: $m/z =$ 749.1808. $[C_{42}H_{35}N_4O_3Pd]^+$ calc.: $m/z = 749.1744$. No correct microanalysis was obtained, due to the presence of a small amount (5–10%) of $[Pd(C(O)Me)(dmphen)_2]SO_3CF_3$.

4b: ^{1}H-NMR ($CDCl_3$): δ 8.04 (d, $J = 8.3$ Hz, H5), 7.6–6.8 (32H, m, *Ph*–P, H3, H4, H9, H10), 3.96 (s, H12), 2.7–2.2 (4H, m, CH_2P), 1.82 (br, C(O)Me). ^{31}P-NMR ($CDCl_3$): δ 37.9 (d, $J = 46$ Hz, P *cis* to Me), 30.3 (d, $J = 46$ Hz, P *trans* to Me). IR (KBr): 1675 cm^{-1}, ν(CO). Mass found: $m/z = 940$. $[C_{54}H_{48}N_2O_3P_2Pd]^+$ calc.: $m/z = 940$. No correct microanalysis was obtained, due to the presence of a small amount (5–10%) of unidentified impurities.

2.5. Reaction of acetylpalladium complexes *1b–4b* with norbornadiene

To a solution of the acetylpalladium complex **1b**–**4b** (ca. 0.02 mmol) in dichloromethane (20 ml) one equivalent of norbornadiene was added. After stirring the mixture at 20°C for 10 min (for **1b**, **2b** and **4b**) or 1 h (for **3b**), the solvent was evaporated and the product was washed with hexane (2 × 20 ml) and dried in vacuo. The products, which had formed quantitatively, were characterized by ^{1}H-NMR spectroscopy, and in the case of **4b** by ^{31}P-NMR spectroscopy aswell. The NMR spectra showed that the known complexes $[Pd(C_7H_8C(O)Me)(p\text{-An-BIAN})]SO_3CF_3$ [13] (**1c**), $[Pd(C_7H_8C(O)Me)(phen)]SO_3CF_3$ [30] (**2c**), **1c** and $[Pd(C_7H_8C(O)Me)(dppe)]SO_3CF_3$ [31] (**4c**) had formed, respectively.

2.6. Structure determination of *1a*

X-ray data were collected for a dark cut-to-size crystal on an Enraf-Nonius CAD4T/Rotating Anode diffractometer. Numerical details have been collected in Table 1. Cell parameters were derived from the setting angles of 25 SET4 reflections [32]. The triclinic unit cell was checked for the presence of possible higher metrical symmetry with the program LEPAGE [33] with negative result. The structure was solved with Patterson techniques using the program DIRDIFF-96 [34] and refined on F^2 using SHELXL-96 [35]. A final difference Fourier map did not show any significant features other than absorption artifacts near Pd and Cl. All geometrical calculations and the illustration were done with PLATON [36]. Full details may be obtained from one of the authors (A.L.S.).

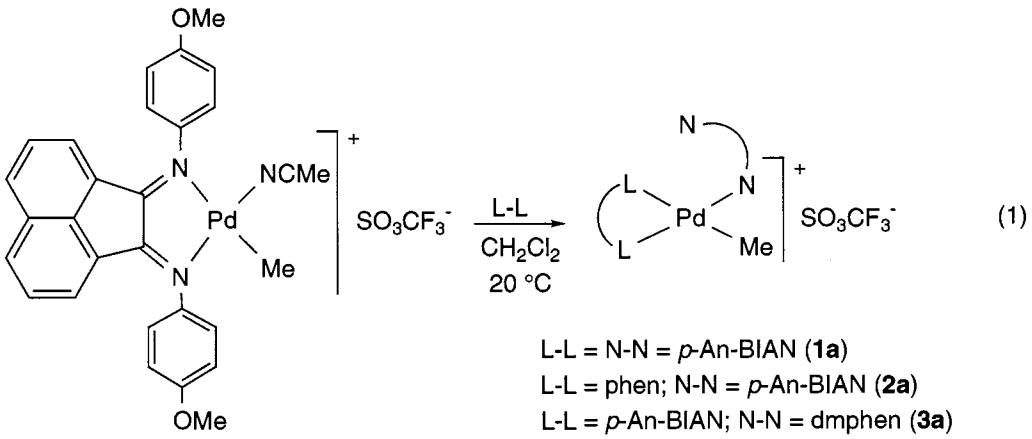
3. Results and discussion

3.1. Synthesis and characterization of complexes *1a–5a*

The reaction of the ionic complex $[Pd(Me)(NCMe)(p\text{–An-BIAN})]SO_3CF_3$ with L–L led to the formation of the stable complexes $[Pd(Me)(p\text{-An-BIAN})(L\text{–}L)]SO_3CF_3$ (L–L = *p*-An-BIAN (**1a**), phen (**2a**), dmphen (**3a**), dppe (**4a**), dppp (**5a**)) (Equation 1).

