Insertion Reactions Involving Palladium Complexes with Nitrogen Ligands, Part. I. Reactivity towards Carbon Monoxide of Methylpalladium (II) Complexes containing Bidentate a-Diimine Ligands; X-Ray Structures of Four Methyl- and Acylpalladium (II) Complex.

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Insertion reactions involving palladium complexes with nitrogen ligands I. Reactivity towards carbon monoxide of methylpalladium(II) complexes containing bidentate α-diimine ligands: crystal structures of four methylpalladium(II) and acylpalladium(II) complexes

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Abstract

Neutral compounds of the type (2,2′-bipyridine)Pd(CH_3)(Cl) and (6-R′-C_5H_3N-2-C(H)=N-R)Pd(CH_3)(Cl) (R = ^{i}Pr; R′ = H: ^{i}Pr–PyCa) (R = ^{t}Bu; R′ = H: ^{t}Bu-PyCa) (R = ^{i}Pr; R′ = CH_3: ^{i}Pr-6-Me–PyCa) (R = $CH_2CH_2C_6H_5$; R′ = H: Phe–PyCa) (R = ^{t}Bu; R′ = CH_3: ^{t}Bu-6-Me–PyCa) (R = ^{i}Pr; R′ = C(H)O: ^{i}Pr–IPA) have been synthesized starting from (1,5-cyclooctadiene)Pd(CH_3)(Cl) and ionic compounds of the type [(N-N)Pd(CH_3)]BF_4 (N–N = bipy, ^{i}Pr–PyCa, ^{t}Bu–PyCa or ^{i}Pr-6-Me–PyCa) by treatment of the methyl(chloro)palladium compounds with silver tetrafluoroborate. All products have been characterized by spectroscopic methods. Reaction of the compounds with carbon monoxide gives the neutral acyl compounds (N–N)Pd(C(O)CH_3)(Cl) and ionic acyl compounds [(N–N)Pd(C(O)CH_3)]BF_4 (N–N = bipy, ^{i}Pr–PyCa, ^{t}Bu–PyCa, ^{i}Pr-6-Me–PyCa or Phe–PyCa). The crystal structures of (^{i}Pr-6-Me–PyCa)Pd(CH_3)(Cl), (^{i}Pr–IPA)Pd(CH_3)(Cl), (bipy)Pd(C(O)CH_3)(Cl) and (^{i}Pr–PyCa)Pd(C(O)CH_3)(Cl), have been determined. Comparison of data for the Pd–N=C–C_5H_4N moieties of the complexes concerned show that the geometries are almost identical, the largest r.m.s. deviation (between (^{i}Pr-6-Me–PyCa)Pd(CH_3)(Cl) and (bipy)Pd(C(O)CH_3)(Cl)) being 0.2 Å. The Pd–C bond distances in the two acetylpalladium complexes are 0.05 Å shorter than those in the two methylpalladium complexes. The Pd–N bond distances for the nitrogen atoms situated *trans* to the organic group are shorter by 0.11 Å in the case of acetyl ligands.

An unprecedented influence of the steric properties of the ligands on the half-life for the CO insertion is observed; substituents adjacent to the nitrogen donor atoms cause strongly acceleration.

Keywords: Palladium; Imine; Carbon monoxide; Catalysis; Crystal structure; Late transition metals

1. Introduction

In many reactions catalyzed by late transition metals, in particular rhodium and palladium, the metal is stabilized by ligands having phosphorus donor atoms. Since late transition metals are soft Lewis acids, the soft Lewis-base phosphorus ligands stabilize a wide variety of oxidation states, thus providing very robust metal complexes, suitable for catalytic reactions under extreme conditions [1].

The number of late transition metal complexes used in catalytic processes bearing the harder nitrogen donor ligands is limited, although most processes involving catalysts containing phosphine ligands can also be carried out with those containing nitrogen ligands [2–5]. Examples are C–C cross-coupling reaction, allylic alkylation, hydrogenation and the Heck reaction, in which nitrogen-based catalysts perform better than phosphine-based catalysts [1,4], but in most cases the phosphine complexes are better, especially in industrial applications. It is known for example that, in the palladium-catalyzed terpolymerization of carbon monoxide, ethene and maleic anhydride, use of bipyridine and phenanthro-

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line ligands gives a considerably higher ethene : MA ratio but a much lower average molecular weight of the terpolymer than does that of diphosphine ligands [3].

In recent years we [6–8] and others [2,5] have shown in model studies of the separate steps of the alternating copolymerization of CO with alkenes that palladium complexes with nitrogen donor ligands are significantly more reactive than analogous palladium phosphine complexes, but they have the major disadvantage of being less stable under catalytic conditions, particularly in respect of their tendency to dissociate from the metal center. For example, the reaction of a palladium complex containing a bidentate α-diimine ligand with an olefin may lead to the dissociation of one nitrogen atom [9], and this under certain conditions may lead to formation of α-diimine-bridged binuclear species [10].

In order to study the steric and electronic effects of nitrogen ligands in carbonylation reactions, we have synthesized a series of neutral and ionic methylpalladium complexes containing bidentate nitrogen ligands 2,2′-bipyridine (bipy)(**1**), 2-(*N*-2-propanecarbaldimino)pyridine (^{i}Pr–PyCa)(**2**),2-(*N*-2-(2-methyl)propanecarbaldimino)-pyridine (^{t}Bu–PyCa)(**3**), 2-(*N*-2-propanecarbaldimino)-6-(methyl)pyridine (^{i}Pr-6-Me–PyCa)(**4**), 2-(*N*-(2-phenyl)ethanecarbaldimino)pyridine (Phe–PyCa)(**5**),2-(*N*-2-(2-methyl)propanecarbaldimino)--(methyl)pyridine (^{t}Bu-6-Me–PyCa)(**6**) and 2-(*N*-propanecarbaldimino)-6-(carbaldimino)pyridine (^{i}Pr-IPA)(**7**). Some palladium and platinum complexes containing some of these ligands have been used in the past by Vitagliano and coworkers [11a,12] in studies of alkene-stabilized five-coordinated palladium and platinum complexes. We have examined the reactivities of the methylpalladium complexes containing the ligands **1–7** towards carbon monoxide (Fig. 1) and also investi-

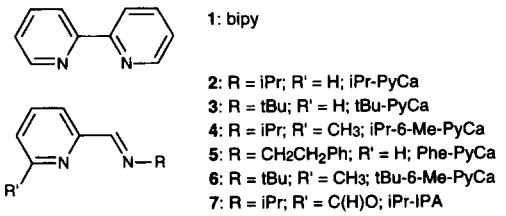


Fig. 1. Structure and numbering of the ligands.

Table 1
Selected ^{1}H NMR data for **2–14b** [a].

Compound [b]	δ(Pd–R) (ppm)	δ(H$^{\alpha}$) (ppm)	δ(H^{3}) (ppm)	δ(H^{6} or 6-R) (ppm)	δ(H^{7}) (ppm)
2	—	3.44	7.81	8.42	8.21
3	—	—	7.96	8.59	8.33
4	—	3.16	7.81	2.57 (Me)	8.35
5	—	3.02	7.99	8.60	8.28
6	—	—	7.86	2.60 (Me)	8.35
7	—	3.59	≈ 7.8	10.10	8.47
1a	1.03	—	8.09, 8.14	8.87, 9.19	—
2a^{c}	1.01	4.31	7.68	9.12	8.37
2a^{t}	1.11	4.43	7.68	8.64	8.27
3a	1.20	—	7.73	8.61	8.20
4a	1.17	4.21	7.50	3.00 (Me)	8.38
5a^{c}	1.09	3.08	7.46	9.05	7.77
5a^{t}	1.07	3.25	7.52	8.62	7.77
6a	1.22	—	7.46	2.92 (Me)	8.36
7a	1.05	4.21	≈ 8.10	10.99	8.68
11a	1.11	—	8.42	8.65, 8.71	—
12a^{c}	1.13	4.12	8.01	8.61	8.57
12a^{t}	1.01	4.20	8.06	8.68	8.67
13a	1.25	—	8.07	8.65	8.53
14a	1.21	4.19	7.86	2.77 (Me)	8.65
1b	2.67	—	—	8.50, 9.02	—
2b^{c}	2.65	4.18	7.63	8.97	8.29
2b^{t}	2.65	4.16	≈ 7.6	8.42	8.19
3b	2.56	—	—	8.41	8.13
4b	2.66	4.00	4.00	2.90 (Me)	8.28
5b^{c}	2.69	2.91	3.95	8.78	7.87
5b^{t}	2.64	3.18	3.98	8.39	7.78
11b	2.32	—	8.30	8.76, 8.82	—
12b	2.68	4.03	4.03	8.40	8.52
13b	2.70	—	—	8.31	8.43
14b	2.71	3.89	3.89	2.72 (Me)	8.55

