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Coordination modes of the novel bifunctional nitrogen ligands 8-(2-pyridyl)quinoline and 8-(6-methyl-2-pyridyl)quinoline towards palladium and platinum. X-ray crystal structures of (8-(2-pyridyl)quinoline)Pd(Me)Cl, (8-(2-pyridyl)quinoline)-Pd(C(O)Me)Cl and (8-(2-pyridyl)quinoline)Pd(PEt_3)Cl_2

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Abstract

The coordination chemistry of the new bidentate nitrogen ligands 8-(2-pyridyl)quinoline (8-PQ) and 8-(6-methyl-2-pyridyl)quinoline) (Me-8-PQ) towards palladium and platinum has been studied. Several (N^N)Pd(R)Cl and (N^N)Pd(alkene) complexes have been synthesised. The complex (8-PQ)Pd(Me)Cl has been characterised by a single crystal X-ray determination (crystal data: triclinic space group $P\bar{1}$ with $a=8.513(5)$, $b=9.338(4)$, $c=10.219(2)$ Å, $\alpha=108.11(2)$, $\beta=89.82(3)$, $\gamma=116.81(4)°$, $V=680.1(6)$ Å^3, $R=0.033$, $Z=2$). A fast CO insertion occurs into the palladium–carbon bond of the complexes (N^N)Pd(Me)Cl providing the (N^N)Pd(C(O)Me)Cl complexes. For (8-PQ)Pd(C(O)Me)Cl an X-ray structure determination has been carried out (crystal data: monoclinic space group $P2_1/c$ with $a=9.084(4)$, $b=10.179(3)$, $c=16.400(3)$ Å, $\beta=95.59(2)°$, $V=1509.2(9)$ Å^3, $R=0.043$, $Z=4$). Unexpected in both molecular structures is the large dihedral angle between the plane of the bidentate nitrogen ligand and the coordination plane of the palladium. Both bidentate coordinating ligands 8-PQ and Me-8-PQ show a relatively large bite angle. A monodentate coordination mode has been observed for the complexes (N^N)M(PEt_3)Cl_2 (M = Pd, Pt), as the pyridyl group of the ligand is coordinated to the metal while the quinoline group is dissociated from the metal, which is shown in the X-ray structure determination for the complex (8-PQ)Pd(PEt_3)Cl_2 (crystal data: monoclinic space group $P2_1/a$ with $a=15.736(2)$, $b=7.782(1)$, $c=18.255(3)$ Å, $\beta=102.98(1)°$, $V=2178.3(6)$ Å^3, $R=0.062$, $Z=4$).

Keywords: Bidentate nitrogen ligand complexes; Palladium complexes; Platinum complexes; CO insertion; Bite angle; Crystal structures

1. Introduction

Over the past years intermediate steps of the palladium catalysed polyketone synthesis [1–6] have been studied. As model reactions, the insertion of CO and alkenes into the palladium–carbon bond of palladium–methyl complexes containing bidentate phosphine [7–11], phosphine–nitrogen [12] or bidentate nitrogen ligands have been investigated [13–15]. Some low temperature NMR studies of in situ systems have provided information about the energetics of migratory insertion reactions [11]. We have focussed our research on insertion reactions involving model complexes of the general formula (L^L)Pd(R)X (R = Me, C(O)Me) [7,8,12–14]. We have found that frequently CO insertion into the Pd–C bond of neutral complexes proved to be faster in complexes containing bidentate nitrogen ligands [14] than insertion into the Pd–C bond of complexes containing bidentate phosphine ligands [7]. An interesting observation was the enhancement of the CO insertion by substituents close to the nitrogen of bidentate nitrogen ligands like 2-(*N*-alkylcarbaldimino)-6-(methyl)pyridine (6-Me-Pyca). Another surprising result was a very fast CO insertion in methanol and even in H_2O observed for the complex [(terpy)Pd(Me)]Cl containing the terdentate bonded terpy ligand [16]. These accelerating effects could be rationalised by a mechanism,

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partly based on the work of Italian groups [17–22], which involves a temporary dissociation of one nitrogen donor atom of the ligand during the substitution steps of the insertion process.

In these studies involving the stability of five-coordinate relative to four-coordinate complexes, it appeared that steric interactions between the *ortho*-substituents of the ligand and the *cis*-ligands on the metal centre in the square-planar rearrangement favour the uptake of an additional ligand. Complexes containing, for example, the very rigid Me_2-phenanthroline ligand or the ligand 6-Me-Pyca form five-coordinate trigonal bipyramidal complexes with π-acceptor ligands like ethylene [20,23], while upon coordination of the poor π-acceptor ONPh to complexes containing Me_2-Phen, a four-coordinate complex is formed in which one nitrogen donor dissociates and is positioned near the axial site of the palladium in a non-coordinating fashion due to the rigidity of the ligand [20]. Interestingly, the rigid bidentate ligand can also adopt coordination positions in between a monodentate and a bidentate form depending on the π-accepting properties of the *trans*-ligand [20].

So far we have used both flexible and rigid bidentate nitrogen ligands with small bite angles in the study of insertion reactions [13,14]. Therefore we have started to investigate in more detail the influence of the bite angle of bidentate nitrogen ligands on insertion reactions [24]. The ligands 8-(2-pyridyl)quinoline (8-PQ) and 8-(6-methyl-2-pyridyl)quinoline (Me-8-PQ) were designed, as they are expected to coordinate with a larger bite angle than other known bidentate nitrogen ligands [14]. The coordination chemistry of these new ligands towards palladium and platinum and the reactivity of the complexes towards CO insertion reactions have been studied.

2. Experimental

2.1. Materials and apparatus

All manipulations were carried out in an atmosphere of purified, dry nitrogen by using standard Schlenk techniques. Solvents were dried and stored under nitrogen. ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a Bruker AMX 300 (300.13, 75.48 and 120.50 MHz respectively). IR spectra were recorded on a Bio-Rad FTS-7 spectrometer. Elemental analyses were carried out by Dornis u. Kolbe Mikroanalytisches Laboratorium, Mühlheim a. d. Ruhr, Germany.

Dibal-H was purchased and used without purification while $Pd(PPh_3)_4$ [25], (COD)PdMeCl [26], $Pd_2Cl_4(PEt_3)_2$ [27], $Pt_2Cl_4(PEt_3)_2$ [28] and 6-bromo-2-picoline [29] were synthesised according to previously reported procedures.

2.2. Synthesis of 8-(2-pyridyl)quinoline, 8-PQ (1)

To a mixture of nBu-Li (18 ml, 36 mmol, 2.0 M in pentane), THF (60 ml) and diethyl ether (60 ml) at −78 °C was added a solution of 8-bromoquinoline (5.1 g, 24 mmol) dissolved in THF (10 ml). After 15 min $ZnCl_2$ (24 ml, 24 mmol, 1.0 M in diethyl ether) was added and the mixture was warmed to 21 °C until a yellow suspension was formed. In a separate flask $(PPh_3)_2PdCl_2$ (200 mg, 0.28 mmol) was suspended in THF (15 ml), to which Dibal-H (0.57 ml, 0.57 mmol, 1.0 M in THF) was added dropwise to give a homogeneous, dark solution of $(PPh_3)_2Pd$ which was added to the 8-(zinc chloride)quinoline via a cannula. 2-Bromopyridine (3.4 ml, 36 mmol) was added dropwise to the reaction mixture followed by 25 h stirring, after which a solution of NaOH (10 g, 0.25 mol) in water (100 ml) was added to the solution. The organic layer was separated from the water fraction, which was extracted twice with dichloromethane (100 ml). The combined organic layers were dried with Mg_2SO_4, the solvent evaporated and the residue brought upon a column with neutral Al_2O_3. Elution with a mixture of hexane and diethyl ether (2/8) yielded the product 8-PQ, which was recrystallised out of pentane at −40 °C. Yield: 2.5 g, 12 mmol, 50%. *Anal.* Calc. for $C_{14}H_{10}N_2$: C, 81.52; H, 4.89; N, 13.58. Found: C, 81.41; H, 4.96; N, 13.46%

2.3. Synthesis of 8-(6-methyl-2-pyridyl)quinoline, Me-8-PQ (2)

The synthesis was carried out according to the procedure followed above for 8-PQ but with the catalyst $Pd(PPh_3)_4$ and the reagent 6-bromo-2-picoline yielding 28% yellow crystalline product. FAB+MS: Found: 221, composition: $C_{15}H_{13}N_2$; Calc.: 221, composition: $C_{15}H_{13}N_2$. No elemental analysis was carried out because of the analogy to **1**.

2.4. Synthesis of {8-(2-pyridyl)quinoline}(methyl)-chloropalladium(II), (8-PQ)Pd(Me)Cl (3)

(COD)Pd(Me)Cl (210 mg, 0.79 mmol) and 8-PQ (195 mg, 0.95 mmol) were dissolved in toluene (20 ml). The pale yellow suspension, which was formed after 15 min, was centrifuged and washed twice with diethyl ether (20 ml) to yield a pale yellow powder (254 mg, 0.70 mmol, 90%). Crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a solution of the product in dichloromethane at 4 °C. *Anal.* Calc. for $C_{15}H_{13}ClN_2Pd$: C, 49.61; H, 3.61; N, 7.71. Found: C, 49.51; H, 3.61; N, 7.74%.

2.5. Synthesis of {8-(2-pyridyl)quinoline}(acetyl)chloro-palladium(II), (8-PQ)Pd(C(O)Me)Cl (4)

CO was bubbled through a solution of (8-PQ)Pd(Me)Cl (100 mg, 0.28 mmol) in dichloromethane (20 ml) for 5 min after which the solution was filtered. The volume of the solution was concentrated to 5 ml and ether (30 ml) was added. The crystalline material (92 mg, 0.23 mmol, 85%) was collected by centrifugation. Crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a solution of the product in dichloromethane at 4 °C. *Anal.* Calc.

for $C_{16}H_{13}ClN_2OPd$: C, 49.13; H, 3.35; N, 7.16. Found: C, 49.17; H, 3.39; N, 7.19%. IR ν(C=O) (CH_2Cl_2): 1695 cm^{-1}.

