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Insertion reactions into palladium–carbon bonds of complexes containing new rigid bidentate nitrogen ligands [1]

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Abstract

The neutral complexes Pd(Me)Cl(DPIA) (**3**) and Pd(Me)Cl(DQIA) (**4**), containing the novel rigid bidentate nitrogen ligands (5,6-dihydro-[1]pyrindin-7-ylidene)-isopropylamine (DPIA) and (6,7-dihydro-5*H*-quinolin-8-ylidene)-isopropylamine (DQIA), respectively, have been synthesized. Complexes **3** and **4** react quantitatively with CO to give the neutral acylpalladium complexes Pd(C(O)Me)Cl(DPIA) (**6**) and Pd(C(O)Me)Cl(DQIA) (**7**), respectively. Complexes **3**, **4**, **6**, and **7**, which were present as mixtures of the *cis* and *trans* isomers, were fully characterized, and in the case of complexes **6** and **7** single crystal X-ray structures have been determined. The molecular structure of **6** and **7** show a square planar geometry with the α-diimine ligands coordinated in a bidentate fashion with comparable bite angles of about 78°. The acylpalladium complexes **6**, **7**, and Pd(C(O)Me)Cl(*i*Pr–PyCa) (**5**), containing the nitrogen ligand 2-(*N*-2-propanecarbaldimino)pyridine (*i*Pr–PyCa), which is the flexible analogue of DPIA and DQIA, react with norbornadiene to yield the ionic alkyl complexes [Pd(C_7H_8C(O)Me)(DPIA)]Cl (**9a**), [Pd(C_7H_8C(O)Me)(DQIA)]Cl (**10a**), and [Pd(C_7H_8C(O)Me)(*i*Pr–PyCa)]Cl (**8a**), respectively. Interestingly, the nature of the α-diimine ligand influences the reaction rate of the norbornadiene insertion in the order N–N = DQIA $\ll$ *i*Pr–PyCa < DPIA. Competition experiments and comparison of the crystal data from **6** and **7** indicate that the complexation strength of the α-diimine ligand is exactly opposite to the reactivity of the corresponding acylpalladium complexes toward norbornadiene, which suggest a mechanism via intermediates containing a unidentate coordinated α-diimine ligand. © 1998 Elsevier Science S.A.

Keywords: Palladium; α-diimine ligand; Bidentate

1. Introduction

The insertion reactions of carbon monoxide and alkenes are key steps in the palladium catalyzed alternating copolymerization of CO and alkenes [1–11]. We and others have conducted a large amount of research on insertion reactions of CO and alkenes into carbon–palladium bonds of complexes containing bidentate phosphorus [12–19], phosphorus–nitrogen [20], bidentate nitrogen [4,21–31], and terdentate nitrogen ligands [32–35]. Extensively studied is the CO insertion into the methyl–palladium bond of complexes of the type Pd(Me)X(P–P) (X = Cl, CF_3SO_3, BF_4; P–P = $PPh_2(CH_2)_nPPh_2$ (n = 2, 3, 4)) [13]. It has been found that complexes containing the diphosphine $PPh_2(CH_2)_4PPh_2$ show the highest reactivity toward CO insertions. This was believed to originate from the flexibility together with the relatively large bite angle of the diphosphine ligand, which lowers the energy of the transition state. This was supported by ab initio calculations, which show that the activation energy of the CO insertion into the methyl–platinum bond of complexes *cis*-Pt(Me)F(CO)(PH_3) decreases upon increase of the angle F–Pt–PH_3 [36]. Surprisingly, methylpalladium complexes containing flexible bidentate nitrogen ligands with rather small bite angles

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[1] Dedicated to Professor Peter M. Maitlis on the occasion of his 65th birthday.

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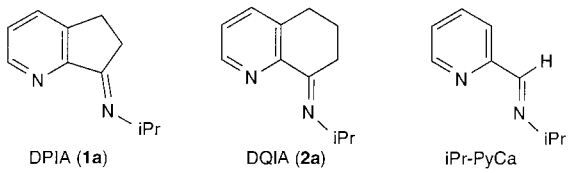


Fig. 1. Structures of DPIA (**1a**), DQIA (**2a**), and *i*Pr–PyCa.

were found to be generally much more reactive toward CO [23,28,37]. Furthermore, complexes containing rigid bidentate nitrogen ligands were not only extremely reactive toward CO [22], but also alkene [22,31] and allene [38,39] insertions were found to occur readily. Up till now, not much is known about the influence of the bite angle and flexibility of bidentate nitrogen ligands on insertion reactions. Very recently, methylpalladium complexes containing the bidentate nitrogen ligands 1,1′-bis(2-pyridyl)ferrocene [29] and 8-(2-pyridyl)quinoline [30], which both coordinate with a large bite angle, were reported to be very reactive toward CO. However, the high reactivity seemed to originate from the flexibility of both ligands. A series of bidentate nitrogen ligands which may be very useful in studying the influence of bite angle and flexibility on insertion reaction is shown in Fig. 1.