[a] In $CDCl_3$ at 293 K, except for the ionic complexes which were examined in CD_3CN at 293 K.
[b] Superscript **t** indicates a *trans* configuration, and superscript **c** a *cis* configuration of the methyl and the imino-nitrogen.

gated the stability and the molecular structures by means of NMR techniques and single-crystal structure analyses. The ligands have in common an α-diimine chelating moiety which has both σ-donating and π-accepting properties [9]. The R–PyCa ligands are non-symmetric and thus can give rise to geometric isomers when coordinated to methyl(chloro)palladium moieties. α-Diimine ligands are known to coordinate in a bidentate fashion [13] but since they are quite flexible, they can if required also adopt a monodentate coordination mode. This was observed even in the case of *cis*-fixed ligands such as phenanthroline, although the non-coordinated nitrogen of the phenanthroline remains in the vicinity of the metal [9].

2. Results

In previous work we showed that (COD)Pd(CH_3)(Cl) readily undergoes substitution by bidentate phosphorus or potentially terdentate nitrogen ligands [7,14]. Although other starting complexes are known, such as [Pd(CH_3)(SMe_2)μ-Cl]$_2$ [15] and (tmeda)Pd(CH_3)(Cl) [2a], use of (COD)Pd(CH_3)Cl proved to be an excellent method for the synthesis of neutral methyl(chloro)palladium complexes containing bidentate and terdentate nitrogen ligands.

The methyl(chloro)palladium complexes **1a–7a**, the methylpalladium tetrafluoroborate complexes **11a–14a**, the acetyl(chloro)palladium complexes **1b–5b** and the acetylpalladium tetrafluoroborate complexes **11b–14b** were isolated with high yields. Compounds **2a–4a** and **2b–4b** gave satisfactory elemental analysis. Compounds **5a**, **6a**, **11a–14a** and **11b–14b** were only stable for a few hours, in precluding elemental analysis. From **7a**, only a very small amount of product was isolated and this was not sufficient for elemental analysis. The structural features of **1a** and **1b** and the elemental analysis data were reported recently [2]. The complexes have been fully characterized by ^{1}H and ^{13}C NMR spectroscopy, and in the case of the acetylpalladium complexes **1b–14b** also by IR spectroscopy. For **4a**, **7a**, **1b** and **2b**, single-crystal structure analyses were carried out. Selected ^{1}H NMR data are presented in Table 1.

2.1. Synthesis and properties of methylpalladium compounds 1a–14a

Substitution of COD in (COD)Pd(CH_3)(Cl) by the appropriate nitrogen ligand in dichloromethane resulted in the rapid formation of complexes of the type (N-N)Pd(CH_3)(Cl), numbered **1a–6a**. The colourless methyl(chloro)palladium complex **7a** was prepared in the same fashion but was isolated by a different procedure (see Section 5). The ionic complexes of the type [(N–N)Pd(CH_3)(acetonitrile)]BF_4 (**11a–14a**) were obtained by reaction of the methylpalladium compounds with silver tetrafluoroborate in acetonitrile. The structure and numbering of the complexes is shown in Fig. 2. For clarity the neutral compounds are numbered **1a**, **1b**, **2a** etc. and the corresponding ionic compounds **11a**, **11b**, **12a** etc.

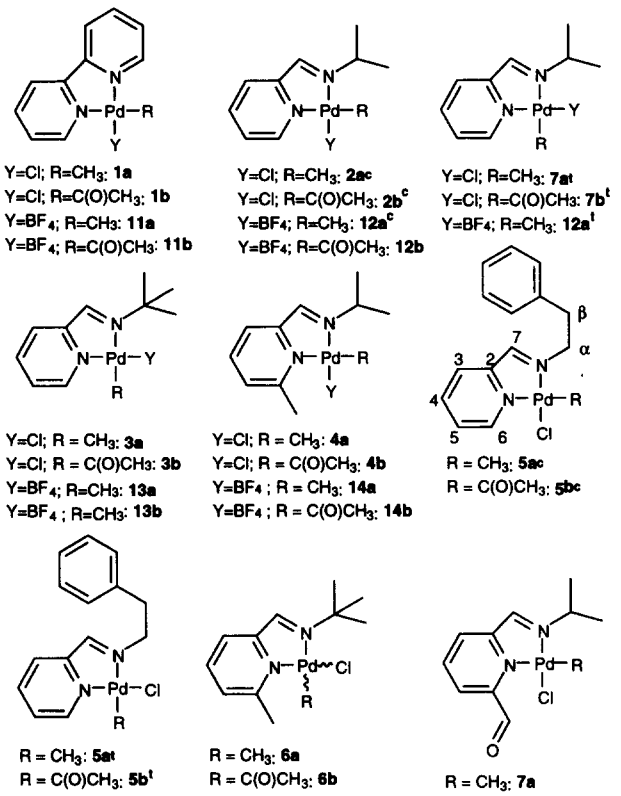


Fig. 2. Structure and numbering of the methyl-and acetylpalladium compounds **1a–14a** and **1b–14b**. The adopted numbering scheme of the R-PyCa ligands **2–7** is shown only for **5**. The superscript **t** indicates a *trans* configuration, and the superscript **c** a *cis* configuration of the methyl and the imino nitrogen.

Since the R–PyCa ligands **2–7** are asymmetric, coordination to methyl(chloro)palladium compounds can lead to the formation of two isomeric forms, which are *cis* and *trans* in respect of the relative positions of the methyl ligand and the imino nitrogen of the R–PyCa ligand on the palladium atom. This is the case for (^{i}Pr–PyCa)Pd(CH_3)(Cl)(**2a**), (Phe–PyCa)Pd(CH_3)(Cl)-(**5a**), [(^{i}Pr-PyCa)Pd(CH_3)]BF_4(**12a**) and the acetylpalladium analogues **2b** and **5b**, as can be concluded from the two sets of resonances in the NMR spectra.

The most sensitive resonances for the assignment of this isomerism are for H^6 and the α-protons of the imino substituents (Table 1). In the *cis* isomers, H^6 has a large chemical shift, owing to the strong deshielding effect of the chloride ligand, which is situated *cis* to the pyridyl group (Fig. 2), whereas the *trans* isomers have the H^6 resonances at a considerably lower chemical shift. For example, the H^6 signal for **2a** appears at 9.12 ppm, and for **2a^t** at 8.64 ppm. The methyl compounds

2a, **5a** and **12a** exist in *cis*:*trans* ratios of 1:0.79, 1:0.30 and 1:0.27 respectively and the acetylpalladium compounds **2b** and **5b** in 1:0.56 and a 1:0.25 ratios respectively, as indicated by the ^{1}H NMR integrals. Interestingly, in the case of **2b**, only the *cis* isomer **2b**(*cis*) was present in the crystal. The ^{1}H and ^{13}C NMR spectra of the complexes of **2** and **5** have sharp resonances indicating that no dynamic processes, such as *cis–trans* isomerization are observed by these complexes on the NMR time scales.