2.6. Synthesis of {8-(2-pyridyl)quinoline}(isobutyryl)-chloropalladium(II), (8-PQ)Pd(C(O)^{i}Pr)Cl (5a)

Pd(dba)$_2$ (360 mg, 0.62 mmol), 8-PQ (144 mg, 0.69 mmol) and isobutyrylchloride (71 μl, 69 mmol) were dissolved in dichloromethane (20 ml) and stirred at 40 °C for 15 min after which the colour of the solution changed from deep purple to yellow. The solution was filtered and concentrated to 5 ml. Diethyl ether was added and the yellow crystalline material was centrifuged and washed with diethyl ether (30 ml). The product was dried under reduced pressure. Yield: 234 mg, 0.56 mmol, 90%. *Anal.* Calc. for $C_{18}H_{17}ClN_2OPd$: C, 51.57; H, 4.09; N, 6.68. Found: C, 51.44; H, 4.13; N, 6.74%. IR ν(C=O) (CH_2Cl_2): 1673 cm^{-1}.

2.7. Synthesis of {8-(2-pyridyl)quinoline}(benzoyl)-chloropalladium(II), (8-PQ)Pd(C(O)Ph)Cl (5b)

The synthesis was carried out according to the procedure followed above for **5a** yielding a yellow crystalline material (258 mg, 0.57 mmol, 92%). *Anal.* Calc. for $C_{21}H_{15}ClN_2OPd$: C, 55.65; H, 3.34; N, 6.18. Found: C, 55.78; H, 3.42; N, 6.10%. IR ν(C=O) (CH_2Cl_2): 1655 cm^{-1}.

2.8. Synthesis of {8-(2-pyridyl)quinoline}(trimethylacetyl)chloropalladium(II), (8-PQ)Pd(C(O)^{t}Bu)Cl (5c)

The synthesis was carried out according to the procedure followed above for **5a** yielding a yellow crystalline material (258 mg, 0.57 mmol, 92%). IR ν(C=O) (CH_2Cl_2): 1668 cm^{-1}. This complex was not stable enough to perform elemental analysis.

2.9. Synthesis of {8-(6-methyl-2-pyridyl}quinoline)-(methyl)chloropalladium(II), (Me-8-PQ)Pd(Me)Cl (6)

The synthesis was carried out according to the procedure followed above for **3** yielding a yellow crystalline material (107.7 mg, 0.286 mmol, 75%). FAB + MS ($C_{16}H_{15}N_2ClPd$-CH_3Cl): Calc.: 326, Found: 325. No elemental analysis was carried out because of the analogy to complex **3**.

2.10. Synthesis of {8-(6-methyl-2-pyridyl)quinoline}-(acetyl)chloropalladium(II), (Me-8-PQ)Pd(C(O)Me)Cl (7)

The synthesis was carried out according to the procedure followed above for **4** yielding a yellow crystalline material (75 mg, 0.19 mmol, 70%). FAB + MS ($C_{17}H_{15}N_2OClPd$-Cl): Calc.: 369, Found: 369. No elemental analysis was carried out because of the analogy to complex **4**.

2.11. Synthesis of {8-(2-pyridyl)quinoline}(maleic anhydride)palladium(0), (8-PQ)Pd(MA) (8a)

Pd(dba)$_2$ (260 mg, 0.45 mmol), 8-PQ (102 mg, 0.49 mmol) and maleic anhydride (50 mg, 0.50 mmol) were dissolved in toluene and stirred for 30 min after which the dark purple solution changed to a pale yellow suspension. The suspension was centrifuged and washed twice with diethyl ether (20 ml). The product was recrystallised from a dichloromethane–diethyl ether mixture yielding a yellow crystalline material (148 mg, 0.36 mmol, 80%). *Anal.* Calc. for $C_{18}H_{12}N_2O_3Pd$: C, 52.64; H, 2.95; N, 6.82. Found: C, 52.78; H, 3.04; N, 6.88%. IR ν(C=O) (KBr): 1719, 1788 cm^{-1}.

2.12. Synthesis of {8-(2-pyridyl)quinoline}(fumaronitrile)-palladium(0), (8-PQ)Pd(FN) (8b)

The synthesis was carried out according to the procedure followed above for **8a** yielding a pale yellow crystalline material (141 mg, 0.36 mmol, 80%). *Anal.* Calc. for $C_{18}H_{12}N_4Pd$: C, 55.33; H, 3.09; N, 14.34. Found: C, 55.46; H, 3.08; N, 14.24%. IR ν(C≡N) (KBr): 2196 cm^{-1}.

2.13. Synthesis of {8-(6-methyl-2-pyridyl)quinoline}-(maleic anhydride)palladium(0), (Me-8-PQ)Pd(MA) (9b)

The synthesis was carried out carried out according to the procedure followed above for **8a** yielding a yellow crystalline material (159 mg, 0.37 mmol, 83%). *Anal.* Calc. for $C_{19}H_{14}N_2PdO_3$: C, 53.73; H, 3.32; N, 6.60. Found: C, 53.57; H, 3.38; N, 6.48%. IR ν(C=O) (KBr): 1724, 1790 cm^{-1}.

2.14. Synthesis of {8-(6-methyl-2-pyridyl)quinoline}-(fumaronitrile)palladium(0), (Me-8-PQ)Pd(FN) (9b)

The synthesis was carried out according to the procedure followed above for **8a** yielding a yellow crystalline material (125 mg, 0.31 mmol, 70%). This complex was not stable enough to perform elemental analysis. IR ν(C≡N) (KBr): 2197 cm^{-1}.

2.15. Synthesis of {8-(2-pyridyl)quinoline}(triethylphosphine)dichloro-palladium(II), (8-PQ)Pd(PEt_3)Cl_2 (10a)

(Pd(PEt_3)Cl_2)$_2$ (85 mg, 0.14 mmol) and 8-PQ (67 mg, 0.32 mmol) were dissolved in dichloromethane (20 ml) and stirred for 30 min. The solution was concentrated to 5 ml and diethyl ether (30 ml) was added. The pale yellow crystalline material was centrifuged and washed twice with diethyl ether (30 ml). Crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether in a solution of the product in dichloromethane at 4 °C. Yield: 124 mg, 0.23 mmol, 95%. *Anal.* Calc. for $C_{20}H_{25}Cl_2N_2PPd$: C, 47.88; H, 5.03; N, 5.58.

Found: C, 47.69; H, 5.18; N, 5.75%. ^{31}P NMR ($CDCl_3$): 35.1 ppm.

2.16. Synthesis of {(8-(2-pyridyl)quinoline}(triethylphosphine)dichloro-platinum(II), (8-PQ)Pt(PEt_3)Cl_2 (10b)

The synthesis was carried out according to the procedure followed above for **10a** except that the solution was stirred for 5 h. Yield: 124 mg, 0.20 mmol, 95%. *Anal.* Calc. for $C_{20}H_{25}Cl_2N_2PPd$: C, 40.69; H, 4.27; N, 4.74. Found: C, 40.74; H, 4.32; N, 4.66%. ^{31}P NMR ($CDCl_3$): −0.92 ppm (^1J(Pt–P) = 3464 Hz).

2.17. Synthesis of {8-(6-methyl-2-pyridyl)quinoline}-(triethylphosphine)dichloro-palladium(II), (Me-8-PQ)-Pd(PEt_3)Cl_2 (11a)

The synthesis was carried out according to the procedure followed above for **10a** yielding 134 mg (0.26 mmol, 96%). FD-MS: Calc.: 516, Found: 516. ^{31}P NMR ($CDCl_3$): 32.9 ppm. No elemental analysis was carried out because of the analogy to complex **10a**.

2.18. Synthesis of {8-(6-methyl-2-pyridyl)quinoline}-(triethylphosphine)dichloro-platinum(II), (Me-8-PQ)-Pt(PEt_3)Cl_2 (11b)

The synthesis was carried out according to the procedure followed above for **10b** yielding 163 mg (0.26 mmol, 96%). FD-MS: Calc.: 604, Found: 604. ^{31}P NMR ($CDCl_3$): −1.79 ppm (^1J(Pt–P) = 3506 Hz). No elemental analysis was carried out because of the analogy to complex **10b**.