Table 1
Crystal data and details of the structure determination for **1a**

Empirical formula	$C_{53}H_{43}N_4O_4Pd$, CF_3O_3S, $2(CH_2Cl_2)$
Formula weight	1225.30
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
a, b, c (Å)	11.332(2), 14.561(4), 17.407(7)
α, β, γ (°)	92.73(3), 94.56(3), 111.833(18)
V (Å^3)	2648.5(14)
Z	2
D_{calcd} (g cm^{-3})	1.536
$F(000)$	1248
μ [Mo–K$_\alpha$] (cm^{-1})	6.6
Crystal size (mm)	$0.12 \times 0.25 \times 0.88$
Temperature (K)	150
Radiation (Å)	Mo–K$_\alpha$ (graphite–monochrom.), 0.71073
$\theta_{min}, \theta_{max}$ (°)	1.2, 25.0
Scan [type and range] (°)	$1.10 + 0.35 \tan\theta$
Hor. and vert. aperture (mm)	3.00, 4.00
Data set	−13:13; −17:17; 0:20
Total, unique data, R_{int}	9652, 9313, 0.097
Observed data	6612 [$I > 2.0\sigma(I)$]
No. of refIns and params	9313, 690
$R, \omega R, S$	0.0608, 0.1510, 1.01
Weighting scheme	$\omega = 1/[\sigma^2(F_0^2) + (0.0703P)^2 + 2.1899P]$ where $P = (F_0^2 + 2F_c^2)/3$
Max. and av. shift/error	0.00, 0.00
Min. and max. resd. dens. (eÅ^{-3})	−1.00, 0.70



L-L = N-N = *p*-An-BIAN (**1a**)
L-L = phen; N-N = *p*-An-BIAN (**2a**)
L-L = *p*-An-BIAN; N-N = dmphen (**3a**)
L-L = dppe; N-N = *p*-An-BIAN (**4a**)
L-L = dppp; N-N = *p*-An-BIAN (**5a**)

The reactions occurred instantaneously and the products were formed in high yield (81–95%). Complexes **2a**–**5a** could also be prepared by the reaction of complexes $[Pd(Me)(NCMe)(L–L)]SO_3CF_3$ with one equivalent of *p*-An-BIAN. Due to the low solubility of the starting complexes $[Pd(Me)(NCMe)(phen)]SO_3CF_3$ and $[Pd(Me)(NCMe)(dmphen)]SO_3CF_3$ in dichloromethane, the preferred way to prepare complexes **2a** and **3a** is the former route.

Complexes **1a**–**5a** were characterized by ^{1}H-NMR and mass spectroscopy. Complexes **1a**–**3a** were further characterized by ^{13}C-NMR spectroscopy and complexes **4a** and **5a** by ^{31}P-NMR spectroscopy. Unfortunately, no correct analytical data could be obtained for **2a**–**5a** due to the presence of small amounts (5–10%) of $[Pd(Me)(L–L)_2]SO_3CF_3$ (for complexes **2a** and **3a**) and unidentified impurities (for complexes **4a** and **5a**). Purification of complexes **2a**–**5a** by crystallisation from dichloromethane/hexane or dichloromethane/diethylether was attempted, but unfortunately failed. In contrast, crystals of **1a** suitable for an X-ray structural determination were obtained from dichloromethane/hexane (vide infra). All methylpalladium complexes **1a**–**5a** show a characteristic *Me*–Pd resonance at 0.3–1.1 ppm in the ^{1}H-NMR spectra and in the case of **1a**–**3a** at 2–10 ppm in the ^{13}C-NMR spectra. As expected, the ^{31}P-NMR spectra of complexes **4a** and **5a** show two resonances. In comparison with complexes Pd(Me)Cl(P–P) and $[Pd(Me)(NCMe)(P–P)]SO_3CF_3$ (P–P = dppe, dppp, dppb, dppf) [26], the lowest frequency resonance is assigned to the phosphorus atom positioned *trans* to the methyl group.