For the palladium complexes **4a**, **14a**, **4b**, **14b** and **7a** containing the 6-substituted ligands ^{i}Pr-6-Me–PyCa and ^{i}Pr–IPA, only the *cis* isomers were observed, whereas the palladium complexes **3a**, **13a**, **3b** and **13b** containing ^{t}Bu–PyCa occur exclusively in the *trans* configuration. The ^{1}H NMR signals from all the R–PyCa palladium compounds are very sharp, except in the case of **6a**, vide infra, indicating that no fluxional processes such as methyl-chloro *cis–trans* isomerization, take place on the NMR time scale.

Surprisingly, the composition of **6a**, containing the sterically demanding ligand **6** proved to be very complex. Adding one equivalent of **6** to (COD)Pd(CH_3)(Cl) led to very poor yields of **6a** (14%). Use of a five fold excess of **6** yielded after washing an aggregate containing **6a** and **6** in a 1:1 ratio. Further washing resulted in formation of Pd black and the recovery of the 1:1 aggregate. The ^{1}H NMR spectrum of this aggregate shows a set of sharp signals of free **6** and a set of broadened signals of coordinated **6**. The structure of **6a** could be analyzed only with difficulty, since the usual indicator protons, H^6 and H^α, are absent. The chemical shift for the methyl ligand in **6a** is close to that in **13a** and suggests a *cis* configuration. The chemical shift of the methyl group, however, may be affected by severe distortions of the methyl and the chloride ligands with respect to the coordination plane. Some nuclear Overhauser effect experiments performed to help to elucidate the configuration of **6a** revealed a chemical exchange of coordinated and free ligand, indicating that **6** is only weakly bonded to Pd(II). This is confirmed by the rapid substitution of **6** to give **4a** when an equimolar amount of **4** was added to **6a**.

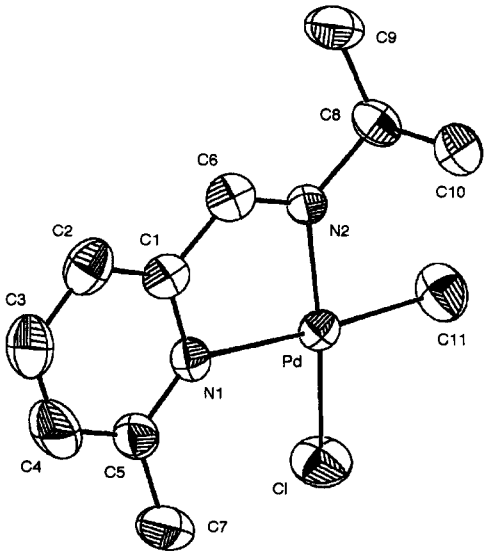


Fig. 3. ORTEP plot (drawn at the 50% probability level) of the molecular structure of [2-(*N*-2-propanecarbaldimino)-6-(methyl) pyridyl]methyl(chloro)palladium(II) (**4a**).

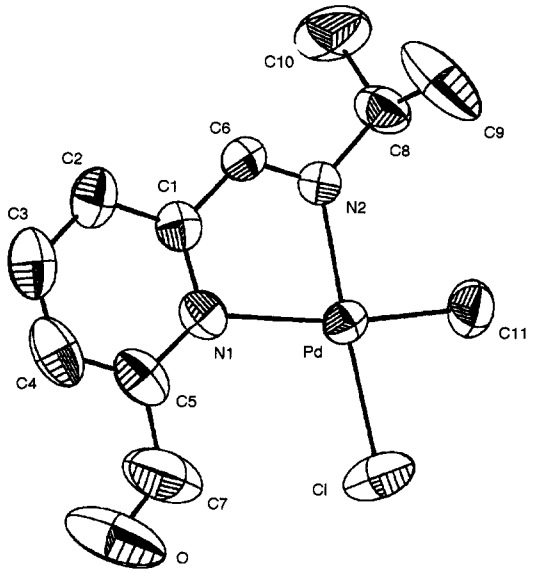


Fig. 4. ORTEP plot (drawn at the 50% probability level) of the molecular structure of 2-(*N*-propanecarbaldimino)-6-(carbaldimino) pyridyl]methyl(chloro)palladium(II) (**7a**).

2.2. Crystallographic section

Crystals suitable for X-ray determination were obtained for **4a**, **7a**, **1b** and **2b** by slow diffusion of diethyl ether into a dichloromethane solution of **4a**, **7a** and **1b**, or by slow evaporation of the solvent from an acetonitrile solution of **2b**. The molecular structures of **4a**, **7a**, **1b** and **2b** are presented in Figs. 3, 4, 5 and 6 respectively. Tables 2 and 3 list the bond distances and selected bond angles respectively, for the non-hydrogen atoms, and Table 5 later gives selected crystal data and refinement details.

The complexes **4a**, **7a**, **1b** and **2b** all have the expected square planar arrangement of the ligands around the palladium metal. The organic group R in **4a**, **7a** and **2b** is *trans* with respect to N(1) and *cis* to N(2), i.e. the *cis* isomers are formed. It is interesting to note that, for **4a**, only the *cis* isomer was found in the crystal, whereas in solution both isomers are present. The α-diimine ligands have bite angles of 77.8(4)–78.5(2)°, which are normal values for these types of ligands [2]. From Fig. 4 it can be seen that the formyl group has turned away from the palladium and does not

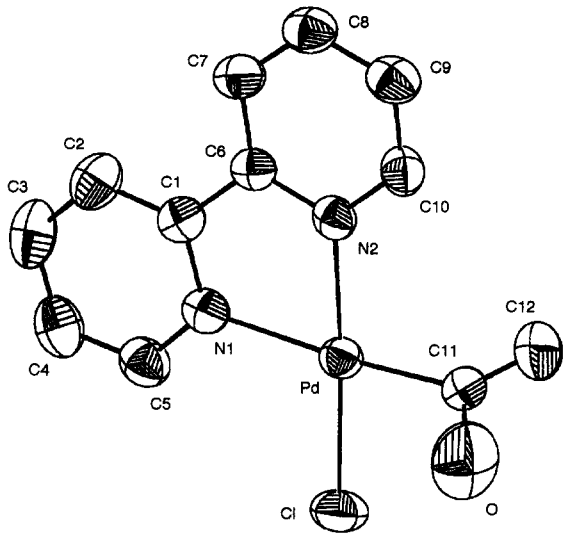


Fig. 5. ORTEP plot (drawn at the 50% probability level) of the molecular structure of (bipyridyl)methyl(chloro)palladium(II) (**1b**).

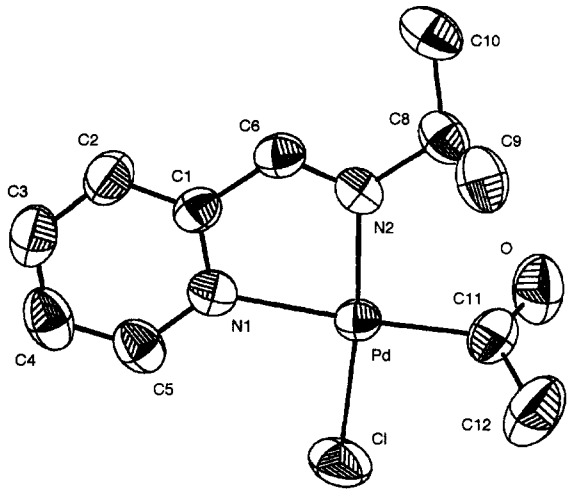


Fig. 6. ORTEP plot (drawn at the 50% probability level) the molecular structure of [2-(*N*-2-propanecarbaldimino)pyridyl] methyl(chloro)palladium(II) (**2b**).