2.19. X-ray structure determination of 3, 4 and 10a

Crystal and refinement data are summarized in Table 1. Data collection for the crystals of complexes **3**, **4** and **10a**

Table 1
Crystal and refinement data for (8-PQ)Pd(Me)Cl (**3**), (BPF)Pd(C(O)Me)Cl (**4**) and (8-PQ)Pd(PEt_3)Cl_2 (**10a**)

	3	**4**	**10a**
Crystal data			
Chemical formula	$C_{15}H_{13}N_2ClPd$	$C_{16}H_{13}N_2OClPd$	$C_{20}H_{25}N_2Cl_2PPd$
Molecular weight	363.1	391.2	501.7
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/a$
a (Å)	8.513(5)	9.084(4)	15.736(2)
b (Å)	9.338(4)	10.179(3)	7.782(1)
c (Å)	10.219(2)	16.400(3)	18.255(3)
α (°)	108.11(2)		
β (°)	89.82(3)	95.59(2)	102.98(1)
γ (°)	116.81(4)		
V (Å^3)	680.1(6)	1509.2(9)	2178.3(6)
D_{calc} (g cm^{-3})	1.77	1.72	1.53
Z	2	4	4
F(000)	360	776	1016
μ (cm^{-1})	15.31 (Mo Kα)	13.9 (Mo Kα)	11.7 (Mo Kα)
Crystal size (mm)	0.50×0.60×0.60	030×0.40×0.50	0.10×0.15×0.40
Data collection			
T (°C)	20	20	20
θ_{min}; θ_{max} (°)	2.1; 29.9	2.3; 29.9	1.1; 24.9
Wavelength (Å)	0.71069 (Mo Kα) (graphite monochr.)	0.71069 (Mo Kα) (graphite monochr.)	0.71069 (Mo Kα) (graphite monochr.)
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
X-ray exposure time (h)	45	55	44
Linear decay (%)	0	0	15
Reference reflection	$1\bar{1}0$, $1\bar{1}3$	033, 100	$\bar{1}\bar{1}1$, 202
Data set	−10:11, −13:0, −13:14	−12:12, 0:14, 0:22	−18:18, −9:0, 0:21
Total unique data	3931	4356	3808
Total observed data	3184	2796	1667
DIFABS correction range	0.78–1.24	0.71–1.43	0.73–1.20
Refinement			
No. refined parameters	225	242	310
Final R [a]	0.033	0.043	0.062
Final Rw [b]	0.052	0.068	0.104
w^{-1}	$7.6+F_o+0.019F_o^2$	$6.9+F_o+0.092F_o^2$	$6.0+F_o+0.039F_o^2$
$(\Delta/\sigma)_{max}$	0.41	0.69	0.10
Min. and max. ρ (e Å^{-3})	−0.9, 0.5	−1.4, 0.7	−0.8, 0.8

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.
[b] $Rw = [\Sigma[w(|F_o| - |F_c|)^2]/\Sigma[w(F_o^2)]]^{0.5}$.

was performed on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation and ω–2θ scan. Two reference reflections were measured hourly and showed no decrease during the course of the data collection for complexes **3** and **4** and 15% decrease for complex **10a**, which was corrected for. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $40 < 2\theta < 42°$ for complexes **3** and **4** and with $38 < 2\theta < 40°$ for complex **10a**. Corrections for Lorentz and polarisation effects were applied. The structure of complexes **4** and **10a** was solved by direct methods while the structure of **3** was solved by the PATTY option of the DIRDIF91 program system [30]. The hydrogen atoms were calculated. Full-matrix least-squares refinement on *F*, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, restraining the latter in such a way that the distance to their carrier remained constant at approximately 1.09 Å, converged to the *R* values given in Table 1. The temperature factor of the H atoms was kept fixed at $U = 0.15$ Å^2 for complex **10a**. An empirical absorption correction (DIFABS [31]) was applied. For complex **3** the secondary isotropic extinction coefficient refined to Ext = 0.02(1) [32,33]. Scattering factors were taken from Cromer and Mann [34]. The anomalous scattering of Pd, P and Cl was taken into account. All calculations were performed with XTAL [35], unless stated otherwise. Positional parameters of the complexes **3**, **4** and **10a** are listed in Tables 2–4, respectively; for the bond distances see Table 9. For the bond angles of complexes **3** and **4** see Table 10, and for complex **10a** see Table 11.

Table 2
Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for (8-PQ)Pd(Me)Cl (**3**) (with e.s.d.s in parentheses)

Atom	*x*	*y*	*z*	U_{eq} [a] (Å^2)
Pd	0.31918(4)	1.01024(3)	0.19054(3)	0.0275(1)
Cl	0.4354(2)	1.3040(1)	0.2496(1)	0.0435(5)
N(1)	0.2445(4)	0.7568(4)	0.1357(3)	0.0299(2)
N(2)	0.3459(4)	1.0274(4)	0.4083(3)	0.0302(2)
C(1)	0.3026(6)	0.6834(5)	0.0248(4)	0.0366(2)
C(2)	0.2771(6)	0.5183(6)	−0.0117(5)	0.0405(2)
C(3)	0.1878(7)	0.4220(5)	0.0696(5)	0.0427(2)
C(4)	0.1263(6)	0.4953(5)	0.1843(5)	0.0372(2)
C(5)	0.1558(5)	0.6637(5)	0.2169(4)	0.0280(2)
C(6)	0.0946(5)	0.7379(5)	0.3436(4)	0.0298(2)
C(7)	−0.0629(6)	0.6316(6)	0.3793(5)	0.0370(2)
C(8)	−0.1173(6)	0.6807(7)	0.5078(5)	0.0446(2)
C(9)	−0.0108(7)	0.8359(7)	0.6066(5)	0.0423(2)
C(10)	0.1515(6)	0.9524(6)	0.5781(4)	0.0358(2)
C(11)	0.2651(7)	1.1150(7)	0.6782(5)	0.0437(2)
C(12)	0.4159(7)	1.2265(6)	0.6443(5)	0.0426(2)
C(13)	0.4495(6)	1.1770(5)	0.5068(4)	0.0365(2)
C(14)	0.2004(5)	0.9094(5)	0.4436(4)	0.0294(1)
C(15)	0.2522(7)	0.9835(7)	−0.0094(5)	0.0442(1)

[a] U_{eq} = 1/3 of the trace of the orthogonalised *U*.

Table 3
Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for (8-PQ)Pd(C(O)Me)Cl (**4**) (with e.s.d.s in parentheses)

Atom	*x*	*y*	*z*	U_{eq} [a] (Å^2)
Pd	0.72806(4)	−0.00142(4)	0.19400(2)	0.0406(2)
Cl	0.7511(2)	−0.2260(2)	0.2184(1)	0.0658(9)
O	0.7146(6)	0.0531(7)	0.3603(3)	0.0815(3)
N(1)	0.7037(5)	0.1961(4)	0.1688(3)	0.0455(4)
N(2)	0.6613(6)	−0.0345(5)	0.0639(3)	0.0516(5)
C(1)	0.6458(7)	0.2762(6)	0.2218(4)	0.0574(4)
C(2)	0.6160(8)	0.4063(7)	0.2073(6)	0.0713(3)
C(3)	0.6448(8)	0.4599(7)	0.1335(6)	0.0768(3)
C(4)	0.7027(7)	0.3797(6)	0.0763(5)	0.0660(5)
C(5)	0.7337(6)	0.2469(5)	0.0953(4)	0.0528(9)
C(6)	0.7966(7)	0.1634(7)	0.0339(4)	0.0585(8)
C(7)	0.8959(9)	0.2226(9)	−0.0149(6)	0.0832(5)
C(8)	0.947(1)	0.159(2)	−0.0817(7)	0.1236(7)
C(9)	0.888(1)	0.040(2)	−0.1082(6)	0.1148(7)
C(10)	0.786(1)	−0.027(1)	−0.0605(4)	0.0889(4)
C(11)	0.726(1)	−0.153(1)	−0.0806(6)	0.1096(3)
C(12)	0.638(1)	−0.207(1)	−0.0353(7)	0.1017(3)
C(13)	0.6095(9)	−0.1509(7)	0.0394(5)	0.0758(6)
C(14)	0.7472(7)	0.0324(6)	0.0136(3)	0.0545(2)
C(15)	0.7985(8)	0.0222(6)	0.3094(4)	0.0582(2)
C(16)	0.956(1)	−0.005(1)	0.3319(6)	0.0864(3)

[a] U_{eq} = 1/3 of the trace of the orthogonalised *U*.

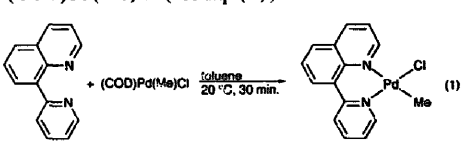
3. Results

3.1. Synthesis of 8-(2-pyridyl)quinoline (1) and 8-(6-methyl-2-pyridyl)quinoline (2)

The new bidentate nitrogen ligands 8-PQ (**1**) and Me-8-PQ (**2**) (see Fig. 1) were obtained by a palladium catalysed cross-coupling reaction of 8-(zinc chloride)quinoline with 6-bromopyridine and 6-bromo-2-picoline, respectively. The transmetallating agent 8-(zinc chloride)quinoline was synthesised in situ by subsequent lithiation with nBuLi and reaction with zinc chloride. The coupling reaction of 6-bromopyridine with 8-(zinc chloride)quinoline was catalysed by $Pd(PPh_3)_2$, which was obtained in situ by reacting $(PPh_3)_2PdCl_2$ with DIBAL-H as a reducing agent, while the coupling of 6-bromo-2-picoline with 8-(zinc chloride)-quinoline was catalysed by $Pd(PPh_3)_4$. The ^{1}H and ^{13}C NMR data are compiled in Tables 5–8.

3.2. Synthesis and properties of (N⌒N)Pd(R)Cl complexes

The complex (8-PQ)Pd(Me)Cl (**3**) can easily be synthesised in high yield by reaction of the ligand 8-PQ with (COD)Pd(Me)Cl (see Eq. (1)).