3.2. Molecular structure of $[Pd(Me)(p\text{-}An\text{-}BIAN)_2]SO_3CF_3$ (**1a**)

The molecular structure of **1a** with the adopted numbering scheme is shown in Fig. 1. Selected bond distances and angles are reported in Table 2. The palladium atom is surrounded by four nitrogen atoms of two *p*-An-BIAN ligands and by the carbon atom of a methyl group. Whereas one *p*-An-BIAN ligand is coordinated in a bidentate fashion (Pd(1)–N(1) = 2.037(4) Å; Pd(1)–N(2) = 2.189(4) Å), the other *p*-An-BIAN ligand is coordinated in an asymmetric fashion with only one nitrogen atom at bonding distance from the palladium center (Pd(1)–N(3) = 2.066(4) Å) and the other nitrogen atom at a much longer distance (Pd(1)–N(4) = 2.714(6) Å). An almost identical asymmetric coordination fashion has been reported for the *p*-An-BIAN ligand in Pd(η^3-$C_5H_8C(O)Me$)Cl(*p*-An-BIAN) [14] and for the dmphen ligand in Pd(η^3-C_5H_9)Cl(dmphen) [37], $PtCl(dmphen)(PPh_3)_2]Cl$ [38] and $PtX_2(dmphen)(L)$ (X = Cl, I; L = PPh_3, CO, N(O)Ph) [38,39]. When Pd(1)–N(4) is considered as a bond, the geometry of **1a** might be described as distorted square pyramidal with the nitrogen atoms N(1), N(2), N(3), and the carbon atom C(100) occupying the basal positions and the nitrogen atom N(4) positioned on the apical site. Elongation of the apical bond is quite common in square pyramidal complexes and several values of the ratio of the axial/equatorial bond length are available, e.g. 1.17 for $[Ni(CN)_5]^{2-}$ [40], 1.16 for $PdBr_2(PR_3)_3$ (PR_3 = 2-phenylisophosphindoline) [41], 1.15 for Pd(η^3-C_5H_9)Cl(dmphen) [37], and 1.14 for PtI_2(dmphen)(CO) [39]. Since these values are considerably smaller than the ratio of 1.31 for complex **1a**, the geometry of **1a** can be regarded as approximately square planar.

The Pd(1)–N(2) distance is longer than the Pd(1)–N(1) distance due to the relatively large *trans* influence [42] of the methyl group. The methyl–palladium distance of 2.029(6) Å and the Pd(1)–N(1), Pd(1)–N(2) and Pd(1)–N(3) distances are as expected and can be compared with those found for other methylpalladium complexes bearing a bi- or terdentate nitrogen ligand [15,16,18,25,43–45].

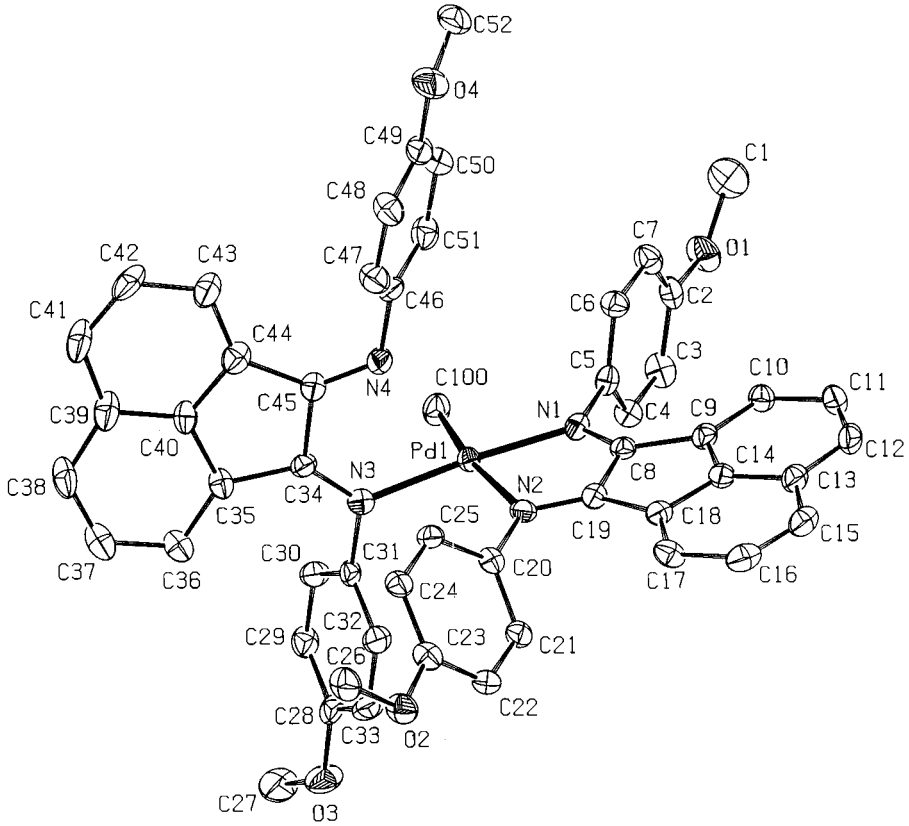


Fig. 1. ORTEP drawing (50% probability level) and adopted numbering scheme of $[Pd(Me)(p\text{-An-BIAN})_2]SO_3CF_3$ (**1a**); hydrogen atoms, SO_3CF_3 anion and CH_2Cl_2 have been omitted for clarity.

3.3. Coordination modes of the bidentate ligands in complexes *1a–5a*

Complexes **1a–5a** contain two bidentate ligands, one of which is coordinated in a bidentate fashion, the other in a unidentate fashion. In the ^{1}H-NMR spectra of **4a** and **5a** the *Me*–Pd resonance appears as doublet of doublets, which indicates that the diphosphine ligand is coordinated in a bidentate fashion and the *p*-An-BIAN ligand in a unidentate fashion. To determine the coordination modes of the nitrogen ligands in complexes **2a** and **3a**, nitrogen chemical shifts were determined for complexes **1a–3a** and for the free ligands *p*-An-BIAN, phen and dmphen (see Table 3) [46].