The novel α-diimines (5,6-dihydro-[1]pyrindin-7-ylidene)-isopropylamine (DPIA) (**1a**) and 6,7-dihydro-5*H*-quinolin-8-ylidene)-isopropylamine (DQIA) (**2a**) can be considered to be the rigid analogues of the well known flexible α-diimine 2-(*N*-2-propanecarbaldimino)pyridine (*i*Pr–PyCa). Since these ligands are expected to have similar electronic properties but may differ only in flexibility and bite angle, the use of these ligands might provide us more insight in the influence of these properties of bidentate nitrogen ligands on insertion reactions in the corresponding palladium complexes. Here, we wish to report the syntheses, characterization, and study of reactivity toward CO and alkenes of palladium complexes containing the α-diimines DPIA and DQIA.

2. Experimental section

2.1. General comments

All manipulations were carried out in an atmosphere of purified dry nitrogen by using standard Schlenk techniques. Solvents were dried and stored under nitrogen. Carbon monoxide 99.5% was purchased from HoekLoos. All other starting chemicals were used as commercially obtained. Silver trifluoromethanesulfonate was stored under nitrogen in the dark. 5,6-dihydro-[1]pyrindin-7-one [40], 6,7-dihydro-5*H*-quinolin-8-one [40], Pd(Me)Cl(COD) (COD = 1,5-cyclooctadiene) [41], and Pd(C(O)Me)Cl(*i*Pr–PyCa) (**5**) (*i*Pr–PyCa = 2-(*N*-2-propanecarbaldimino)pyridine) [28] were prepared according to the literature. ^{1}H and ^{13}C NMR spectra (300.13 and 75.48 MHz, respectively) were recorded on a Bruker AMX 300 and a Bruker DRX 300 spectrometer. Chemical shifts are in ppm relative to TMS as external standard. IR spectra were obtained on a Bio-Rad FTS-7 spectrophotometer and mass spectra on a JEOL JMS SX/SX1O2A four-sector mass spectrometer equipped with a fast atom bombardment source.

*2.2. Synthesis of DPIA (**1a**) and DQIA (**2a**)*

A solution of 5,6-dihydro-[1]pyrindin-7-one (0.49 g, 3.69 mmol) in 20 ml of isopropylamine, to which 2 drops of formic acid were added, was stirred at 20°C. After 2 h, the amine was evaporated in vacuo and the residue was extracted with diethyl ether (2 × 20 ml). Evaporation of the diethyl ether resulted in a brown oil, which was further purified by chromatography over neutral alumina with hexane/diethyl ether (4:1) as eluent, yielding a brown oil (2.69 mmol, 73%). IR (KBr): 3398 cm^{-1} (broad), υ(N–H). Mass found: $m/z = 174$. $C_{11}H_{14}N_2$ calc.: $m/z = 174$.

The compound DQIA (**2a**) was obtained from 6,7-dihydro-5*H*-quinolin-8-one and isopropylamine as a yellow oil (68%) in a similar way as described for compound **1a**. IR (KBr): 3385 cm^{-1} (broad), υ(N–H). Mass found: $m/z = 188$. $C_{12}H_{16}N_2$ calc.: $m/z = 188$.

*2.3. Synthesis of Pd(Me)Cl(DPIA) (**3**) and Pd(Me)Cl(DQIA) (**4**)*

To a solution of Pd(Me)Cl(COD) (0.64 g, 2.41 mmol) in 15 ml of dichloromethane was added **1** (0.47 g, 2.70 mmol) and the mixture was stirred at 20°C. After 30 min, the solution was evaporated to dryness and the product was washed with diethyl ether (2 × 20 ml) and dried in vacuo, yielding complex **3** as a yellow solid (2.24 mmol, 93%). Anal. found: C, 43.65; H, 5.16; N, 8.37. $C_{12}H_{17}ClN_2Pd$ calc.: C, 43.52; H, 5.18; N, 8.46.