1 3

Table 4
Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for (8-PQ)$PdCl_2(PEt_3)$ (**10a**) (with e.s.d.s in parentheses)

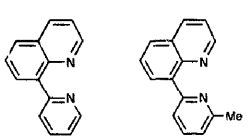
Atom	x	y	z	U_{eq} [a] ($Å^2$)
Pd	0.31562(8)	0.3456(2)	0.19830(7)	0.0370(7)
Cl(1)	0.1906(3)	0.2174(8)	0.1321(4)	0.0744(4)
Cl(2)	0.4384(3)	0.4945(8)	0.2561(3)	0.0636(3)
P	0.4025(3)	0.1558(8)	0.1605(3)	0.0486(3)
N(1)	0.2373(9)	0.547(2)	0.2310(8)	0.0413(1)
N(2)	0.354(1)	0.697(2)	0.438(1)	0.0491(2)
C(1)	0.195(1)	0.651(3)	0.177(1)	0.0575(1)
C(2)	0.151(2)	0.797(3)	0.184(1)	0.0691(1)
C(3)	0.152(1)	0.834(3)	0.261(1)	0.0580(9)
C(4)	0.194(1)	0.732(3)	0.317(1)	0.0583(9)
C(5)	0.235(1)	0.581(2)	0.3036(9)	0.0362(1)
C(6)	0.273(1)	0.460(2)	0.3623(9)	0.0376(1)
C(7)	0.258(1)	0.291(3)	0.357(1)	0.0526(1)
C(8)	0.294(1)	0.177(2)	0.414(1)	0.0471(1)
C(9)	0.346(1)	0.232(2)	0.480(1)	0.0404(1)
C(10)	0.364(1)	0.410(2)	0.4901(1)	0.0470(1)
C(11)	0.423(1)	0.474(3)	0.557(1)	0.0580(1)
C(12)	0.442(2)	0.644(3)	0.563(1)	0.0605(9)
C(13)	0.404(1)	0.744(3)	0.500(1)	0.0587(2)
C(14)	0.330(1)	0.526(2)	0.4293(9)	0.0352(3)
C(15)	0.347(2)	−0.038(3)	0.112(2)	0.0753(2)
C(16)	0.407(3)	−0.166(5)	0.084(2)	0.1060(3)
C(17)	0.460(2)	0.250(5)	0.095(2)	0.0920(2)
C(18)	0.399(3)	0.335(6)	0.029(2)	0.1217(2)
C(19)	0.491(2)	0.077(4)	0.235(2)	0.0813(8)
C(20)	0.457(3)	−0.008(4)	0.298(2)	0.1033(1)

[a] $U_{eq} = 1/3$ of the trace of the orthogonalised U.

The pale yellow complex **3** was characterised by ^1H (see Table 5), COSY and ^{13}C NMR (see Table 6), elemental analysis and a single crystal X-ray structure determination. The atomic numbering of complex **3** is given in Table 5.

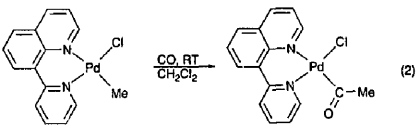
From the ^1H NMR spectrum it can be deduced that the major product is the isomer (8-PQ)Pd(Me)Cl which is drawn in Eq. (1) with the methyl group *cis* to the pyridyl group of the ligand. The chloride on the palladium causes a high downfield shift to 9.42 ppm of the proton H-2 adjacent to the nitrogen of the quinoline [36]. The signal of the methyl protons can be observed at 1.05 ppm which is as expected for a palladium–methyl complex containing a bidentate nitrogen ligand [13,14,37]. The other isomer of the complex with the methyl group *trans* to the pyridyl group is formed in 5% yield. There is no equilibration between the two isomers, as the minor isomer is not formed after dissolving the pure major isomer in $CDCl_3$.

A fast and quantitative CO insertion into the palladium–methyl bond of complex **3** occurs when CO is bubbled through a solution of **3** in dichloromethane for 5 min at 21 °C (Eq. (2)).



1 2

Fig. 1. 8-PQ (**1**) and Me-8-PQ (**2**).

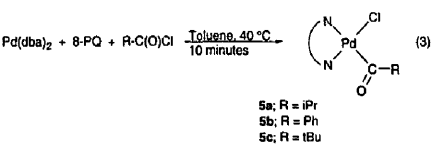


(2)

3 4

The pale yellow product **4** was characterised by ^1H and ^{13}C NMR, IR, elemental analysis and a single crystal X-ray structure determination. The ^1H NMR and ^{13}C NMR values for the ligand (see Tables 5 and 6) of complex **4** are comparable with the spectra of complex **3** except for the methyl signal. Upon CO insertion this signal shifts in the ^1H NMR from 1.05 to 2.48 ppm and in the ^{13}C NMR from 0.5 to 36.6 ppm, which are normal shifts [13–15,37].

Other acyl complexes like (8-PQ)Pd(C(O)iPr)Cl (**5a**), (8-PQ)Pd(C(O)Ph)Cl (**5b**) and (8-PQ)Pd(C(O)tBu)Cl (**5c**) can be synthesised in reasonably high yield starting from $Pd(dba)_2$ in reaction with the appropriate acid chloride and the ligand (see Eq. (3)).



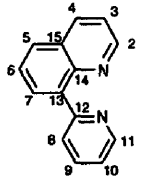
(3)

5a; R = iPr
5b; R = Ph
5c; R = tBu

The yellow products were characterised by ^1H NMR (see Table 5) and ^{13}C NMR (see Table 6), IR and elemental analysis, except for complex **5c** which is not stable enough to perform a ^{13}C NMR measurement and elemental analysis. The other complexes are stable in crystalline form for months and in solution for days. In these reactions also 95% of the isomer is formed with the R group *cis* to the pyridyl group, which may be deduced from the large downfield shift, as in **3** and **4**, of H-2 adjacent to the nitrogen of the quinoline group.

The complex (Me-8-PQ)Pd(Me)Cl (**6**) was obtained by the same method as that used for complex **3**. From the ^1H NMR (see Table 7), however, it may be concluded that in complex **6** the methyl group on palladium is positioned *trans* to the pyridyl group. The proton H-2, adjacent to the nitrogen of the quinoline group, can be observed at 9.13 ppm, which is normal for such a pyridyl proton *cis* to a methyl on the palladium [14,36]. The methyl on the pyridyl group shifts from 2.67 ppm in the free ligand to 3.25 ppm in complex **6**. The ^1H NMR signal of the methyl on the palladium resonates at significantly lower ppm value (0.77 ppm) than that in complex **3**. It is clear that the steric interaction between the methyl group on the pyridyl and the methyl group on palladium is the cause of the reversal of the configuration with respect to **3**. Analogous to **3**, also in complex **6** a fast CO insertion occurs upon bubbling CO through a solution of the starting complex in dichloromethane providing (Me-8-

Table 5
^{1}H NMR data for the complexes containing the ligand 8-PQ [a]



	H2	H3	H4	H5	H6	H7	H8	H9	H10	H11	Other groups
1	8.97 dd	7.45 dd	8.24 dd	7.90 dd	7.68 t	8.13 dd	8.08 d	7.83 dd	7.32 dd	8.79 dd	
	(4.2; 1.7)	(8.2, 4.2)	(8.3, 1.8)	(8.2, 1.5)	(7.6)	(8.2, 1.5)	(8.9)	(7.9, 1.6)	(4.8, 1.6)	(4.8, 1.6)	
3	9.42 dd	7.54 dd	8.31 dd	8.09 d	7.73 dd	8.10 d	7.62 d	7.95 dt	7.43 dd	8.86 dd	CH_3: 1.05
	(4.7, 1.6)	(8.3, 4.7)	(8.3, 1.6)	(7.8)	(7.8)	(7.8)	(7.9)	(7.8, 1.5)	(7.8, 5.5)	(5.5, 1.6)	
4	9.21 dd	7.54 dd	8.35 dd	8.09 d	7.78 t	8.09 d	7.61 d	7.97 dt	7.50 dt	9.19 dd	CH_3: 2.48 s
	(4.6; 1.7)	(8.2; 4.6)	(8.2; 1.7)	(7.5)	(7.5)	(7.5)	(7.8)	(7.8; 1.6)	(5.2; 1.6)	(5.2; 1.6)	
5a	9.19 dd	7.53 dd	8.35 dd	8.08 d	7.78 t	8.11 d	7.61 d	7.96 dt	7.47 dt	9.14 dd	iPr CH: 3.21 sept (7.0)
	(4.6, 1.7)	(8.3, 4.7)	(8.3, 1.7)	(7.6)	(7.6)	(7.6)	(7.8)	(7.8, 1.6)	(5.6, 1.6)	(5.6, 1.6)	iPr CH_3: 0.98 d (7.0)
5b	9.21 dd	7.54 dd	8.44 dd	8.16 d	7.83 t	8.16 d	7.63 d	7.95 dt	7.42 dt	8.96 dd	Ph: *ortho*: 8.11 dd (8.4; 1.5)
	(4.7, 1.7)	(8.3, 4.6)	(8.3, 1.7)	(7.7)	(7.7)	(7.7)	(8.1)	(8.1, 1.7)	(5.2, 1.5)	(5.2, 1.5)	Ph: *meta*: 7.26 t (7.1 Hz)
											Ph: *para*: 7.37 t (7.3 Hz)
5c	9.20 dd	7.54 dd	8.34 dd	8.12 d	7.77 t	8.09 d	7.62 d	7.96 dt	7.43 dt	8.98 dd	tBu: 1.04 s
	(4.6; 1.7)	(8.3; 4.6)	(8.3; 1.7)	(7.7)	(7.7)	(7.7)	(7.8)	(7.8; 1.6)	(5.6; 1.6)	(5.6; 1.6)	
8a	9.15 dd	7.58 dt	8.42 dd	8.06 m	7.74 t	8.06 m	7.73 d	7.98 dt	7.43 m	8.96 dd	CH=: 3.95 br
	(4.8, 1.7)	(8.3, 4.8)	(8.3, 1.7)		(8.2)		(7.8)	(7.8, 1.7)		(5.3, 1.7)	3.66 br
8b	9.30 dd	7.58 dd	8.44 dd	8.07 m	7.76 t	8.07 m	7.75 d	7.99 dt	7.45 m	9.13 dd	CH=: 2.94 br
	(4.6, 1.6)	(8.3, 4.8)	(8.3, 1.6)		(8.2)		(7.8)	(7.8, 1.7)		(5.2, 1.3)	2.77 br
10a	8.95 dd	7.43 dd	8.22 dd	7.98 dd	7.77 t	8.74 dd	7.84 m	7.86 m	7.43 m	8.97 m	Et: CH_2: 1.75 dq
	(4.2; 1.7)	(8.3; 4.2)	(8.3; 1.7)	(7.8; 1.0)	(7.8)	(7.8; 1.0)					^3J(H–H) = 7.6; ^3J(P–H) = 11.4
											Et CH_3: 1.05 dt
											^3J(H–H) = 7.6; ^2J(P–H) = 17.5
10b	8.94 dd	7.42 dd	8.21 dd	7.96 dd	7.73 t	8.66 dd	7.83 d	7.87 dt	7.46 t	8.99 m	Et CH_2: 1.70 dq
	(4.2; 1.8)	(8.3; 4.2)	(8.3; 1.8)	(7.3; 1.4)	(7.3)	(7.3; 1.4)	(7.1)	(7.9; 1.5)	(7.5)		^3J(H–H) = 7.6; ^3J(P–H) = 11.0
											Et CH_3: 0.99 dt
											^3J(H–H) = 7.6; ^2J(P–H) = 16.9

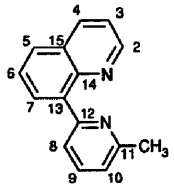
[a] Recorded at 300.13 MHz in $CDCl_3$ at 21 °C with J in parentheses (s = singlet, d = doublet, dd = doublet doublets, t = triplet, m = multiplet, br = broad).