Table 2
Bond distances (with estimated standard deviations in parentheses) for the non-hydrogen atoms of **4a**, **7a**, **1b**, and **2b**

	Bond distance (Å)			
	4a	**7a**	**1b**	**2b**
Pd–Cl	2.307(2)	2.312(2)	2.32(1)	2.319(1)
Pd–C(11)	2.009(9)	2.012(8)	1.94(1)	1.964(5)
Pd–N(1)	2.260(5)	2.253(5)	2.16(1)	2.170(4)
Pd–N(2)	2.070(5)	2.060(4)	2.07(1)	2.063(3)
C(1)–C(2)	1.37(1)	1.397(10)	1.36(2)	1.392(7)
C(1)–C(6)	1.450(9)	1.456(7)	1.47(2)	1.465(6)
C(1)–N(1)	1.363(7)	1.341(7)	1.37(1)	1.343(5)
C(2)–C(3)	1.40(1)	1.390(10)	1.38(2)	1.400(7)
C(3)–C(4)	1.36(1)	1.34(1)	1.39(2)	1.347(9)
C(4)–C(5)	1.38(1)	1.39(1)	1.35(2)	1.389(8)
C(5)–C(7)	1.48(1)	1.47(1)	—	—
C(5)–N(1)	1.347(8)	1.357(7)	1.33(2)	1.331(6)
C(6)–N(2)	1.272(8)	1.283(8)	1.36(1)	1.285(6)
C(8)–C(9)	1.51(1)	1.50(1)	1.38(1)	1.516(8)
C(8)–C(10)	1.50(1)	1.51(1)	—	1.523(7)
C(8)–N(2)	1.495(8)	1.488(8)	—	1.490(6)
C(11)–C(12)	—	—	1.52(2)	1.509(9)
C(11)–O	—	—	1.20(2)	1.174(7)
C(7)–C(8)	—	—	1.39(2)	—
C(6)–C(7)	—	—	1.39(2)	—
C(9)–C(10)	—	—	1.36(2)	—
C(10)–N(2)	—	—	1.36(2)	—
C(7)–O	—	1.20(1)	—	—

Table 3
Selected bond angles (with estimated standard deviations in parentheses) for the non-hydrogen atoms of **4a**, **7a**, **1b** and **2b**

	Bond angle (°)			
	4a	**7a**	**1b**	**2b**
Cl–Pd–C(11)	85.9(2)	86.6(2)	88.3(4)	88.1(1)
Cl–Pd–N(1)	101.6(1)	102.0(1)	97.2(6)	96.1(1)
C(11)–Pd–N(2)	94.5(3)	92.9(3)	96.7(7)	97.7(2)
N(1)–Pd–N(2)	78.4(2)	78.5(2)	77.8(4)	78.1(1)
Pd–C(11)–C(12)	—	—	117(1)	115.4(5)
Pd–C(11)–O	—	—	123.0(8)	122.1(4)
C(12)–C(11)–O	—	—	120(1)	122.5(5)

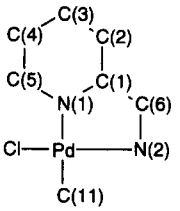


Fig. 7.

coordinate to the metal center. In **1b** and **2b**, the acetyl ligand lies in perpendicular position to the palladium coordination plane, in keeping with earlier reports [2a,16].

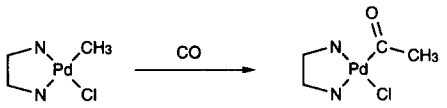
Comparison of the data for the corresponding compounds Pd, Cl, N(1), N(2), C(1), C(2), C(3), C(4), C(5), C(6) and C(11) (Fig. 7) in structures **4a–2b** led to the following results. Taking **4a** as reference the matching led to the following r.m.s. values: **4a–7a** r.m.s., 0.08 Å; **4a–1b** r.m.s., 0.20 Å; **4a–2b** r.m.s., 0.16 Å. The greatest variation in distances are for those involving the chloride atoms of the compounds, with r.m.s. values of 0.15, 0.39 and 0.34 Å respectively.

2.3. Carbonylation reactions of methylpalladium compounds 1a–14a

The methyl(chloro)palladium compounds **1a–5a** (Scheme 1) and the methylpalladium tetrafluoroborate compounds **11a–14a** were treated with CO in order to investigate their reactivity in CO insertion.

For preparative purposes, Schlenk vessels containing a solution of **1a–5a** in dichloromethane or **11a–14a** in acetonitrile were evacuated, flushed twice with CO and then filled with CO, and the mixture was stirred for 30 min, during which a little palladium black was formed. Filtration gives the pure acetyl compounds **1b–14b**.

The half-lives for CO insertion were obtained by measuring the CO uptake with a gas buret (Table 4). Although use of high pressure ^{1}H NMR spectroscopy for the determination of CO insertion half-lives was successful in the case of diphosphine palladium complexes [6a,17], this method was unsuitable for most compounds containing nitrogen ligands, because insertion half-lives are too short for reliable measurement.



Scheme 1.

3. Discussion

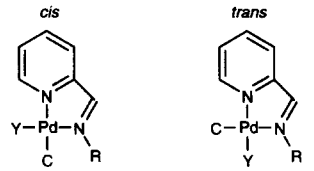
Several features in the ^{1}H NMR data are note worthy. Whereas for the free ligands the resonances of the pyridine protons appear in the sequence H^5, H^4, H^3, H^6, those for the R–PyCa complexes normally appear in the sequence H^5, H^3, H^4, H^6. The negative coordination-induced shift (CIS) of H^3 can be attributed to the *E-trans* conformation of the free ligand. In this conformation, the nitrogen of the imino group points towards H^3 and the interaction between the hydrogen and the lone pair of the imine induces a low field shift for H^3. The CIS of H^6 depends strongly on the arrangement of the ligands around the palladium center. If the complex has a *cis* configuration, the chloride ligand is close to H^6 and the strong deshielding effect of the chloride ligand increases the chemical shift for H^6.

The *cis* configuration is apparently the most favourable configuration for methyl(chloro)palladium complexes with non-symmetric R–PyCa ligands, in keeping with previous reports [11a,12]. The differences between the energies of the *cis* and the *trans* configurations are clearly small, since minor changes on either side of the ligand can affect the configuration. Apparently, a very delicate balance is reached in the case of the configurations of **2a**, **2b**, **5a** and **5b** for which both isomers occur, while the steric requirement of the acetyl ligand compared with that of the methyl ligand changes the *cis* : *trans* ratio in favour of the *cis* configuration. This is also clear for the ionic isomer **12a**, in which the

Table 4
Half-lives for the carbonylation of **1a–14a**, and IR data for **1b–14b** [a] and related compounds taken from the literature

Compound	Half-life (min:s)	(ν(CO) cm^{-1})
(^{i}Pr-6-Me–PyCa)Pd(CH_3)(Cl) (**4a**)	4:15 (±0:30)	1697
[(^{i}Pr-6-Me–PyCa)Pd(CH_3)]BF_4 (**14a**)	8:00 (±0:30)	1705
[(bipy)Pd(CH_3)]BF_4, (**11a**)	8:30 (±0:30)	1690
[(^{t}Bu-PyCa)Pd(CH_3)]BF_4 (**13a**)	12:00 (±0:30)	1700
(^{t}Bu-PyCa)Pd(CH_3)(Cl) (**3a**)	12:30 (±0:30)	1692
[(^{i}Pr-PyCa)Pd(CH_3)]BF_4 (**12a^c** and **12a^t**)	14:00 (±0:30)	1703
(^{i}Pr-PyCa)Pd(CH_3)(Cl) (**2a^c** and **2a^t**)	19:00 (±0:30)	1695
(Phe–PyCa)Pd(CH_3)(Cl) (**5a^c** and **5a^t**)	23:45 (±0:30)	1694
(bipy)Pd(CH_3)(Cl) (**1a**)	28:30 (±0:30)	1690
(^{t}Bu–PyCa)Pd(CH_3)(Cl)–^{t}Bu–PyCa (**6a**)	instantaneous Pd blackening	—

[a] [Pd] = 40 mM; P(CO) = 2 bar; T = 293 K.