Complex Pd(Me)Cl(DQIA) (**4**) was synthesized in a similar way as described for complex **3** (81%). Anal. found: C, 44.78; H, 5.58; N, 7.83. $C_{13}H_{19}ClN_2Pd$ calc.: C, 45.24; H, 5.56; N, 8.12.

2.4. Synthesis of Pd(C(O)Me)Cl(DPIA) (6) and Pd(C(O)Me)Cl(DQIA) (7)

A solution of Pd(Me)Cl(DPIA) (**3**) (0.22 g, 0.67 mmol) in 20 ml of dichloromethane was stirred at 20°C for 30 min in a CO atmosphere. The solution was filtered through Celite filter aid and the residue was extracted with dichloromethane (5 ml). The combined filtrates were evaporated to dryness and the product was washed with diethyl ether (2×20 ml) and dried in vacuo, giving **6** as a yellow solid (0.58 mmol, 86%). IR (KBr): 1711 cm^{-1}, υ(CO). Anal. found: C, 43.20; H, 4.79; N, 7.68. $C_{13}H_{17}ClN_2OPd$ calc.: C, 43.48; H, 4.77; N, 7.80.

Complex Pd(C(O)Me)Cl(DQIA) (**7**) was synthesized from Pd(Me)Cl(DQIA) (**4**) in a similar way as described for complex **6** (89%). IR (KBr): 1689 cm^{-1}, υ(CO). Anal. found: C, 45.22: H, 5.16; N, 7.35. $C_{14}H_{19}ClN_2OPd$ calc.: C, 45.06; H, 5.14; N, 7.51.

2.5. Synthesis of [Pd(C7H8C(O)Me)(iPr–PyCa)]Cl (8a), [Pd(C7H8C(O)Me)(DPIA)]Cl (9a), and [Pd(C7H8C(O)Me)(DQIA)]Cl (10a)

Norbornadiene (0.21 ml, 2.00 mmol) was added to a solution of Pd(C(O)Me)Cl(*i*Pr–PyCa) (**5**) (0.13 g, 0.41 mmol) in 20 ml of dichloromethane. After being stirred at 20°C for 1 h, the solution was evaporated to dryness and the residue was washed with diethyl ether (2×20 ml), yielding **8a** as a yellow solid (0.37 mmol, 92%), which was too unstable in the solid state to allow microanalysis. IR (KBr): 1600 cm^{-1}, υ(CO). Mass found: $m/z = 389$. $C_{18}H_{23}N_2OPd$ calc.: $m/z = 389$.

The complexes Pd(C_7H_8C(O)Me)(DPIA)]Cl (**9a**) and [Pd(C_7H_8C(O)Me)(DQIA)]Cl (**10a**) were obtained in a similar way as described for **8a** (92 and 85% yield, respectively) and were also too unstable in the solid state to allow microanalysis.

9a: IR (KBr): 1604 cm^{-1}, υ(CO). Mass found: $m/z = 415$. $C_{20}H_{25}N_2OPd$ calc.: $m/z = 4l5$.

10a: IR (KBr): 1611 cm^{-1}, υ(CO). Mass found: $m/z = 429$. $C_{21}H_{27}N_2OPd$ calc.: $m/z = 429$.

2.6. Synthesis of [Pd(C7H8C(O)Me)(iPr–PyCa)]SO3CF3 (8b), [Pd(C7H8C(O)Me)(DPIA)]SO3CF3 (9b) and [Pd(C7H8C(O)Me)(DQIA)]SO3CF3 (10b)

To a solution of [Pd(C_7H_8C(O)Me)(*i*Pr–PyCa)]Cl (**8a**) (80.8 mg, 0.19 mmol) in a mixture of 20 ml of dichloromethane and 0.5 ml of acetonitrile was added $AgSO_3CF_3$ (56.0 mg, 0.22 mmol), and the mixture was stirred in the dark at 20°C. After 10 min, the mixture was evaporated to dryness and 20 ml of dichloromethane were added. After filtering the solution through Celite aid and extracting the residue with dichloromethane (5 ml), the combined filtrates were evaporated to dryness. Washing the residue with diethyl ether (2×20 ml) and drying in vacuo, yielded **8b** as a yellow solid (0.17 mmol, 89%). No correct analytical data could be obtained, probably due to the presence of small amounts of $AgSO_3CF_3$. IR (KBr): 1604 cm^{-1}, υ(CO). Mass found: $m/z = 389$. $C_{18}H_{23}N_2OPd$ calc.: $m/z = 389$.