Table 6
^{13}C NMR data for the complexes containing the ligand 8-PQ [a] (adopted numbering scheme is shown in Table 5)

	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	Other groups
1	150.9	121.5	137.0	129.3	127.0	131.7	127.4	136.0	122.7	150.1	157.6	139.4	146.3	129.1	
3	156.3	122.6	138.9	131.8	127.4	133.0	128.1	138.9	124.7	152.6	156.1	134.9	144.1	129.1	CH_3: 0.5
4	156.2	122.6	139.3	131.3	127.5	133.3	128.5	139.3	124.4	150.6	156.5	134.7	144.6	129.1	CH_3: 36.6 C=O: 229.2
5a	156.2	122.6	139.3	132.0	127.4	133.0	128.5	139.3	124.2	150.4	156.6	134.8	144.6	129.2	iPr CH: 48.5 iPr CH_3: 18.9 C=O: 236.5
5b	151.0	122.7	139.8	130.8	127.9	130.8	128.9	139.7	124.8	151.0	156.4	134.7	144.5	129.4	Ph: quat: 138.9 *ortho*: 133.9 *meta*: 128.5 *para*: 132.3 C=O: 226.4
8a	156.4	122.4	139.8	132.1	127.9	135.2	127.8	139.6	124.7	152.9	154.8	134.4	143.9	130.2	C=C: 42.2, 42.0 C=O: 173.5, 173.4
8b	156.9	122.4	139.9	132.0	127.7	134.9	127.9	139.3	124.5	153.8	155.8	135.0	144.8	130.4	C=C: 19.36 CN: 124.0
10a	152.2	122.7	137.9	130.8	127.1	134.2	130.8	137.5	124.6	151.9	159.9	140.0	147.4	129.7	Et CH_2: 17.1 (^1J(C–P) = 32.4) CH_3: 9.4
10b	151.5	121.8	137.1	130.7	125.9	133.9	129.9	136.6	124.1	150.9	159.3	138.5	146.6	128.7	Et CH_2: 14.4 (^1J(C–P) = 39.2) CH_3: 8.0

[a] Recorded at 75.48 MHz in $CDCl_3$ at 21 °C.

Table 7
^{1}H NMR data for the complexes containing the ligand Me-8-PQ [a]



	H2	H3	H4	H5	H6	H7	H8	H9	H10	CH_3	Other groups
2	8.96 dd	7.42 dd	8.21 dd	7.87 dd	7.61 t	8.09 dd	7.81 d	7.69 t	7.18 d	2.67	
	(4.1, 1.7)	(8.3, 4.2)	(8.3, 1.8)	(8.1, 1.4)	(7.9)	(7.1, 1.4)	(7.7)	(7.7)	(7.5)		
6	9.13 dd	7.49 dd	8.30 dd	8.02 dd	7.74 dd	8.21 d	7.46 d	7.80 t	7.41 d	3.25	CH_3: 0.77
	(4.7, 1.7)	(8.4, 4.7)	(8.3, 1.7)	(8.2, 1.2)	(7.6)	(7.4, 1.3)	(8.0)	(7.8)	(7.7)		
7 [b]	8.97 d	7.54 dd	8.32 dd	8.05 d	7.85 t	8.24 d	7.46 d	7.81 t	7.40 d	3.12	CH_3: 2.47
	(4.6)	(8.3, 4.6)	(8.3, 1.1)	(8.0)	(7.8)	(7.8)	(7.9)	(7.8)	(7.7)		
9a	9.03 dd	7.58 dd	8.37 dd	7.98 t	7.71 t	8.00	7.42 d	7.83 t	7.42 d	2.95	CH=: 3.66 br
	(4.9, 1.9)	(8.3, 4.6)	(8.3, 1.7)	(7.1)	(7.8)	(7.8, 1.3)	(7.8)	(7.9)	(7.8)		
9b	9.12 dd	7.56 dd	8.40 dd	8.01 d	7.73 t	8.01 d	7.44 d	7.83 t	7.44 d	3.07	CH=: 2.64 br
	(4.5, 1.6)	(8.3, 4.5)	(8.3, 1.6)	(7.6)	(7.6)	(7.6)	(7.8)	(7.8)	(7.8)		
11a	8.91 dd	7.41 dd	8.20 dd	7.97 dd	7.76 t	8.62 dd	7.46 d	7.76 t	7.32 d	3.31	Et CH_2: 1.69 dq
	(4.1, 1.7)	(8.3, 4.1)	(8.3, 1.7)	(8.1, 1.4)	(8.2)	(8.1, 1.4)	(7.8)	(7.8)	(7.7)		^3J(H–H) = 7.6; ^3J(P–H) = 11.5
											Et CH_3: 0.96 dt
											^3J(H–H) = 7.6; ^2J(P–H) = 17.6
11b	8.91 dd	7.41 dd	8.20 dd	7.96 dd	7.71 t	8.50 dd	7.48 d	7.78 t	7.39 t	3.29	Et CH_2: 1.62 dq
	(4.1, 1.7)	(8.2, 4.1)	(8.3, 1.7)	(8.3, 1.3)	(7.8)	(7.2, 1.4)	(7.7)	(7.7)	(7.7)		^3J(H–H) = 7.6; ^3J(P–H) = 11.0
											Et CH_3: 0.88 dt
											^3J(H–H) = 7.5; ^2J(P–H) = 17.0

[a] Recorded at 300.13 MHz in $CDCl_3$ at 21 °C with J in parentheses (s = singlet, d = doublet, dd = doublet doublets, t = triplet, m = multiplet, br = broad).
[b] Recorded at $T = -23$ °C.

Table 8
^{13}C NMR data for the complexes containing the ligand Me-8-PQ [a] (adopted numbering scheme is shown in Table 7)

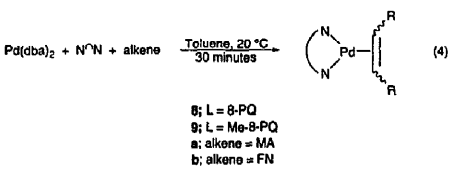
	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	CH_3	Other groups
2	150.8	121.5	136.9	129.1	127.1	131.7	124.3	136.2	122.2	158.7	157.1	140.0	146.5	129.2	25.3	
6	155.9	122.8	138.5	131.7	127.6	131.7	125.4	138.7	125.0	162.0	157.1	136.2	145.0	129.0	29.7	CH_3: −5.7 CH_3: 36.2
7 [b]	155.5	122.1	138.6	131.2	127.1	131.9	125.2	138.8	124.7	160.5	156.5	135.1	144.8	128.0	29.0	C=O: 222.7 C=C: - [c]
9a [b]	156.3	123.4	140.3	132.5	129.2	135.3	126.6	140.3	125.9	161.0	157.1	137.4	145.4	131.0	31.2	C=O: 162.6
11a	150.2	121.0	135.6	128.9	126.0	133.3	125.2	136.7	124.3	158.9	158.0	138.3	146.2	128.1	25.7 Et CH_3: 15.2	(^1J(C–P) = 32.8) CH_3: 7.5
11b	150.0	120.9	135.5	128.6	126.5	134.0	124.9	136.6	124.9	159.3	158.6	137.8	146.0	127.9	25.2 Et CH_2: 13.4	(^1J(C–P) = 39.4) CH_3: 7.1

[a] Recorded at 75.48 MHz in $CDCl_3$ at 21 °C, unless stated otherwise.
[b] Recorded at $T = -23$ °C.
[c] Not observed.

PQ)Pd(C(O)Me)Cl (**7**), which, in contrast to complex **4**, is rather unstable especially in solution. The ^1H NMR was recorded at −23 °C, because the spectrum at 20 °C shows broadened signals for the methyl group on palladium, for the methyl group on the ligand and for proton 7.

3.3. Synthesis of (N⌒N)Pd(alkene) complexes

The zerovalent palladium complexes (8-PQ)Pd(MA) (**8a**), (8-PQ)Pd(FN) (**8b**), (Me-8-PQ)Pd(MA) (**9a**) and (Me-8-PQ)Pd(FN) (**9b**) were synthesised in high yield by reaction of $Pd(dba)_2$, the bidentate nitrogen ligand and the electron poor alkenes maleic anhydride (MA) or fumaronitrile (FN) (see Eq. (4)).



This general procedure [38] is only suitable for strongly electron-accepting alkenes. When weaker electron-accepting alkenes like dimethyl maleate or dimethyl fumarate were employed, no zerovalent palladium complexes could be isolated. The bright yellow crystalline products **8a** and **8b** are stable in air for months and in solution for days, while the products **9a** and **9b** decompose within a few hours in solution. The ^1H and ^{13}C NMR spectra are compiled in Tables 5–8.