12b:	1	0	R=iPr; C=C(O)CH$_3$; Y=CH$_3$CN/BF$_4$.
5b:	1	0.25	R=Phe; C=C(O)CH$_3$; Y=Cl.
12a:	1	0.27	R=iPr; C=CH$_3$; Y=CH$_3$CN/BF$_4$.
5a:	1	0.30	R=Phe; C=CH$_3$; Y=Cl.
2b:	1	0.56	R=iPr; C=C(O)CH$_3$; Y=Cl.
2a:	1	0.79	R=iPr; C=CH$_3$; Y=Cl.

Fig. 8. *cis*:*trans* ratios of **2a**, **2b**, **5a**, **5b**, **12a** and **12b**.

chloride ligand has been replaced by an acetonitrile molecule. The preference for the *cis* configuration increases in the order **12b** > **5b** > **12a** > **5a** > **2b** > **2a** (Fig. 8).

The fact that the acetylpalladium compounds have a larger preference for the *cis* configuration can be attributed to the perpendicular position of the acetyl group with respect to the coordination plane. In this conformation the acetyl group is less bulky than the methyl group and is sterically less constrained by the bulk of the substituent on the imino-nitrogen. The *trans* influence of the acetyl group, which is larger than that of the methyl group [18], also increases the preference for the *cis* configuration. The effect of acetonitrile on the stereochemistry can also be attributed to the lower steric hindrance.

The higher *trans* influence of the methyl and the acetyl ligand than of the chloride ligand [18] is reflected in the longer Pd–N(1) distance (by 0.19 Å for the methylpalladium compounds and by 0.09–0.11 Å for the acetylpalladium compounds) with respect to the Pd–N(2) distance. The shorter Pd–C(11) distances in the acetylpalladium complexes **1b** and **2b** than in the methylpalladium complexes **4a** and **7a** (by about 0.05 Å) can be attributed to the shorter bonds found for sp^2-hybridized carbon atoms in general. An intriguing discrepancy, however, is found for the Pd–N(1) bond distances, which are severely affected by the nature of the organic ligand in the *trans* position. These Pd–N(1) distances in **1b** and **2b** are about 0.11 Å shorter than those in **4a** and **7a**, while the Pd–Cl and Pd–N(2) bond distances are not affected, and this must be due to the differences between the *trans* influences of the methyl and the acetyl ligands.

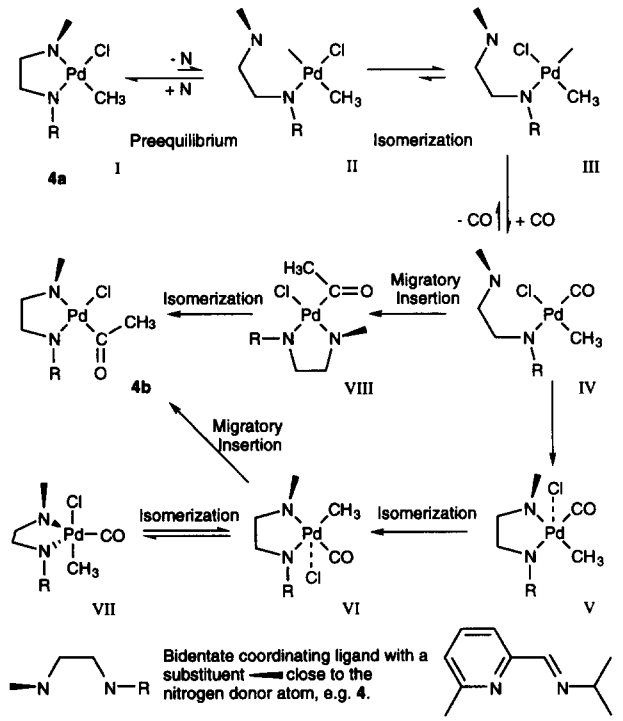
The acetyl ligand is known to have a larger *trans* influence than the methyl ligand [18] and this would be expected to lead to longer Pd–N(1) distances owing to σ-bond destabilization of the Pd–N bond. However, shorter bonds are, in fact, found in **1b** and **2b**. Since the R–PyCa and bipy ligands have suitable $p\pi_*$ orbitals for π back donation, the *trans* influence of the acetyl ligand causes an increased $d_{xz} \rightarrow p\pi_*$ back donation from the palladium to the pyridyl moiety. Hence, a push–pull process is present which causes the Pd–N(1) distances in **1b** and **2b** to be shorter than in the methylpalladium complexes **4a** and **7a**.

The half-lives of the CO insertion for the neutral compounds **1a–3a** are only slightly longer than those for the ionic methylpalladium analogues **11a–13a**, and that for the neutral compound **4a** is even shorter than that for the ionic compound **14a**. However, different solvents were used for the neutral and the ionic compounds and so the half-lives cannot be compared, since not only are the solubilities of CO in the two solvents different, but also different mechanistic routes may apply, vide infra. Nevertheless, it is expected that the presence of acetonitrile will lower the rate of CO insertion since it acts as a competing ligand.

The large differences in the half-lives between the various methylpalladium compounds are unexpected. The half-life clearly decreases with increasing steric hindrance on either side of the ligand. This surprising accelerating effect of a substituent adjacent to one nitrogen donor atom was very recently also observed for complexes with trinitrogen ligands [19]. The accelerating effect of a bulky group close to the N-donor function, however, reaches a limit. For example, when **6a** is treated with CO in dichloromethane, instantaneous formation of Pd-black is observed, and this is understandable since too much steric hindrance will cause inefficient bonding of the bidentate nitrogen ligand to the palladium atom, vide supra.

We showed previously that compounds (P–P)-Pd(CH_3)(Y) (Y = Cl^-, $CF_3SO_3^-$ or BF_4^-) containing flexible diphosphine ligands P–P with large bite angles show short half-lives for CO insertion, since the transition state energy is when the CO and CH_3 groups will be forced closer together in the intermediate (P–P)Pd(CH_3)(CO) [6a]. Therefore, we were rather surprised to find that methylpalladium compounds containing these flexible bidentate nitrogen ligands **1–5** with small bite angles (76–80°) underwent much faster CO insertion than those containing diphosphines [7]. We observed similar fast insertion of CO into the Pd–C bond recently also for methylpalladium complexes with rigid bidentate nitrogen ligands that have comparable small bite angles.

When we look at our earlier results [6,7] and those reported here in the light of other work [9a,20] we note that Natile and coworkers found that bidentate nitrogen ligands containing bulky groups adjacent to the N-donor functions cause deviations from planarity, as for example in (dmphen)Pd(CH_3)(Cl) (dmphen = 2,9-dimethyl-1,10-phenanthroline) [20], and these ligands also show a greater tendency to form five-coordinated complexes with alkenes [9b,11,20]. Strikingly, dmphen can, depending on the donor and acceptor properties of the ligand, bond in the *trans* position as a bidentate ligand



Scheme 2. Mechanism accounting for the accelerating effect of substituents adjacent to the nitrogen donor in the insertion reactions of CO with the complexes (N–N)Pd(CH_3)(Cl).

(acceptor in the *trans* position) or as a monodentate ligand (donor in the *trans* position) and can even adopt a coordination mode in between monodentate and bidentate [9b].

In a recent article on the rigid bidentate nitrogen ligand Ar-BIAN (Ar-BIAN = bis(arylimino)acenaphtene) we have tentatively proposed a mechanism involving dissociation of Cl^- to allow CO coordination, while the rigid N–N ligand remains bonded as a bidentate throughout the CO insertion [7a,b]. However, in the light of the previous discussion one might also propose for compounds (N–N)Pd(CH_3)(Cl) the mechanism outlined in Scheme 2 for the carbonylation of **4a**, which is partly based on results reported by Natile and coworkers [9a].

According to Natile and coworkers, the first step involves (partial) dissociation of the nitrogen donor containing the bulky substituent. The resulting T-shaped intermediate II then isomerizes to the more stable T-shaped intermediate III with CH_3 *trans* to Cl. Addition of CO gives intermediate IV; such species with CO *cis* to the CH_3 group have recently been observed [8].