Complexes Pd(C_7H_8C(O)Me)(DPIA)]SO_3CF_3 (**9b**) and [Pd(C_7H_8C(O)Me)(DQIA)]SO_3CF_3 (**10b**) were obtained in a similar way as described for complex **8b** (93 and 92% yield, respectively). No correct analytical data could be obtained, probably due to the presence of small amounts of $AgSO_3CF_3$.

9b: IR (KBr): 1609 cm^{-1}, υ(CO). Mass found: $m/z = 415$. $C_{20}H_{25}N_2OPd$ calc.: $m/z = 415$.

lOb: IR (KBr): 1611 cm^{-1}, υ(CO). Mass found: $m/z = 429$. $C_{21}H_{27}N_2OPd$ calc.: $m/z = 429$.

2.7. X-ray structure determination of 6 and 7

Crystals suitable for X-ray structure determination were mounted on a Lindemann-glass capillary and transferred to an Enraf–Nonius CAD4-Turbo diffractometer on rotating anode. Accurate unit-cell parameters and an orientation matrix were determined by least-squares fitting of the setting angles of 25 well-centered reflections (SET4, [42]). Reduced-cell calculations did not indicate higher lattice symmetry [43]. Crystal data and details on data collection and refinement are presented in Table 1. Data were collected at 150 K in ω scan mode, and were corrected for *Lp* effects and for the observed linear decay of the reference reflections. An empirical absorption/extinction correction based on measured ψ-scans (PLATON/ABSP [44]) was applied for compound **6**. The structures were solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-96 [45]). Refinement was performed on F^2 by full-matrix least-squares techniques (SHELXL-96 [46]); no observance criterion was applied during refinement. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms, allowing the C–H distance to refine. The methyl groups were refined as rigid groups, allowing for rotation around the C–C bonds. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed

Table 1
Crystallographic data for **6** and **7**

Complex	**6**	**7**
Crystal data		
Formula	$C_{13}H_{17}ClN_2OPd$	$C_{14}H_{19}ClN_2OPd$
Molecular weight	359.16	373.19
Crystal system	orthorhombic	monoclinic
Space group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)
a, Å	12.0908(16)	8.7427(15)
b, Å	13.673(2)	9.213(3)
c, Å	17.035(3)	19.496(4)
β, deg	–	112.996(14)
V, Å^3	2816.2(7)	1445.5(6)
D_{calc}, g cm^{-3}	1.694	1.715
Z	8	4
F(000)	1440	752
μ, cm^{-1} [Mo K α]	15.0	14.6
Crystal size, mm	0.27×0.29×0.55 (yellow)	0.1×0.3×0.3 (yellow)
Data collection		
θ_{min}, θ_{max} deg	1.20, 27.49	1.13, 27.00
SET 4 θ_{min}, θ_{max} deg	11.50, 14.06	10.03, 13.74
$\Delta\omega$, deg	0.53+0.35 tan θ	0.75+0.35 tan θ
Hor., ver. aperture, mm	3.00+1.50 tan θ, 4.00	3.00, 4.00
X-ray exposure time, h	15	17
Linear instability, %	3	2
Reference reflections	2 4 0, 3 2 4, 2 $\bar{3}$ $\bar{2}$	$\bar{2}$ 2 2, $\bar{2}$ 2 1, $\bar{2}$ 4 4
Data set	0:15, −16:17, −22:0	−11:8, 0:11, −23:25
Total data	6817	5404
Total unique data	3224 [R_{int} = 0.049]	3146 [R_{int} = 0.078]
ABSP corr. range	0.845, 0.946	–
Refinement		
No. of refined params	175	189
Final R[a]	0.0300 [2587 $F_o > 4\sigma(F_o)$]	0.0600 [2021 $F_o > 4\sigma(F_o)$]
Final $wR2$[b]	0.0676	0.1304
Goodness of fit	1.045	1.014
Weighting scheme[c]	$[\sigma^2(F^2)+(0.0178P)^2+0.96P]^{-1}$	$[\sigma^2(F^2)+(0.0376P)^2]^{-1}$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.000, 0.001	0.000, 0.000
Min. and max. Residual density, e Å^{-3}	−0.47, 0.53	−1.22, 1.00 [near Pd]

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.
[c] $P = (\mathrm{Max}(F_o^2, 0)+2F_c^2)/3$.