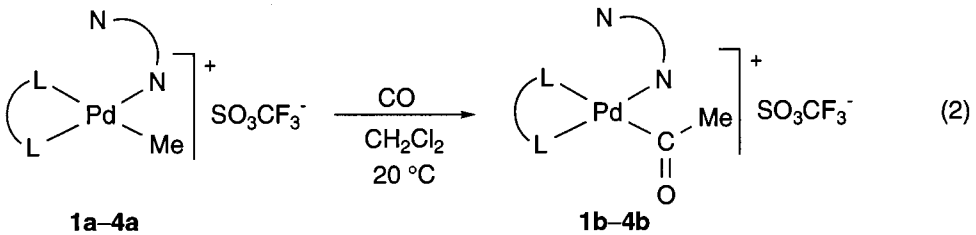
Table 2
Selected bond distances (Å) and angles (°) for complex **1a** (with estimated S.D.s in parentheses)

Bond distances (Å)			
Pd(1)–N(1)	2.037(4)	N(2)–C(19)	1.294(7)
Pd(1)–N(2)	2.189(4)	N(3)–C(34)	1.281(8)
Pd(1)–N(3)	2.066(4)	N(4)–C(45)	1.270(8)
Pd(1)–N(4)	2.714(6)	C(8)–C(19)	1.489(8)
Pd(1)–C(100)	2.029(6)	C(34)–C(45)	1.515(8)
N(1)–C(8)	1.302(6)		
Bond angles (°)			
N(1)–Pd(1)–N(2)	79.54(16)	N(3)–Pd(1)–C(100)	87.2(2)
N(1)–Pd(1)–N(3)	174.01(18)	N(4)–Pd(1)–C(100)	88.4(2)
N(1)–Pd(1)–N(4)	115.61(17)	Pd(1)–N(1)–C(8)	114.2(4)
N(1)–Pd(1)–C(100)	91.1(2)	Pd(1)–N(1)–C(5)	128.5(3)
N(2)–Pd(1)–N(3)	101.85(15)	Pd(1)–N(2)–C(19)	110.3(3)
N(2)–Pd(1)–N(4)	97.92(17)	Pd(1)–N(2)–C(20)	128.1(3)
N(2)–Pd(1)–C(100)	170.3(2)	Pd(1)–N(3)–C(31)	114.7(4)
N(3)–Pd(1)–N(4)	70.10(17)	Pd(1)–N(3)–C(34)	124.4(4)

Table 3
^{15}N-NMR data of *p*-An-BIAN, phen, dmphen and complexes **1a–3a** (with CIS values in parentheses)[a]

Compound	^{15}N Chemical shift (ppm)[b]
p–An-BIAN	−40.3
phen	−74.4
dmphen	−80.2
$[Pd(Me)(p-An\text{-}BIAN)_2]SO_3CF_3$ (**1a**)	−97.1 (−56.8)
$[Pd(Me)(p\text{-An-BIAN})(phen)]SO_3CF_3$ (**2a**)	−138.0 (−63.6), phen N; −79.7 (−39.4), BIAN N
$[Pd(Me)(p\text{-An-BIAN})(dmphen)]SO_3CF_3$ (**3a**)[c]	−114.0 (−33.8), dmphen N

[a] Recorded in $CDCl_3$ at 20°C.
[b] CIS values are given in parentheses.
[c] Signal of BIAN nitrogen atoms was not observed.



(2)

1a–4a **1b–4b**

In the range 253–293 K, the ^{15}N-NMR spectra of **1a** in $CDCl_3$ show an averaged signal for the four BIAN nitrogen atoms at −79.7 ppm. In the case of complex **2a**, the ^{15}N-NMR spectrum at 293 K shows averaged signals for the phen and BIAN nitrogen atoms at −138.0 and −79.7 ppm, respectively. In the range 223–293 K, the ^{15}N-NMR spectra of **3a** in $CDCl_3$ exhibit an averaged signal of the dmphen nitrogen atoms at ca. −114 ppm, whereas signals of the BIAN nitrogen atoms were not observed. It is known that signals of nitrogen atoms show a dramatic low-frequency shift ranging from −50 to −90 ppm upon coordination to palladium [47,48]. Whereas the averaged coordination induced shift (CIS, $\Delta\delta$) of −63.6 ppm for the phen nitrogen atoms in **2a** indicates that the phen ligand is coordinated in a bidentate fashion, the relatively low averaged CIS value of −39.4 ppm for the BIAN nitrogen atoms in **2a** suggests a unidentate coordination fashion of the BIAN ligand. Similarly, the low averaged CIS value of −33.8 ppm for the dmphen nitrogen atoms in **3a** suggests that a unidentate coordination of the dmphen ligand and, as a consequence, a bidentate coordination of the BIAN ligand.