A conceivable alternative pathway would involve an initial migratory insertion to give the product **4b** via intermediate VIII. This is less likely, since CH_3 migration would not be expected to occur for CH_3 *trans* to Cl. The more likely pathway involves the dissociation of Cl *trans* to CH_3 to give V, in which has a strong *trans* influence, so favoring isomerization to VI. Depending on the solvent, this intermediate could be present as an ion pair, with a cationic palladium moiety and Cl^-, or as separated ions. Migratory insertion might now occur in the (N–N)Pd(CH_3)(CO) plane to give, after reassociation of Cl^-, the final product **4b**. It is also possible that V isomerizes to the TBP-shaped intermediate VII. Since migratory insertion from VII is unlikely [21], this five-coordinated intermediate will be an unreactive species. This mechanism is attractive since it accounts for the rate-enhancing effect of bulky substituents on the nitrogen and is in line with the observation that both flexible and rigid bidentate nitrogen ligands may be in a monodentate bonding [9a,b,10]. The possibility cannot be excluded, however, that intermediate V is formed directly from intermediate I by association of CO, facilitated by distortion from planarity induced by the substituent close to one N-donor function.

Enhancement of the rate of CO insertion was also observed in acetonitrile for the compounds [(N–N)Pd(CH_3)($NCCH_3$)]Y containing weakly coordinating groups Y such as OTf or BF_4. A similar mechanism may be proposed but with acetonitrile taking the coordination position occupied by Cl^- in the neutral compounds. It may well be, however, that in the case of weakly coordinating groups there is a direct substitution by CO, while the N^N ligand remains bonded in a bidentate fashion. The rate-enhancing effect of steric bulk close to one of the N-donor atoms is then less easily explained.

It remains likely that the mechanisms of CO insertion will differ for bidentate phosphine and nitrogen ligands. They may differ not only in terms of the dissociation of ligands and anions but also in respect of the sequence in which such processes take place, and different mechanisms could even operate simultaneously.

4. Conclusions

The methyl(chloro)palladium compounds discussed undergo a very interesting isomerism, caused by the steric interactions of the substituents on the ligand. These interactions also have a large influence on the rate of CO insertion. The exact reason for this acceleration is not yet clear, and only a tentative but plausible mechanism can at present be put forward.

5. Experimental details

5.1. Materials and apparatus

All manipulations were carried out under purified dry nitrogen by use of standard Schlenk techniques. Sol-

vents were dried and stored under nitrogen. Starting chemicals from Aldrich Chemicals, and carbon monoxide 2.5 grade from HoekLoos were used without further purification except where otherwise indicated explicitly. The complex (COD)Pd(CH_3)(Cl) was made from (COD)$PdCl_2$ by published methods [14,22].

Elemental analyses were carried out by the Elemental Analyses Section of ITC–TNO, Zeist, The Netherlands. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 100 and AMX 300 spectrometers, and IR spectra on a Perkin–Elmer PE 283 spectrometer.

5.2. Compounds

5.2.1. Synthesis of 2-(N-R-carbaldimino)-6-(R')-pyridine

Compounds **2–6** were made by the procedure described by Lavery and Nelson [23] from pyridine-2-carboxaldehyde, 6-methylpyridine-2-carboxaldehyde or 2,6-pyridinedicarboxaldehyde. Ligands **2**, **3** and **6** were vacuum distilled and all ligands were purified over activated basic alumina prior to use. Ligand **7** was obtained as a side product from the trinitrogen analogue 2,6-bis(isopropylcarbaldimino)pyridine [24] and was not purified, vide infra.

2: green oil. ^{1}H NMR ($CDCl_3$): δ 1.09 (d, 6H, ^{i}Pr), 3.44 (septet, ^{i}Pr), 7.08 (dd, H^5), 7.51 (t, H^4), 7.81 (d, H^3), 8.21 (s, H^7), 8.42 (d, H^6) ppm.

3: pale-yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.28 (d, 9H, ^{t}Bu), 7.23 (dd, H^5), 7.68 (t, H^4), 7.96 (d, H^3), 8.33 (s, H^7), 8.59 (d, H^6) ppm.

4: orange oil. ^{1}H NMR ($CDCl_3$): δ 1.25 (d, 6H, ^{i}Pr), 2.57 (s, 6-Me), 3.16 (septet, ^{i}Pr), 7.18 (d, H^5), 7.59 (t, H^4), 7.81 (d, H^3), 8.35 (s, H^7) ppm.

5: orange oil. ^{1}H NMR ($CDCl_3$): δ 3.02 (t, 2H, H^α), 3.91 (t, 2H, H^β), 7.22 (m, 6H, H^5 + phenyl), 7.67 (t, H^4), 7.96 (d, H^3), 8.28 (s, H^7), 8.60 (d, H^6) ppm.

6: yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.31 (s, 9H, ^{t}Bu), 2.60 (s, 3H, 6-Me), 7.17 (d, H^5), 7.62 (t, H^4), 7.86 (d, H^3), 8.35 (s, H^7) ppm.

7: ^{1}H NMR ($CDCl_3$): δ 1.25 (d, 6H, ^{i}Pr), 3.59 (septet, ^{i}Pr), approximately 7.8 (m, 3H, H^3, H^4 and H^5), 8.47 (s, H^7), 10.10 (s, $-CHO$) ppm.

5.2.2. Synthesis of methyl(chloro)palladium compounds 1a–5a

Compounds **1a–7a** have been synthesized by substitution of COD in (COD)Pd(CH_3)(Cl) in dichloromethane as reported recently [14].

1a: pale-yellow microcrystals; yield, 85%. ^{1}H NMR ($CDCl_3$): δ 1.03, (s, 3H, Pd–Me) 7.51 (t, $H^{5'}$), 7.54 (t, $H^{5'}$), 7.96 (t, $H^{4'}$), 8.06 (t, H^4), 8.09 (d, H^3), 8.14 (d, $H^{3'}$), 8.87 (d, $H^{6'}$), 9.19 (d, H^6) ppm.

2a: yellow microcrystals; yield, 96%. ^{1}H NMR ($CDCl_3$): **2a**^{c} δ 1.01 (s, 3H, Pd–Me), 1.44 (d, 6H, ^{i}Pr), 4.31 (septet, ^{i}Pr), 7.62 (dd, H^5), 7.68 (d, H^3), 7.98 (t, H^4), 8.37 (s, H^7), 9.12 (d, H^6); **2a**^{t} δ 1.11 (s, 3H, Pd–Me), 1.48 (d, 6H, ^{i}Pr), 4.43 (septet, ^{i}Pr), 7.58 (dd, H^5), 7.68 (d, H^3), 8.37 (t, H^4), 8.27 (s, H^7), 8.64 (d, H^6) ppm. Anal. Found: C, 39.39; H, 4.89; N, 9.04. $C_{10}H_{15}ClN_2Pd$ calc.: C, 39.37; H, 4.96; N, 9.18%.

3a: yellow microcrystals; yield, 97%. ^{1}H NMR ($CDCl_3$): δ 1.20 (s, 3H, Pd–Me), 1.57 (d, 9H, ^{t}Bu), 7.58 (dd, H^5), 7.73 (d, H^3), 8.08 (t, H^4), 8.20 (s, H^7), 8.61 (d, H^6) ppm. Anal. Found: C, 41.27; H, 5.23; N, 8.66. $C_{11}H_{17}ClN_2Pd$ calc.: C, 41.40; H, 5.37; N, 8.78%.

4a: pale-yellow microcrystals; yield, 94%. ^{1}H NMR ($CDCl_3$): δ 1.17 (s, 3H, Pd–Me), 1.38 (d, 6H, ^{i}Pr), 3.00 (s, 6-Me), 4.21 (septet, ^{i}Pr), 7.38 (d, H^5), 7.80 (t, H^4), 7.50 (d, H^3), 8.38 (s, H^7). Anal. Found: C, 41.43; H, 5.51; N, 8.76. $C_{11}H_{17}ClN_2Pd$ calc.: C, 41.40; H, 5.37; N, 8.78%.