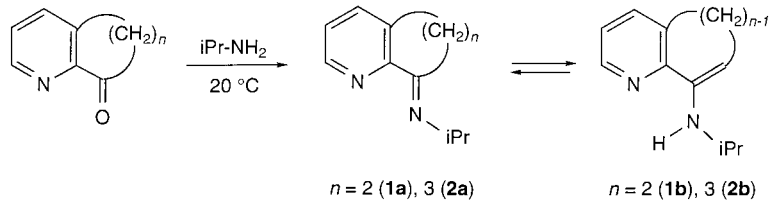
isotropic thermal parameter related to the value of the equivalent isotropic thermal parameter of their carrier atoms by a factor amounting to 1.5 for the methyl hydrogen atoms and 1.2 for the other hydrogen atoms. The crystal structure of **7** contains a 4% disorder component related to the major component by reflection in the [221] netplane. Only the minor Pd site has been included in the structure factor calculation. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography [47]. Geometrical calculations and illustrations were performed with PLATON [44]; all calculations were performed on a DECstation 5000. Full details may be obtained from one of the authors (ALS).

3. Results

3.1. Synthesis and characterization of compounds *1–10*

The pyridine–ketones 5,6-dihydro-[1]pyrindin-7-one and 6,7-dihydro-5*H*-quinolin-8-one reacted with isopropylamine in the presence of a catalytic amount of formic acid to give mixtures of (5,6-dihydro-[1]pyrindin-7-ylidene)-

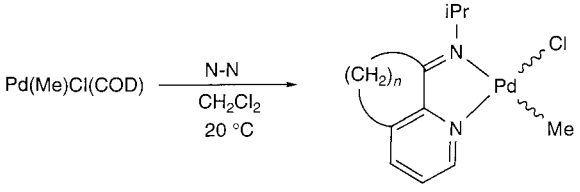
isopropylamine (DPIA) (**1a**) and isopropyl-(5*H*-[1]pyrindin-7-yl)-amine (**1b**) and 6,7-dihydro-5*H*-quinolin-8-ylidene)-isopropylamine (DQIA) (**2a**) and (5,6-dihydro-quinolin-8-yl)-isopropylamine (**2b**), respectively (Eq. (1)).



n = 2 (**1a**), 3 (**2a**) *n* = 2 (**1b**), 3 (**2b**) (1)

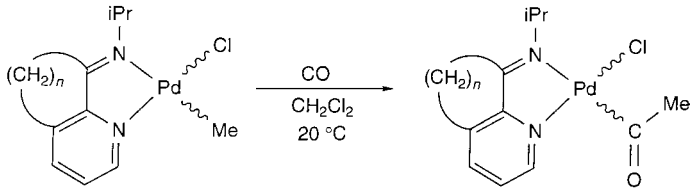
The reactions were completed within 2 h and the products were formed in reasonable yield (73 and 68%, respectively). Compounds **1** and **2** are in the pure form as well as in solution only moderately stable and decompose within a few hours at 20°C, resulting in several unidentified products. However, they can be stored at −80°C for several days without decomposition. Compounds **1** and **2** have been characterized by ^{1}H and ^{13}C NMR spectroscopy (Tables 2 and 3, respectively), IR, and mass spectroscopy (see Section 2). The ^{1}H NMR spectra of **1** and **2** in $CDCl_3$ show two sets of resonances due to the presence of the two tautomers **a** and **b** in a ratio of 1:5 and 1:10, respectively. In both cases, the major isomer proved to be the pyridine–enamine **b**, as corroborated by ^{1}H NMR spectroscopy (for the major isomer a triplet and a broad signal, representing one proton each, were observed in the 4–6 ppm region), ^{13}C NMR spectroscopy (the chemical shift of C_7 of the major isomer is about 95 ppm, which is characteristic of sp^2 carbon atoms), and IR (a N–H stretching frequency was observed at about 3390 cm^{-1}). The ^{1}H and ^{13}C NMR spectra of 1 and 2 show sharp signals at 20°C, indicating that tautomerization does not occur on the NMR time scales. However, the disappearance of the H_7 resonances from **1b** and **2b** in the ^{1}H NMR spectrum upon addition of a drop of D_2O to a solution of **1** and **2** in $CDCl_3$ indicates that tautomerization does proceed on the laboratory time scale (within 10 min).