From these results it is evident that the coordination mode of the *p*-An-BIAN ligand in complexes [Pd(Me)(*p*-An-BIAN)(L–L)]SO_3CF_3 (**1a**–**5a**) is highly dependent on the nature of the L–L ligand. In the case of L–L = dppe (**4a**) and dppp (**5a**), which coordinate more strongly to a palladium(II) center than the *p*-An-BIAN ligand, a bidentate coordination mode of the L–L ligand is preferred, while the BIAN ligand is coordinated in a unidentate fashion. The large σ-coordinating ability of the phen ligand as compared with that of the *p*-An-BIAN ligand [49] favours for **2b** a structure in which the *p*-An-BIAN ligand is coordinated as a unidentate. The bidentate coordination of the *p*-An-BIAN ligand in complex **3a** is most probably caused by the more favorable unidentate coordination of the dmphen ligand, which bears two sterically demanding methyl groups adjacent to the nitrogen donor atoms. Coordination of the dmphen ligand in a bidentate fashion may lead to considerable steric interactions between these methyl groups and the other ligands, as has been observed for the complexes $PtCl_2$(dmphen) [50] and Pd(Me)Cl(dmphen) [43].

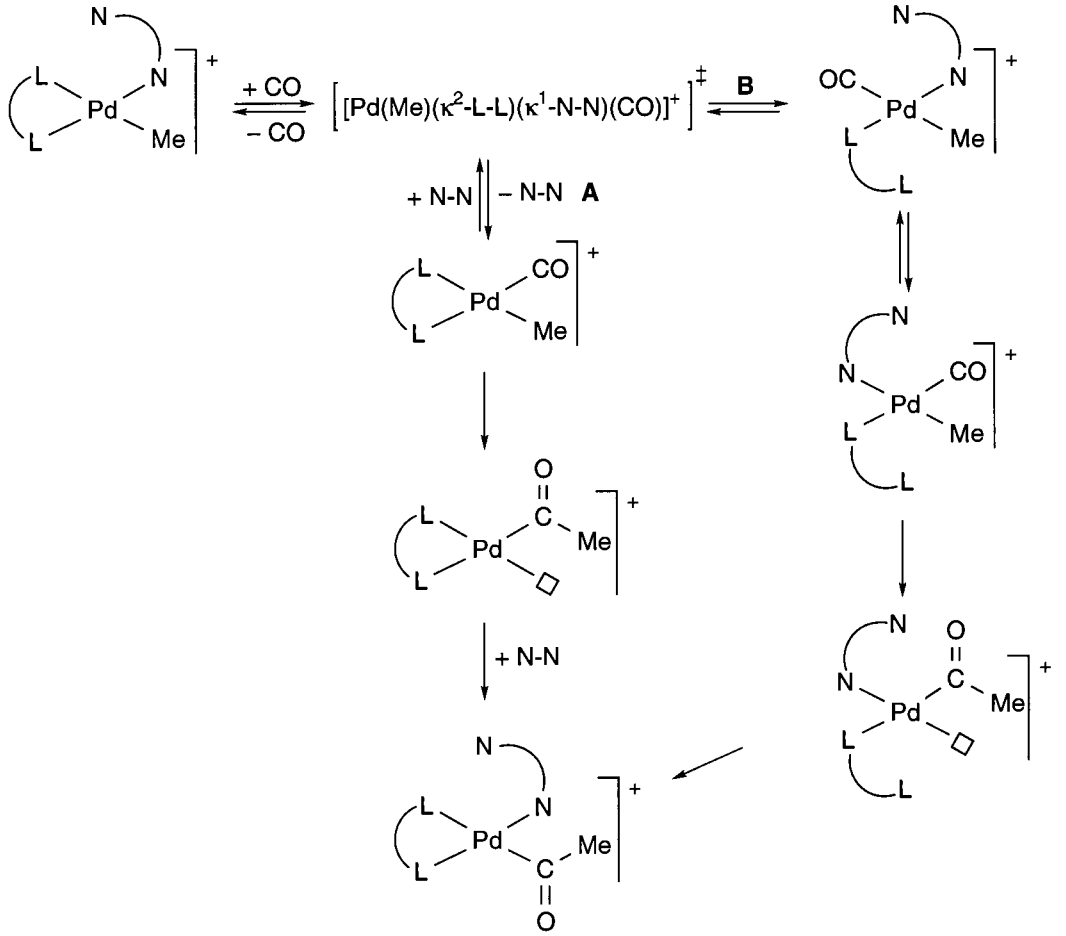
*3.4. Synthesis and characterization of complexes **1b–4b***

Methylpalladium complexes **1a**–**4a** reacted with CO to give the corresponding acetylpalladium complexes **1b**–**4b** (Equation 2).