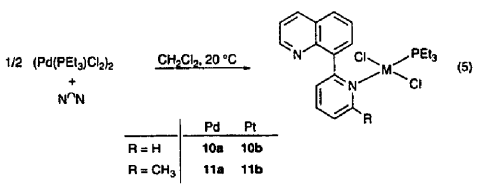
The signals of the vinylic protons and unsaturated carbons of MA and FN shift 3.0–3.5 (^1H NMR) and 90–120 (^{13}C NMR) to lower ppm values, respectively. These changes in chemical shift are characteristic of zerovalent PdL_2(alkene) complexes [38].

For the zerovalent palladium complexes **8** and **9** a fluxional behaviour on the NMR time scale can be observed. At low temperature (−73 °C) the alkene proton signals show a distinct AB pattern in the slow exchange limit while at higher temperature broadening and coalescence of the signals occurs leading to one signal for both alkene protons in the fast exchange limit.

From the results of the variable temperature NMR experiments the rotation barrier $\Delta G^{\neq}_{rot}$ of the alkenes can be calculated using the formula $\Delta G^{\neq}_{rot} = -RT_c \ln[\pi\Delta\nu h/(2^{1/2}kT_c)]$ in which T_c is the coalescence temperature and $\Delta\nu$ the chemical shift difference in Hz of the alkene protons in the slow exchange limit. At 300.13 MHz the $\Delta G^{\neq}_{rot}$ is 65 ± 1 kJ mol^{-1} for complex **8a** ($\Delta\nu = 94$ Hz, $T_c = 318$ K) and 63 ± 1 kJ mol^{-1} for complex **8b** ($\Delta\nu = 63$ Hz, $T_c = 300$ K). The value for complex **9a** is somewhat lower at 55 ± 1 kJ mol^{-1} ($\Delta\nu = 129$ Hz, $T_c = 285$ K), which seems unexpected in view of the higher steric demands of the ligand Me-8-PQ. The rotational barriers calculated for complexes **8** and **9a** are in the range found for other palladium complexes containing bidentate nitrogen ligands [38].

3.4. Synthesis of (N^N)M(PEt$_3$)Cl$_2$ (M = Pd, Pt)

An almost quantitative yield of the complexes (8-PQ)-Pd(PEt$_3$)Cl$_2$ (**10a**) and (8-PQ)Pt(PEt$_3$)Cl$_2$ (**10b**) can be obtained when the chloro bridged dimers (Pd(PEt$_3$)Cl$_2$)$_2$ and (Pt(PEt$_3$)Cl$_2$)$_2$ are stirred with the ligand in dichloromethane for 30 min and 5 h, respectively (see Eq. (5)).



	Pd	Pt
R = H	10a	10b
R = CH$_3$	11a	11b

The pale yellow complexes are very stable in solution and as a solid. The products were characterised by ^{1}H (see Table 5), COSY, ^{13}C NMR (see Table 6) and elemental analysis. An X-ray structure determination was carried out for the complex (8-PQ)Pd(PEt$_3$)Cl$_2$ (**10a**).

In **10a** and **10b** the ligand is coordinated in a monodentate fashion, the quinoline group being dissociated, as can be deduced from the molecular structure (vide infra) and the ^{1}H NMR spectra of both the Pd and Pt complexes. The platinum complex shows only platinum satellites on the proton adjacent to the nitrogen of the pyridyl group while no satellites can be observed on the protons adjacent to the nitrogen of the quinoline group. The ^{1}H NMR spectra of complexes Pd and Pt show almost no chemical shift difference for the protons of the quinoline group in comparison with the free ligand except for proton H7 which is shifted in the Pd and Pt complex by 0.6 and 0.5 ppm to a higher ppm value, respectively. This is an indication that this proton H7 points towards the metal centre and that the nitrogen of the quinoline group is pointed away from the metal centre.

Analogous complexes (Me-8-PQ)Pd(PEt$_3$)Cl$_2$ (**11a**) and (Me-8-PQ)Pt(PEt$_3$)Cl$_2$ (**11b**) have been obtained with the pyridyl moiety coordinated to the metal centre. The proton adjacent to the nitrogen of the quinoline group does not show platinum satellites for complex **11b**, while for both complexes **11a** and **11b** a downfield shift of proton H7 can be observed in the ^{1}H NMR spectrum (see Table 7). This indicates that proton H7 is in close proximity to the metal centre.

The ^{31}P NMR spectrum of complex **10a** shows one phosphorus resonance at 35.1 ppm, while the resonance of complex **10b** can be observed at 0.92 ppm with ^1J(Pt–P) = 3464 Hz. The ^{31}P resonances of complexes **11a** and **11b** are found at 32.9 and −1.79 ppm, with ^1J(Pt–P) = 3506 Hz for the latter. These chemical shifts are as expected [39–41], while the ^1J(Pt–P) coupling constants are consistent with a *trans* configuration of the pyridyl moiety with respect to the phosphine [40,42].

3.5. Molecular structure of (8-PQ)Pd(Me)Cl (3)

A view of the molecular structure of complex **3** is shown in Fig. 2. Tables 9 and 10 contain the bond lengths and the bond angles of the non-hydrogen atoms, respectively.

The ligand 8-PQ, which forms a six-membered metallacycle, coordinates as a bidentate, while the ligands around the palladium are situated in a planar arrangement. The methyl group is *cis* with respect to the pyridyl group as was inferred from the ^{1}H NMR spectrum (vide supra).

The Pd–N2 distance of 2.185(4) Å (*trans* to the methyl group) is significantly longer than the Pd–N1 distance of 2.035(4) Å (*trans* to the chloride) because of the higher *trans* influence of the methyl group [43]. The Pd–Cl distance of 2.323(1) Å is as expected [14,37], while the Pd–C15 bond of 2.031(5) Å is relatively long when compared to other Pd–C bond lengths [14]. Interesting is the relatively large bite angle of the ligand, which is 87.7(1)°. This angle is at least 10° larger than those of other palladium complexes

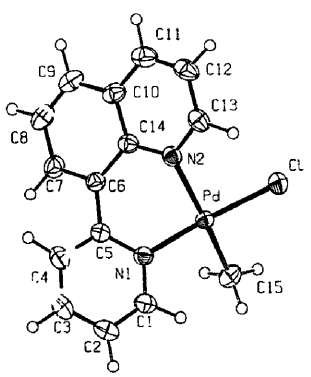


Fig. 2. An ORTEP plot at 50% probability level of complex (8-PQ)-Pd(Me)Cl (3).

containing bidentate nitrogen ligands like Ar-BIAN, R-PyCa and Bipy [13–15]. The most interesting feature of this molecule is that instead of a relatively flat structure a structure is formed with large dihedral angles between the Cl–Pd–Me plane and both the pyridyl and quinoline planes, as can be observed very clearly in Fig. 3, where a side view of complex **3** is projected. The dihedral angle between the Cl–Pd–Me plane and the quinoline plane is 50.9(2)° and this angle is 46.4(4)° between the former and the pyridyl plane.

3.6. Molecular structure of (8-PQ)Pd(C(O)Me)Cl (4)

A view of the molecular structure of complex **4** is shown in Fig. 4. In this structure the same geometry is observed as in complex **3** which means that the C(O)Me group is situated *cis* to the pyridyl group. The coordination of the acetyl group is as expected, with the plane of the acetyl almost perpendicular to the coordination plane of the palladium. The bond

Table 9
Bond distances (Å) of (8-PQ)Pd(Me)Cl (**3**), (8-PQ)Pd(C(O)Me)Cl (**4**) and (8-PQ)Pd(PEt_3)Cl_2 (**10a**) (with e.s.d.s in parentheses)

Bond	(8-PQ)Pd(Me)Cl	(8-PQ)Pd(C(O)Me)Cl	(8-PQ)Pd(PEt_3)Cl_2
Pd–Cl1	2.323(1)	2.326(2)	2.294(5)
Pd–Cl2			2.296(5)
Pd–P			2.225(6)
Pd–N(1)	2.035(4)	2.060(4)	2.16(2)
Pd–N(2)	2.185(4)	2.186(5)	
Pd–C(15)	2.031(5)	1.952(6)	
P–C15			1.87(3)
P–C17			1.81(3)
P–C19			1.82(3)
O–C(15)		1.226(9)	
N(1)–C(1)	1.348(6)	1.336(8)	1.33(3)
N(1)–C(5)	1.366(5)	1.363(8)	1.35(2)
N(2)–C(13)	1.328(4)	1.323(9)	1.27(3)
N(2)–C(14)	1.375(6)	1.371(8)	1.38(2)
C(1)–C(2)	1.380(8)	1.357(9)	1.35(3)
C(2)–C(3)	1.386(7)	1.38(1)	1.43(4)
C(3)–C(4)	1.392(7)	1.39(1)	1.35(3)
C(4)–C(5)	1.402(7)	1.410(8)	1.38(3)
C(5)–C(6)	1.480(6)	1.475(9)	1.45(2)
C(6)–C(7)	1.392(7)	1.40(1)	1.33(3)
C(6)–C(14)	1.452(4)	1.436(9)	1.44(2)
C(7)–C(8)	1.401(7)	1.39(2)	1.39(3)
C(8)–C(9)	1.361(8)	1.38(2)	1.37(2)
C(9)–C(10)	1.420(6)	1.44(2)	1.42(3)
C(10)–C(11)	1.415(5)	1.42(2)	1.45(3)
C(10)–C(14)	1.424(6)	1.431(9)	1.44(2)
C(11)–C(12)	1.367(7)	1.27(2)	1.35(3)
C(12)–C(13)	1.408(6)	1.40(1)	1.42(3)
C(15)–C(16)		1.47(1)	1.54(5)
C(17)–C(18)			1.51(5)
C(19)–C(20)			1.52(5)

lengths and angles of the non-hydrogen atoms are reported in Tables 9 and 10, respectively.