Addition of **1** and **2** to a solution of Pd(Me)Cl(COD) resulted in substitution of COD by **1** and **2** and led to the rapid and exclusive formation of methylpalladium complexes Pd(Me)Cl(DPIA) (**3**) and Pd(Me)Cl(DQIA) (**4**), respectively (Eq. (2)). No formation has been observed of any palladium compound in which the pyridine–enamine tautomers of **1** and **2** (**1b** and **2b**, respectively) are coordinated in a unidentate fashion, as reported earlier for 1-(isopropylamino)-6-(isopropylimino)-cyclohex-1-ene [48].



n = 2 (**3**), 3 (**4**) (2)

Complexes **3** and **4** reacted rapidly with CO to give the corresponding acylpalladium complexes Pd(C(O)Me)Cl(DPIA) (**6**) and Pd(C(O)Me)Cl(DQIA) (**7**), respectively, in high yield (Eq. (3)). Complexes **3**, **4**, **6**, and **7** are very stable in the solid state and can be stored at 20°C for several months without decomposition. Complexes **3** and **4** are also stable in solution and did not show any decomposition after several days in chloroform at 20°C. In contrast, the acylpalladium complexes **6** and **7** slowly decomposed in solution (dichloromethane and chloroform) at 20°C, which resulted in palladium black.



n = 2 (**3**), 3 (**4**) *n* = 2 (**6**), 3 (**7**) (3)

All complexes show correct analytical data and were further characterized by ^{1}H and ^{13}C NMR spectroscopy (Tables 2 and 3, respectively), and in the case of the acylpalladium complexes **6** and **7** also by IR spectroscopy

Table 2
^{1}H NMR data for compounds **1**–**10**[a]

	H_1	H_2	H_3	H_7	H_8	H_9	H_{10}	H_{11}	Other signals
1a	8.58 dd (4.7, 0.9)	7.19 dd (7.7, 4.7)	[b]	2.73 m	–	2.99 m	3.70 sep (6.4)	1.25 d (6.4)	–
1b	8.36 dd (5.0, 1.0)	7.03 dd (7.4, 5.0)	7.58 dd (7.4, 1.0)	5.20 t (2.6)	–	3.25 d (2.6)	3.55 sep (6.4)	1.23 d (6.4)	4.31 br, NH
2a	8.68 d (3.5)	7.20 dd (7.6, 3.5)	7.48 d (7.6)	2.75 t (6.6)	1.99 m	2.86 t (6.3)	3.96 sep (6.2)	1.27 d (6.2)	–
2b	8.32 d (4.9)	7.03 dd (7.2, 4.9)	7.38 d (7.2)	4.89 t (4.4)	2.37 m	2.79 t (7.8)	3.51 sep (6.3)	1.22 d (6.3)	4.82 br, NH
cis-**3**	8.70 d (5.4)	[c]	7.83 d (7.7)	[c]	–	2.93 m	4.10 sep (6.4)	1.41 d (6.4)	1.05 s, Pd–Me
trans-**3**	8.33 d (5.4)	7.50 dd (7.7, 5.4)	7.90 d (7.7)	3.39 m	–	2.83 m	3.90 sep (6.4)	1.52 d (6.4)	1.22 s, Pd–Me
cis-**4**	9.10 d (5.3)	[c]	7.69 d (7.8)	[c]	[c]	[c]	4.43 sep (6.5)	1.44 d (6.5)	0.99 s, Pd–Me
trans-**4**	8.47 d (5.3)	7.45 dd (7.8, 5.3)	7.77 d (7.8)	2.80 t (6.3)	2.04 m	2.96 t (5.9)	4.27 sep (6.5)	1.57 d (6.5)	1.07 s, Pd–Me
cis-**6**	8.45 d (5.3)	[c]	7.88 d (7.6)	[c]	–	2.95 m	3.73 sep (6.3)	1.24 d (6.3)	[c]
trans-**6**	8.06 d (5.3)	7.51 dd (7.6, 5.3)	7.94 d (7.6)	3.34 m	–	2.83 m	3.80 sep (6.3)	1.41 d (6.3)	2.63 s, C(O)Me
cis-**7**	8.94 d (5.2)	[c]	7.68 d (7.7)	[c]	[c]	[c]	4.27 sep (6.4)	1.30 d (6.4)	[c]
trans-**7**	8.19 d (5.2)	7.43 dd (7.7, 5.2)	7.77 d (7.7)	2.78 t (6.4)	2.00 m	2.95 t (6.0)	4.13 sep (6.4)	1.50 d (6.4)	2.63 s, C(O)Me
8a[d]	8.42 d (5.0)	7.74 m	8.19 m	–	–	–	4.21 sep (6.4)	1.41 d (6.4) 1.38 d (6.4)	9.46 s, H_6 8.87 d (7.6), H_4 2.57 s, C(O)Me
8b[e]	8.45 d (5.1)	7.81 m	8.17 m	–	–	–	4.10 sep (6.4)	1.39 d (6.4) 1.37 d (6.4)	8.71 s, H_6 8.17 m, H_4 2.55 s, C(O)Me
9a[f]	8.30 d (5.3)	7.90 dd (7.8, 5.3)	8.27 d (7.8)	3.56 m	–	2.96 m	3.94 sep (6.3)	1.30 d (6.3) 1.27 d (6.3)	2.58 s, C(O)Me
9b[g]	8.27 d (5.3)	7.78 dd (7.9, 5.3)	8.09 d (7.9)	3.46 m	–	2.91 m	3.89 sep (6.3)	1.30 d (6.5) 1.27 d (6.5)	2.53 s, C(O)Me
10a[h]	8.32 d (5.0)	7.84 dd (7.7, 5.0)	8.11 (7.7)	2.91 m	2.07 m	3.07 t (6.0)	4.29 sep (6.4)	1.32 d (6.4) 1.29 d (6.4)	2.58 s, C(O)Me
10b[i]	8.37 d (5.3)	7.76 dd (7.8, 5.3)	7.99 (7.8)	2.92 m	2.10 m	3.04 t (6.0)	4.32 sep (6.4)	1.37 d (6.4) 1.34 d (6.4)	2.56 s, C(O)Me