In the case of complexes **1a** and **2a** the reactions were completed within 1 min under ambient conditions in dichloromethane (1 bar CO pressure, 20°C), showing rates comparable with those found for the neutral complexes Pd(Me)Cl(Ar-BIAN) [13,24], but the rates were lower than those observed for the ionic complexes [Pd(Me)(NCMe)(Ar-BIAN)]SO_3CF_3 [13]. Complexes **3a** and **4a** reacted much more slowly with CO and a CO pressure of 15 and 25 bar, respectively, was required for a rapid conversion. Complex **5a** also reacted with CO as could be concluded from the disappearance of the resonances of **5a** in the ^{1}H- and ^{31}P-NMR spectra. However, only uncharacterized compounds were obtained.

Interestingly, the insertion of CO into the methyl–palladium bond of **1a** was strongly retarded by addition of free *p*-An-BIAN. Whereas carbonylation of **1a** was completed within 1 min in the absence of free *p*-An-BIAN, in the presence of 1.5 equivalents of *p*-An-BIAN, the conversion of **1a** to **1b** was only 5% after 1 min. Similar to **1a**, the carbonylation of **4a** is inhibited by free *p*-An-BIAN (75% conversion to **4b** after 30 min in the absence of free *p*-An-BIAN, 15% conversion after 30 min in the presence of 1.5 equivalents of free *p*-An-BIAN). Unfortunately, the influence of free nitrogen ligand on the carbonylation rates of **2a** or **3a** could not be studied due to nitrogen ligand substitution reactions.

The stable acetylpalladium complexes **1b**–**4b** were isolated and characterized by ^{1}H-NMR, IR, and mass spectroscopy. Complexes **1b**–**3b** were further characterized by ^{13}C-NMR spectroscopy and complex **4b** by ^{31}P-NMR spectroscopy. Unfortunately, no correct analytical data could be obtained for **2b**–**4b** due to the presence of small amounts (5–10%) of [Pd(C(O)Me)(L–L)$_2$]SO_3CF_3 (for complexes **2b** and **3b**) and unidentified impurities (for complex **4b**). Formation of complexes **1b**–**4b** after the reaction of complexes **1a**–**4a** with CO is clear from the high-frequency



Scheme 1. Two proposed mechanisms for CO insertion reaction in complexes **1a**–**4a**.

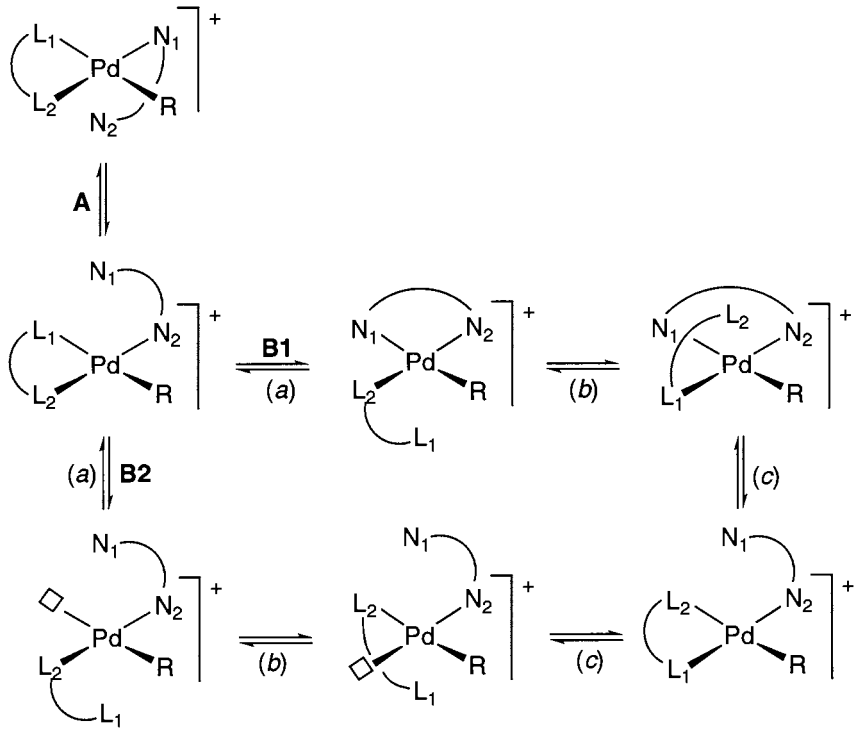
shift of the methyl resonance from 0.3–1.1 to 1.7–2.6 ppm in the ^{1}H-NMR spectra, the observation of a CO stretching frequency in the IR spectra (1690–1710 cm^{-1}), and in the case of **1a**–**3a** from the resonances of the C(O)Me group in the ^{13}C-NMR spectra (ca. 225 ppm (CO) and ca. 32 ppm (Me)). Insertion of CO into the methyl–palladium bond of **4a** is also evident from the low-frequency shift of the phosphorus resonances from 59.1/39.1 to 37.9/30.3 ppm in the ^{31}P-NMR spectrum [26]. The small shift of the phosphorus *trans* to the R group as compared with that of the phosphorus in *cis* position and the increasing coupling constant ^{2}J(P,P) from 27 to 46 Hz upon carbonylation of **4a** have been observed before for the carbonylation of complexes Pd(Me)Cl(P–P) and [Pd(Me)(NCMe)(P–P)]SO_3CF_3 (P–P = dppe, dppp, dppb, dppf) [26].