5a: orange microcrystals; yield, 89%. ^{1}H NMR ($CDCl_3$): **5a** (*cis*) δ 1.09 (s, 3H, Pd–Me), 3.08 (t, 2H, H^α), 4.01 (t, 2H, H^β), 7.20 (m, phenyl), 7.46 (d, H^3), 7.60 (ddd, H^5), 7.77 (s, H^7), 7.91 (dt, H^4), 9.05 (d, H^6); **5a** (*trans*) δ 1.07 (s, 3H, P–Me), 3.25 (t, 2H, H^α), 4.09 (t, 2H, H^β), 7.20 (m, phenyl), 7.52 (d, H^3), 7.59 (ddd, H^5), 7.77 (s, H^7), 8.01 (dt, H^4), 8.62 (d, H^6) ppm.

5.2.3. Synthesis of [2-(N-2-(2-methyl)propanecarbaldimino)-6-methylpyridyl]methyl(chloro)palladium(II) (6a)

To a solution of 1.11 g (4.20 mmol) (COD)-Pd(CH_3)(Cl) in 50 ml of CH_2Cl_2 were added 3.6 ml (19.8 mmol; 4.7 equivalents) ^{t}Bu-6-Me–PyCa(**6**). The mixture was stirred for 1 h, the solvent then removed in vacuo, and the resulting green oil washed with 3 × 30 ml of hexane and dried to constant weight. According to ^{1}H NMR spectrum, the orange product **6a** contains approximately 1 equivalent of the free ligand. ^{1}H NMR ($CDCl_3$): δ 1.22 (s, Me), 1.55 (s, 9H, ^{t}Bu), 2.92 (s, 3H, 6-Me), 7.39 (d, H^5), 7.46 (d, H^3), 7.82 (t, H^4), 8.36 (s, H^7) ppm.

5.2.4. Synthesis of 2-(N-propanecarbaldimino)-6-(carbaldimino)pyridine 7 and 2-(N-propanecarbaldimino)-6-(carbaldimino)pyridyl]methyl(chloro)palladium(II) (7a)

A solution of 279.6 mg (2.1 mmol) of 2,6-pyridinedicarboxaldehyde and 176 μl (121 mg, 2.1 mmol, 1.0 equivalent) of isopropylamine in 35 ml of dry diethyl ether was stirred over 3Å molecular sieves for 4 days. After filtration and evaporation of the solvent, 195 mg of a mixture of the unsubstituted, monosubstituted and bis-substituted ligands in a 3:1:3 ratio was obtained.

Without separation of the products 26.5 mg (0.1 mmol) of (COD)Pd(CH_3)(Cl) in 5 ml of acetonitrile was treated with 25 μl of the mixture containing 13% of **7**. The products were precipitated by the addition of 5 ml of diethyl ether. The precipitate was isolated by

decantation washed with 3 ml of diethyl ether and dried in vacuo. This precipitate consists of 17% of **7a** and 83% of (2,6-bis(isopropylcarbaldimino)pyridyl)Pd-(CH_3)(Cl) [24] as indicated by ^{1}H NMR spectroscopy. Selective crystallization from acetonitrile yielded colourless cubic crystals of **7a** with about 15% yield and the red crystals of (NNN)Pd(CH_3)(Cl) with about 80% yield.

7a: ^{1}H NMR ($CDCl_3$): δ 1.05 (s, 3H, Pd–Me), 1.39 (d, 6H, ^{i}Pr), 4.21 (septet, ^{i}Pr), approximately 8.10 (m, 3H, H^3, H^4 and H^5), 8.68 (d, H^7), 10.99 (s, $-CHO$) ppm.

5.2.5. Synthesis of ionic methylpalladium tetrafluoroborate complexes 11a–14a

To a stirred solution of 0.05 mmol of **1a–4a** in 3 ml of dry acetonitrile was added 0.05 mmol of silver tetrafluoroborate. The immediately formed white precipitate was filtered off and the ionic methylpalladium complexes **11a–14a** were precipitated by addition of 5 ml of diethyl ether. The precipitate was isolated by decantation, washed with 2 ml of diethyl ether and 2 ml of pentane and dried in vacuo.

11a: pale-yellow microcrystals; yield, 95%. ^{1}H NMR (CD_3CN): δ 1.11 (s, 3H, Pd–Me), 7.78 (m, 2H, H^5 and $H^{5'}$), 8.31 (m, 2H, H^4 and $H^{4'}$), 8.42 (m, H^3 and $H^{3'}$), 8.65 (d, $H^{6'}$), 8.71 (H^6) ppm.

12a: yellow microcrystals; yield, 73%. ^{1}H NMR (CD_3CN): **12a**^{c} δ 1.13 (s, 3H, Pd–Me), 1.44 (d, 6H, ^{i}Pr), 4.12 (septet, ^{i}Pr), 7.19 (dd, H^5), 8.01 (d, H^3), 8.31 (t, H^4), 8.57 (s, H^7), 8.61 (d, H^6); **12a**^{t} δ 1.01 (s, 3H, Pd–Me), 1.45 (d, 6H, ^{i}Pr), 4.20 (septet, ^{i}Pr), 7.87 (dd, H^5), 8.06 (d, H^3), 8.67 (s H^7), 8.68 (d, H^6), (H^4 concealed) ppm.

13a: orange microcrystals; yield, 78%. ^{1}H NMR (CD_3CN): δ 1.25 (s, 3H, Pd–Me), 1.53 (s, 9H, ^{t}Bu), 7.82 (dd, H^5), 8.07 (d, H^3), 8.33 (t, H^4), 8.53 (s, H^7), 8.65 (d, H^6) ppm.

14a: yellow microcrystals; yield, 81%. ^{1}H NMR (CD_3CN); δ 1.21 (s, 3H, Pd–Me), 1.48 (d, 6H, ^{i}Pr), 2.77 (s, 3H, 6-Me), 4.19 (septet, ^{i}Pr), 7.72 (d, H^5), 7.86 (d, H^3), 8.14 (t, H^4), 8.65 (s, H^7) ppm.

5.3. Carbonylation reactions

5.3.1. Synthesis of acetylpalladium compounds 1b–4b and 11b–14b

Synthesis on a preparative scale was carried out by keeping an evacuated Schlenk vessel containing a dichloromethane solution of about 20 mg of the methylpalladium compound filled with CO at 1 bar for 45 min [6,7]. The solution was filtered and the solvent removed in vacuo.

1b: yellow crystals; yield, 82%. ^{1}H NMR ($CDCl_3$): δ 2.67 (s, 3H, C(O)Me), 7.50 (t, H^5 and $H^{5'}$), 7.99 (t, H^4 and $H^{4'}$), 8.07 (d, $H^{3'}$), 8.15 (d, H^3), 8.50 (d, $H^{6'}$), 9.02 (d, H^6) ppm.

2b: orange crystals; yield, 97%. ^{1}H NMR ($CDCl_3$): **2b**^{c} δ 1.36 (d, 6H, ^{i}Pr), 2.65 (s, C(O)Me), 4.18 (septet, ^{i}Pr), 7.59 (dd, H^5), 7.63 (d, H3), 7.97 (t, H^4), 8.29 (s, H^7), 8.97 (d, H^6); **2b**^{t} δ 1.44 (d, 6H, ^{i}Pr), 2.65 (s, C(O)Me), 4.16 (septet, ^{i}Pr), approximately 7.6 (concealed, H^5 and H^3), 8.05 (t, H^4), 8.19 (s, H^7), 8.42 (d, H^6) ppm. Anal. Found: C, 39.61; H, 4.57; N, 8.31. $C_{11}H_{15}ClN_2OPd$ calc.: C, 39.66; H, 4.54; N, 8.41%.