The bond angles of this structure are slightly different from the bond angles of complex **3**. The bite angle N1–Pd–N2 (86.6(2)°) is slightly smaller. Comparison of the bond lengths of complexes **3** and **4** shows interesting features. The Pd–N1 (2.060(4) Å) of complex **4** is enlarged significantly with regard to complex **3** (2.031(5) Å). The Pd–N2 (2.186(5) Å) bond however is not enlarged at all, while we would have expected the opposite because of the higher *trans* influence of the acetyl group with regard to the methyl group [44]. The Pd–C15 distance of complex **4** is shorter (1.952(6) Å) because of the sp^2 character of the acetyl carbon atom C15.

Also, in this structure large dihedral angles between the coordination plane of the palladium and the quinoline plane, and between the coordination plane of palladium and the pyridyl plane are observed. The former angle is larger (52.2(2)°) and the latter is significantly smaller (39.1(3)°) than those in complex **3**.

3.7. Molecular structure of (8-PQ)Pd(PEt_3)Cl_2 (10a)

A view of the molecular structure of complex **10a** is shown in Fig. 5. In this structure it can be observed that the ligand 8-PQ coordinates as a monodentate via the pyridyl group and the quinoline group is bent away from the metal centre as deduced from ^{1}H NMR (vide supra). The phosphine is coordinated *trans* to the pyridyl group while the two chloride ligands complete the square planar surrounding of the palladium.

The pyridyl plane makes an angle of 66° with the coordination plane of the palladium and an angle of 48° with the quinoline plane. Selected bond lengths and bond angles are reported in Tables 9 and 11, respectively.

The Pd–Cl distances of 2.294(5) and 2.296(5) Å are comparable with those found for other complexes with a *trans* Cl–Pd–Cl configuration [45–48]. The Pd–N1 bond distance of 2.16(2) Å is relatively long with respect to other Pd–N1 [45–47] distances of analogous complexes but comparable to the analogous distance in the complex *trans*-$PdCl_2$(2-NH_2-3-Mepy)(PEt_3) [48]. The Pd–P distance of 2.225(6) Å is normal for *trans* N1–Pd–P complexes [45–47,49]. The Cl1–Pd–Cl2 and P–Pd–N1 bond angles deviate relatively much from linearity, being 174.5(2) and 175.0(4)°, respectively.

4. Discussion

The new bifunctional nitrogen ligands 8-(2-pyridyl)-quinoline (**1**) and 8-(6-methyl-2-pyridyl)quinoline (**2**) can

Table 10
Bond angles (°) for (8-PQ)Pd(Me)Cl (3) and (8-PQ)Pd(C(O)Me)Cl (4) (with e.s.d.s in parentheses)

	(8-PQ)Pd(Me)Cl	(8-PQ)Pd(C(O)Me)Cl
Cl–Pd–N(1)	173.8(1)	178.1(2)
Cl–Pd–N(2)	93.0(1)	91.6(1)
Cl–Pd–C(15)	88.6(2)	86.5(2)
N(1)–Pd–N(2)	87.7(1)	86.6(2)
N(1)–Pd–C(15)	91.7(2)	95.3(2)
N(2)–Pd–C(15)	170.7(2)	176.6(3)
Pd–N(1)–C(1)	118.8(3)	120.4(4)
Pd–N(1)–C(5)	122.0(3)	121.4(4)
C(1)–N(1)–C(5)	118.6(4)	118.0(5)
Pd–N(2)–C(13)	120.0(3)	119.4(5)
Pd–N(2)–C(14)	115.3(2)	113.0(4)
C(13)–N(2)–C(14)	118.2(3)	117.9(6)
N(1)–C(1)–C(2)	123.5(4)	124.2(7)
C(1)–C(2)–C(3)	118.7(5)	119.0(7)
C(2)–C(3)–C(4)	118.6(5)	118.7(7)
C(3)–C(4)–C(5)	120.4(4)	119.7(7)
N(1)–C(5)–C(4)	120.1(4)	120.5(6)
N(1)–C(5)–C(6)	121.8(4)	120.7(5)
C(4)–C(5)–C(6)	118.0(4)	118.9(6)
C(5)–C(6)–C(7)	118.5(3)	117.2(6)
C(5)–C(6)–C(14)	123.8(3)	124.0(6)
C(7)–C(6)–C(14)	117.2(4)	118.1(6)
C(6)–C(7)–C(8)	123.0(3)	122.1(9)
C(7)–C(8)–C(9)	119.9(4)	121(1)
C(8)–C(9)–C(10)	120.5(4)	120(1)
C(9)–C(10)–C(11)	122.0(4)	123.5(9)
C(9)–C(10)–C(14)	119.9(3)	119.2(9)
C(11)–C(10)–C(14)	118.1(4)	117.3(8)
C(10)–C(11)–C(12)	120.1(4)	120(1)
C(11)–C(12)–C(13)	118.1(3)	121(1)
N(2)–C(13)–C(12)	124.3(4)	122.8(8)
N(2)–C(14)–C(6)	120.1(3)	120.3(5)
N(2)–C(14)–C(10)	120.9(3)	120.3(6)
C(6)–C(14)–C(10)	118.9(3)	119.4(6)
Pd–C(15)–O		121.7(5)
Pd–C(15)–C(16)		116.1(5)
O–C(15)–C(16)		122.2(7)

easily be synthesised starting from 8-bromoquinoline in a palladium catalysed cross coupling reaction with 2-bromopyridine and 6-bromo-2-picoline, respectively. These ligands readily form Pd^0 and Pd^{II} complexes comparable to other bidentate nitrogen ligands like α-diimine ligands [13–15]. The carbonylation reaction of the Pd–methyl complex **3** leading to the acetyl complex **4** can be performed at room temperature and atmospheric pressure within several minutes which is characteristic of palladium complexes containing bidentate nitrogen ligands [13,14,37]. Carbonylation of complex **6** containing the ligand Me-8-PQ also shows these characteristics but the product is less stable than complex **4**. A closer look at the molecular structures and the NMR of the products of the complexation and carbonylation reactions, however, shows that the coordination behaviour of the ligand 8-PQ and Me-8-PQ is rather different from other bidentate nitrogen ligands. In both complexes **3** and **4** the ligand coordinates with a relatively large bite angle of 87.7(1) and 86.6(2)°, respectively. Unexpectedly the complexes show large dihedral angles between the plane Cl–Pd–Me and the pyridyl and quinoline planes (see Fig. 3). To compare the distortion, found in complex **3**, with other complexes with such a phenemenon, the dihedral angle between the least-squares plane N1–N2–C9–C14 and the Cl–Pd–Me plane has been calculated, being 39.8(2)°, which is comparable to those in the complexes (Me_2-Phen)Pd(Me)Cl [18], (Me_2-Phen)Pt(Cl)$_2$, (Me_2-Phen)Pt(Br)$_2$ and (Me_2-Phen)Pt(I)$_2$ containing the very rigid bidentate nitrogen ligand Me_2-phenanthroline (Me_2-Phen) [17]. In these complexes the angles are 39.3, 38.8, 41.9 and 44.0°, respectively, which is clearly a consequence of the large steric interactions of the *ortho*-substituents on the phenanthroline and the other ligands on the metal.

Complex **4** exhibits, to an even larger extent, the same type of distortion and the analogous angle amounts to 52.7(3)°, which is significantly larger than that in complex **3** and the other complexes mentioned before [17,18].

In addition, the ligand in complexes **3** and **4**, is also highly distorted from planarity, which is illustrated by the dihedral angle between the quinoline and the pyridyl planes of 41.0(1)° in complex **3** and 39.8(2)° in complex **4**.

The large dihedral angles of complexes **3** and **4** can be explained by both the ring size of the formed metallacycle and the rigidity of the ligand. In a flat, six-membered metallacycle with Pd–N distances of more than 2 Å a very acute bite angle of about 60° would be expected, which is not possible in view of the overlap of both nitrogen lone pairs with the empty palladium $d_{x^2-y^2}$ orbitals. Thus, the out of plane bending of the aromatic rings is essential for efficient coordination of this ligand in a bidentate fashion and therefore must lead to a large bite angle.

To gain more insight into the direction of the nitrogen lone pairs with regard to the empty palladium $d_{x^2-y^2}$, the angles of both the lines C3–N1 through the pyridyl and C11–N2 through the quinoline group with the plane Cl–Pd–C15 of complexes **3** and **4** have been calculated. The ideal angle for overlap would be 0° but the angles between the lines C3–N1 and C11–N2 with the plane Cl–Pd–C15 in complex **3** are 12.84(4) and 33.7(2)°, respectively and in complex **4** 5.04(6) and 28.5(2)°, respectively. From these values it may be concluded that the lone pair of the quinoline nitrogen makes a very unfavourable angle with the empty $d_{x^2-y^2}$ orbitals of the palladium upon coordination. The angles between C3–N1 through the pyridyl moiety with the plane Cl–Pd–C15 are smaller and are forced to a more common situation, we think, because of the relatively strong bonding of the pyridyl group to palladium with respect to the quinoline group (vide infra).