3.5. Mechanism of CO insertion in complexes *1a*–*4a*

The observation that the rate of CO insertion in complexes [Pd(Me)(*p*-An-BIAN)(L–L)]SO_3CF_3 decreases in the order L–L = *p*-An-BIAN (**1a**) ≫ dmphen (**3a**), i.e. with increasing steric demand of the unidentate nitrogen ligand, indicates an associative substitution of a ligand donor atom by CO, i.e. the making of the Pd–CO bond occurs before the breaking of a ligand–palladium bond. A possible mechanism for CO insertion in complexes **1a**–**4a** involves CO association, dissociation of the unidentate nitrogen ligand, a rate-determining migratory CO insertion, and coordination of the dissociated nitrogen ligand (Scheme 1, pathway A).

Such a mechanism is in agreement with the retardation of the CO insertion in complex **1a** and **4a** upon addition of an excess free *p*-An-BIAN and it explains the observation that rate of CO insertion for [Pd(Me)(dppe)(L)]SO_3CF_3 and [Pd(Me)(*p*-An-BIAN)(L)]SO_3CF_3 decreases in the order L = MeCN ≫ *p*-An-BIAN, i.e. with increasing Pd–L bond strength. Furthermore, CO insertion in [Pd(Me)(dppe)(*p*-An-BIAN)]SO_3CF_3 (**4a**) via pathway A is completely in agreement with extensive studies of CO [26,51–53] and alkene insertion reactions [31,53] in complexes of the type [Pd(R)(P–P)(L)]Y (R = Me, Ph, C(O)Me; P–P = bidentate phosphine ligand; Y = SO_3CF_3, BF_4; L = MeCN, PPh_3), which revealed that insertion predominantly occurs via dissociation of the L ligand.

An alternative pathway (Scheme 1, pathway B) involves formation of species containing two unidentate bonded



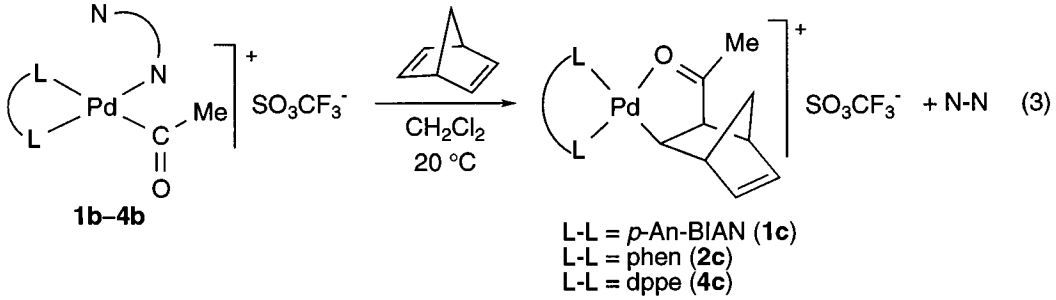
Scheme 2. Proposed mechanisms for exchange processes in complexes **1**–**5**.

bidentate ligands via dissociation of the L atom positioned *trans* to the methyl group, which has a relatively large *trans* influence [42]. Isomerization followed by a rate-determining CO insertion and association of the L atom leads to the product. Recently, formation of similar species containing two unidentate N–N ligands has been proposed to explain the retardation of alkene and allene insertion reactions of complexes of the type Pd(R)X(N–N) upon addition of free nitrogen ligand [19,24]. Furthermore, coordination of two bidentate nitrogen ligands in a unidentate fashion has been observed recently for $[Rh(nbd)(i\text{Pr-6-Me-PyCa})_2]SO_3CF_3$ (*i*Pr-6-Me-PyCa = 2-(*N*-2-propanecarbaldimino)-6-methylpyridine) [54]. Pathway B explains the increase of the rate of CO insertion for complexes $[Pd(Me)(L–L)(p\text{-An-BIAN})]SO_3CF_3$ in the order L–L = dppe ≪ *p*-An-BIAN ≈ phen, i.e. with increasing Pd–L bond strength. However, this pathway does not account for the observed retardation of the CO insertion in **1a** and **4a** upon addition of free *p*-An-BIAN. Therefore, we prefer pathway A for CO insertion in complexes **1a**–**4a**.