3b: pale-yellow microcrystals; yield, 87%. ^{1}H NMR ($CDCl_3$): δ 1.50 (s, 9H, ^{t}Bu), 2.56 (s, 3H, C(O)Me), 7.55–8.05 (m, 3H, H^3, H^4, H^5), 8.13 (s, H^7), 8.41 (d, H^6) ppm. Anal. Found: C, 40.44; H, 4.85; N, 7.78. $C_{12}H_{17}ClN_2OPd$ calc.: C, 41.52; H, 4.94; N, 8.07%.

4b: orange microcrystals; yield, 80%. ^{1}H NMR ($CDCl_3$): δ 1.35 (d, 6H, ^{i}Pr), 2.66 (s, 3H, C(O)Me), 2.90 (s, 3H, 6-CH_3), 4.00 (septet, ^{i}Pr), 7.36 (d, H^5), 7.44 (d, H^3), 7.81 (t, H^4), 8.28 (s, H^7) ppm. Anal. Found: C, 40.58; H, 4.72; N, 7.67. $C_{12}H_{17}ClN_2OPd$ calc.: C, 41.52; H, 4.94; N, 8.07%.

5b: orange microcrystals: yield, 77%. ^{1}H NMR ($CDCl_3$): **5b**^{c} δ 2.69 (s, 3H, C(O)Me), 2.91 (t, 2H, H^α), 3.95 (t, 2H, H^β), 7.2 (m, 5H, phenyl), 7.54 (m, H^3), 7.87 (s, H^7), 7.91 (dt, H^4), 8.78 (d, H^6); **5b**^{t} δ 2.64 (s, 3H, C(O)Me), 3.18 (t, 2H, H^α), 3.98 (t, 2H, H^β), 7.2 (m, 5H, phenyl), 7.54 H^3), 7.78 (s, H^7), 8.01 (t, H^4), 8.39 (d, H^6) ppm.

11b: pale-yellow microcrystals; yield, 96%. ^{1}H NMR (CD_3CN): δ 2.32 (s, 3H, C(O)Me), 7.78 (m, 2H, H^5 and $H^{5'}$), 8.30 m (2H, H^3 and $H^{3'}$), 8.41 (t, 2H, H^4 and $H^{4'}$), 8.76 (d, H^6), 8.82 (d, $H^{6'}$) ppm.

12b: yellow microcrystals; yield, 67%. ^{1}H NMR (CD_3CN): δ 1.42 (d, 6H, ^{i}Pr), 2.68 (s, 3H, C(O)Me), 4.03 (septet, ^{i}Pr), 7.82 (dd, H^5), 7.98 (d, H^3), 8.29 (t, H^4), 8.40 (d, H^6), 8.52 (s, H^7) ppm.

13b: orange microcrystals; yield, 69%. ^{1}H NMR (CD_3CN): δ 1.49 (s, 9H, ^{t}Bu), 2.70 (s, 3H, C(O)Me), 7.9 (dd, H^5), 8.01 (d, H^3), 8.31 (m, 2H, H^4 and H^6), 8.43 (s, H^7) ppm.

14b: yellow microcrystals; yield, 73%. ^{1}H NMR (CD_3CN): δ 1.41 (d, 6H, ^{i}Pr), 2.71 (s, 3H, C(O)Me), 2.72 (s, 3H, 6-Me), 3.89 (septet, ^{i}Pr), 7.67 (d, H^5), 7.80 (d, H^3), 8.10 (t, H^4), 8.55 (s, H^7) ppm.

5.3.2. Determination of the half-life for insertion of CO

The half-lives were determined at 293 K by use of a home-made gas buret. In a typical experiment, a 12 ml vessel was filled under nitrogen with 5 ml of a 0.4 mM solution of the methylpalladium complex (see Table VII for the solvent) and the solution was stirred. The vessel was carefully evacuated three times and connected to the CO-filled gas buret. The measurement was started by opening the valve betwen the CO and the vigorously stirred solution of the methylpalladium compound. When the equilibrium was reached, the time for take-up of

every 0.25 ml of CO was recorded until the CO uptake had stopped (i.e. at least three half-lives) and the half-life was calculated. Blank experiments in several solvents showed that the time for diffusion of CO was about 20 s.

5.3.3. X-ray data collection and structure refinement

Data for all four crystals were collected on a Enraf–Nonius CAD-4 diffractometer using graphite monochromated radiation, Cu Kα for **1b** and **2b** and Mo Kα for **4a** and **7a**, and ω–2θ scan. The number of reflections measured was 3909 of which 2834 were treated as observed (significance level of 2.5 $\sigma(I)$) in the range $0 \leqslant h \leqslant 35$, $0 \leqslant k \leqslant 35$, $0 \leqslant l \leqslant 11$, maximum $(\sin\theta)/\lambda = 0.70$ for **4a**, 5630/3225, $-13 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 18$, $0 \leqslant l \leqslant 21$, $(\sin\theta)/\lambda = 0.80$ for **7a**, 1318/1272, $-9 \leqslant h \leqslant 0$, $-13 \leqslant k \leqslant 0$, $0 \leqslant l \leqslant 18$, $(\sin\theta)/\lambda = 0.63$ for **1b** and 2626/2476, $-9 \leqslant h \leqslant 0$, $-9 \leqslant k \leqslant 9$, $-14 \leqslant l \leqslant 14$, $(\sin\theta)/\lambda = 0.63$ for **2b**. All structures were solved by direct methods.

The positions of the hydrogen atoms were calculated. Full-matrix least-squares refinement on F anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, with the latter restrained in such a way that the distance to their carrier remained constant at approximately 1.09 Å, converged to the values tabulated in Table V. The weighting scheme used was $w^{-1} = (A + F_{obs} + BF_{obs}^2)^{-1}$. An empirical absorption correction was applied [26]. The anomalous scattering of Pd and Cl was taken into account. Scattering factors were taken from the litterature [27]. All calculations were performed with XTAL [28] unless stated otherwise. For **1b**, which has chiral overall packing, the absolute structure was determined by additional refinement of the inverted structure (Table 5).

Tables of thermal parameters and H atom coordinates, and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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Table 5
Crystal and refinement data for **4a**, **7a**, **1b** and **2b**

	4a	**7a**	**1b**	**2b**
Chemical formula	$C_{11}H_{17}ClN_2Pd$	$C_{11}H_{15}ClN_2OPd$	$C_{12}H_{11}ClN_2OPd$	$C_{11}H_{15}ClN_2OPd$
Formula weight	319.1	333.1	341.1	333.1
a (Å)	25.644(2)	8.683(1)	7.5083(8)	7.3003(4)
b (Å)	—	11.475(4)	10.840(1)	7.8791(5)
c (Å)	7.907(1)	13.339(5)	15.173(1)	11.603(1)
α (°)	—	—	—	87.525(9)
β (°)	—	104.09(4)	—	86.286(6)
γ (°)	—	—	—	74.272(6)
V (Å^3)	5199.8(9)	1289.1(8)	1234.9(2)	640.85(9)
T (K)	293	293	293	293
Crystal size (mm)	0.25 × 0.38 × 0.5	0.2 × 0.5 × 0.5	0.15 × 0.4 × 0.4	0.15 × 0.25 × 0.4
λ (Å)	0.71069	0.71069	1.5418	1.5418
Crystal class	Tetragonal	Monoclinic	Orthorhombic	Triclinic
Space group	$I4_1/a$	$P2_1/c$	$Pna2_1$	P1
Z	16	4	4	2
d_x (g cm^{-3})	1.54	1.72	1.84	1.72
μ (cm^{-1})	15.9	22.32	134.42	137.72
R	0.041	0.045	0.033; 0.037 [a]	0.034
R_w	0.084	0.061	0.044; 0.050 [a]	0.047
Weights (A, B)	6.8, 0.013	6.0, 0.115	8.1, 0.006	2.6, 0.005
Extinction [25]	0.08(6)	—	—	0.006(2)
Absorption	0.81–1.18	0.67–1.28	0.74–1.44	0.67–1.47
Residual electron density (electrons)	−0.7–0.6	−1.1–0.7	−0.5–0.7	−0.8–0.7

[a] Value for inverted structure

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