The major configuration of the (8-PQ)Pd(R)Cl complexes is the one with the R group *cis* to the pyridyl group, while only a small amount of the other isomer has been observed. Since the pK_a value for pyridine is larger than for quinoline [50], the former group is expected to have better

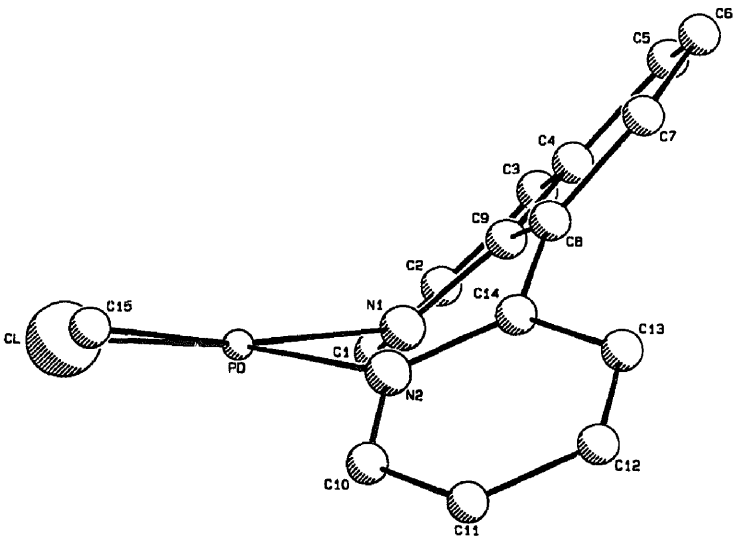


Fig. 3. Side view of complex **3**.

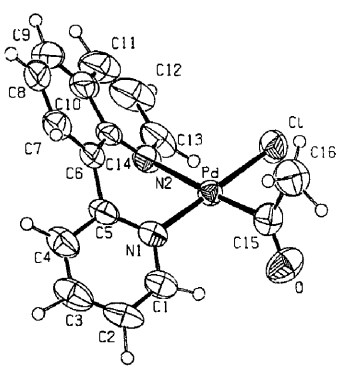


Fig. 4. An ORTEP plot at 50% probability level of complex (8-PQ)-Pd(C(O)Me)Cl (**4**).

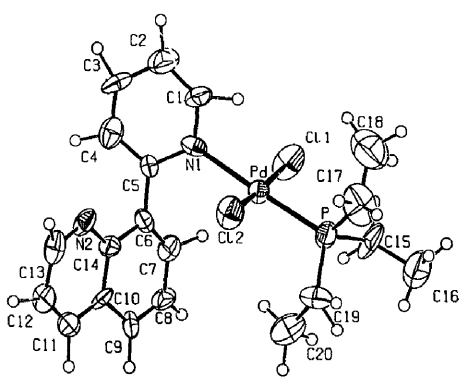


Fig. 5. An ORTEP plot at 50% probability level of complex (8-PQ)-$Pd(PEt_3)Cl_2$ (**10a**).

σ-donating capabilities, which induces the methyl group to coordinate *cis* to this pyridyl group, as it has better σ-donating properties than the chloride. The conformation in complex **6** is reversed due to the steric hindrance of the methyl on the pyridyl group with the methyl group on palladium.

The Pd–N2 distance *trans* to the R group in complex **4** of 2.186(5) Å is equal to the Pd–N2 distance in complex **3**. Since the acetyl group is expected to have a larger *trans* influence and thus a larger σ-bond destabilisation than the methyl group [44], the Pd–N2 distance in complex **4** would be expected to be larger. However, for analogous complexes containing the bidentate nitrogen ligands iPr-Pyca and Bipy even shorter Pd–N bonds *trans* to an acetyl group than *trans* to a methyl group have been reported [14]. These observations have been rationalised by suggesting a relatively large $d_{xz} \rightarrow p_{\pi*}$ back-donation from the palladium to the pyridyl moiety induced not only by the large σ-donation of the acetyl group to the palladium but also by the presence of suitable $p_{\pi*}$ orbitals on the pyridyl group. This electronic push–pull effect does not apply for complexes **3** and **4**, which may be explained by the large angle between the quinoline and the coordination plane of the palladium, making π-back-donation rather difficult.

An unexpected coordination mode of the ligands **1** and **2** is shown in complexes **10** and **11** where the pyridyl group is coordinated to the metal centre with the quinoline group turned away from the metal centre, as the former group is a stronger σ-donor than the quinoline group (vide supra). The X-ray crystal determination of the Pd complex **10a** and the ^{31}P NMR spectrum of the Pt complexes **10b** and **11b** show that all four-coordinate complexes have a *trans* configuration.

Table 11
Bond angles (°) for (8-PQ)$PdCl_2(PEt_3)$ (**10a**) (with e.s.d.s in parentheses)

Cl(1)–Pd–Cl(2)	174.5(2)	N(1)–C(5)–C(6)	120(2)
Cl(1)–Pd–P	93.6(2)	C(4)–C(5)–C(6)	123(2)
Cl(1)–Pd–N(1)	89.2(4)	C(5)–C(6)–C(7)	123(2)
Cl(2)–Pd–P	88.0(2)	C(5)–C(6)–C(14)	118(1)
Cl(2)–Pd–N(1)	88.9(4)	C(7)–C(6)–C(14)	119(2)
P–Pd–N(1)	175.0(4)	C(6)–C(7)–C(8)	123(2)
Pd–P–C(15)	115.4(8)	C(7)–C(8)–C(9)	122(2)
Pd–P–C(17)	112(1)	C(8)–C(9)–C(10)	119(2)
Pd–P–C(19)	114(1)	C(9)–C(10)–C(11)	121(2)
C(15)–P–C(17)	105(1)	C(9)–C(10)–C(14)	119(2)
C(15)–P–C(19)	107(1)	C(11)–C(10)–C(14)	120(2)
C(17)–P–C(19)	103(1)	C(10)–C(11)–C(12)	120(2)
Pd–N(1)–C(1)	117(1)	C(11)–C(12)–C(13)	115(2)
Pd–N(1)–C(5)	124(1)	N(2)–C(13)–C(12)	129(2)
C(1)–N(1)–C(5)	119(2)	N(2)–C(14)–C(6)	123(2)
C(13)–N(2)–C(14)	119(2)	N(2)–C(14)–C(10)	118(1)
N(1)–C(1)–C(2)	128(2)	C(6)–C(14)–C(10)	119(2)
C(1)–C(2)–C(3)	112(2)	P–C(15)–C(16)	115(2)
C(2)–C(3)–C(4)	121(2)	P–C(17)–C(18)	112(2)
C(3)–C(4)–C(5)	122(2)	P–C(19)–C(20)	112(2)
N(1)–C(5)–C(4)	117(2)		

Rotation of the quinoline group around the pyridyl–quinoline axes of both complexes **10** and **11** causes proton H7 of the quinoline group to be in close proximity of the palladium atom. The calculated Pd–H7 distance observed in the molecular structure of complex **10a** shown in Fig. 5 amounts to 2.8(3) Å, which is within the distance of 3.2 Å expected for van der Waals contacts. This short distance causes a shift of 0.5 ppm in the ^1H NMR to lower field, as observed before in the complex $[PtCl_2PBu_3]_2$(tBuN=CH–CH=NtBu) [41]. This shift is relatively large as compared to the shifts found for the complexes *trans*-$PdCl_2$[2-(N=CHR)-3-methylpyridine}(PEt_3) (R = substituted aryl group) [48] but small as compared to the shifts found for the complexes [Pd(dmp)(bquin)(OH_2)][ClO_4] and Pd(dmp)(bquin)-NO_3 (dmp = {2-dimethylaminomethyl)phenyl-*N*}, bquin = benzo[*h*]quinoline) [51].

The zerovalent complexes (8-PQ)Pd(alkene) (**8**) and (Me-8-PQ)Pd(MA) (**9a**) show a fluxional behaviour, causing coalescence of the vinylic protons at higher temperatures (27 °C). Since the coordinated maleic anhydride has a C_s symmetry, coalescence is not self-evident when the asymmetry of the ligand coordinated to the palladium is taken into account. Two atropisomers exist of the ligand 8-PQ when this is coordinated in a bidentate fashion of which one is shown in the molecular structure of complex **3** (see Fig. 3). The two atropisomers for the (N^N)Pd(alkene) complexes, shown in Fig. 6, have not been observed separately in solution in low temperature NMR experiments, indicating that there is a low energetic barrier between both isomers. A fast exchange on the NMR time scale between the two atropisomers causes a nett mirror plane through the coordination plane of the palladium. Providing this is a fast process on the NMR time scale with respect to the rotation of the alkene as

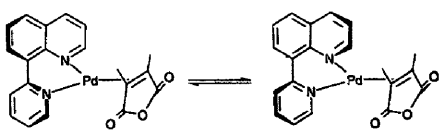


Fig. 6. Atropisomerism in (N^N)Pd(alkene) complexes.

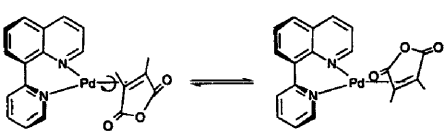


Fig. 7. Alkene rotation around the Pd–alkene axes.

shown in Fig. 7, coalescence of the alkene proton signals is feasible.

The two si- and re-face isomers, principally formed upon coordination of the *E*-alkene fumaronitrile, are equivalent on the NMR time scale when taking into account the fast interconversion of the two atropisomers. Coalescence of the fumaronitrile protons can now be rationalised by rotation of the alkene around the Pd–alkene axes, as the coordinated fumaronitrile has C_2 symmetry.

5. Concluding remarks

From the molecular structures of complex **3**, **4** and **10a** it can be concluded that the coordination characteristics of the ligand 8-PQ, forming a six-membered metallacycle upon coordination, are comparable to the coordination characteristics of a bidentate nitrogen ligand with substituents close to

the nitrogens as in Me_2-Phen although the bite angle is consistently larger. Both ligands form complexes having large dihedral angles between the plane of the bidentate nitrogen ligand and the coordination plane of palladium. An additional ligand like PEt_3 causes dissociation of one nitrogen donor of both the ligand 8-PQ and the very rigid ligand Me_2-Phen. The large dihedral angle and the relatively large bite angle of the ligand 8-PQ does not seem to have a large effect on the CO insertion into the palladium carbon bond of complexes **3** and **6** when compared with other known systems [14].

6. Supplementary material

Further details of the structure determinations, including atomic coordinates, bond lengths and angles and thermal parameters for **3**, **4** and **10a** are available from the authors on request.

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