3.6. Fluxional behavior of complexes *1a,b–4a,b* and *5a*

In the range 203–293 K, the ^{1}H-NMR spectra of **1a**,**b**–**4a**,**b** and **5a** show averaged signals for each pair of protons on either sides of the unidentate bonded nitrogen ligand. In the same temperature range, the ^{1}H-NMR spectra of complexes **1a**,**b** and **2a**,**b** also show that both sides of the bidentate bonded nitrogen ligand (*p*-An-BIAN and phen, respectively) are magnetically equivalent, indicating nitrogen donor atom site exchange that is fast on the ^{1}H-NMR time scale. In contrast, at 203 K the ^{1}H-NMR spectra of **3a**,**b** exhibit separate signals for the acenaphthene protons on both sides of the *p*-An-BIAN ligand, which are sharp for **3a** and broadened for **3b**. Coalescence of these signals is reached at 273 K for **3a** and at 243 K for **3b**. Intermolecular nitrogen ligand exchange can be excluded as source of the observed exchange processes, since addition of free *p*-An-BIAN to **1a** gave sharp signals for the individual resonances of free and coordinated *p*-An-BIAN. In the range 203–293 K the ^{31}P-NMR spectra of complexes **4a**,**b** and **5a** show two sharp doublets, indicating that phosphorus donor atom site exchange is slow on the ^{31}P-NMR time scale.

Analogous to what has been proposed for the platinum(II) complexes $[PtX(N–N)(PR_3)_2]X$ (X = Cl, Br, I, BF_4; R = Et, *n*-Bu, Ph; N–N = phen, dmphen, 1,8-naphthyridine) [38,55] and $PtX_2(dmphen)(PPh_3)$ (X = Cl, Br, I) [38], the equivalence of both sides of the unidentate nitrogen ligand in complexes **1**–**4** and **5a** can be explained by a dynamic process involving fast exchange of the two nitrogen atoms at the same coordination site (flipping) (Mechanism A in Scheme 2). Since flipping of the unidentate nitrogen ligand is fast on the NMR time scale, even at the lowest temperature used, a detailed study of this dynamic process could not be performed. A mechanism (Scheme 2, mechanism B1) which explains the nitrogen donor atom site exchange in complexes **1**–**3** involves (a) substitution of the nitrogen atom positioned *trans* to the R group by the uncoordinated nitrogen atom,



which may occur rather easily due to the large *trans* influence [42] of the R group, (b) flipping of the unidentate L–L ligand (vide supra), and (c) nitrogen substitution similar to (a).

An alternative mechanism (Scheme 2, mechanism B2) which may explain the nitrogen donor atom site exchange in complexes **1**–**3** involves (a) dissociation of the nitrogen atom positioned *trans* to the R group, resulting in a T-shaped intermediate, in which both nitrogen ligands are coordinated in a unidentate fashion, (b) a *cis*–*trans* isomerization, which is known to proceed fast in T-shaped intermediates [56], and (c) nitrogen association. Both mechanisms B1 and B2 explain the fast nitrogen donor atom site exchange in complexes **1**–**3** as compared with the phosphorus donor atom site exchange in complexes **4a**,**b** and **5a**, which contain strongly coordinating bidentate phosphine ligands. Furthermore, mechanisms B1 and B2 explain the slow nitrogen donor atom exchange in complex **3a** as compared with that in complex **3b**, which contains an acetyl group with a relatively large *trans* influence [42]. Only mechanism B1, however, explains the slow nitrogen donor atom exchange process in complex **3a** as compared with those in **1a** and **2a**; a bidentate coordination fashion of the dmphen ligand is unfavorable because of the sterically demanding methyl groups of the dmphen ligand (vide supra). Therefore, we prefer a mechanism involving intermediates in which the initially unidentate nitrogen ligand is bound as a bidentate, i.e. mechanism B1.

3.7. Norbornadiene insertion in complexes *1b*–*4b*

The reaction of the acetylpalladium complexes **1b**–**4b** with norbornadiene led to insertion of the alkene into the acetyl–palladium bond, resulting in formation of the alkylpalladium complexes $[Pd(C_7H_8C(O)Me)(p\text{-An-BIAN})]SO_3CF_3$ (**1c**) [13], $[Pd(C_7H_8C(O)Me)(phen)]SO_3CF_3$ (**2c**) [30], **1c** [13], and $[Pd(C_7H_8C(O)Me)(dppe)]SO_3CF_3$ (**4c**) [31] together with the free nitrogen ligands *p*-An-BIAN, *p*-An-BIAN, dmphen and *p*-An-BIAN, respectively (Equation 3).

The reactions of complexes **1b**, **2b**, and **4b** with norbornadiene occurred within 5 min, showing rates comparable with those found for the neutral complexes Pd(C(O)Me)Cl(Ar-BIAN [13,24], but the rates were lower than that observed for the ionic complex $[Pd(C(O)Me)(NCMe)(p\text{-An-BIAN})]SO_3CF_3$ [13]. In contrast, complex **3b** reacted much more slowly with norbornadiene and conversion to **1c** and free dmphen was only completed after 1 h. Since the products **1c**, **2c**, and **4c** are similar to those obtained after reaction of norbornadiene with complexes $[Pd(C(O)R)(NCMe)(L–L)]SO_3CF_3$ and Pd(C(O)R)X(L–L) (R = Me, Et, *i*Pr, Ph; L–L = N–N, P–P; X = Cl, Br, I), which mechanisms have been studied extensively [13,22,24,31,53], norbornadiene insertion in complexes **1b**–**4b** was not studied any further.

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