[a] Recorded at 300.13 MHz in $CDCl_3$ at 20°C, unless noted otherwise, J (Hz) in parentheses (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, sep = septet, m = multiplet, br = broad).
[b] Signal of H_3 is overlapping with signal of H_4 from **1b**.
[c] Signal is overlapping with signals from the *trans* isomer.
[d] Signals of C_7H_8 moiety: 6.28 dd (5.3, 3.0 Hz), 6.20 dd (5.3, 2.9 Hz), =CH; 3.18 br, 2.97 br, CHC=; 2.32 dd (6.3, 2.3 Hz), PdCH; 1.82 d (9.1 Hz), 1.53 d (9.1 Hz), CH_2; signal of C*H*C(O)Me is overlapping with signal of C(O)Me.
[e] Signals of C_7H_8 moiety: 6.39 dd (5.1, 3.0 Hz), 6.24 dd (5.1, 2.7 Hz), =CH; 3.25 br, 2.98 br, CHC=; 2.59 d (6.3 Hz), C*H*C(O)Me; 2.34 dd (6.3, 2.1 Hz), PdCH; 1.75 d (9.0 Hz), 1.48 d (9.0 Hz), CH_2.
[f] Signals of C_7H_8 moiety: 6.30 dd (5.3, 3.0 Hz), 6.21 dd (5.3, 3.0 Hz), =CH; 3.16 br, 2.88 br, CHC=; 2.60 d (5.9 Hz), PdCH; 2.50 dd (5.9, 1.8 Hz), C*H*C(O)Me; 1.80 d (9.1 Hz), 1.49 d (9.1 Hz), CH_2.
[g] Signals of C_7H_8 moiety: 6.40 dd (4.9, 2.7 Hz), 6.26 dd (4.9, 2.7 Hz), =CH; 3.26 br, 2.98 br, CHC=; 2.58 m, PdCH; 2.49 d (5.8 Hz), C*H*C(O)Me; 1.79 d (9.3 Hz), 1.46 d (9.3 Hz), CH_2.
[h] Signals of C_7H_8 moiety: 6.26 m, 6.17 m, =CH; 3.18 br, 2.87 br, CHC=; 2.62 d (5.8 Hz), C*H*C(O)Me; 2.23 d (5.8 Hz), PdCH; 1.70 d (8.0 Hz), 1.53 d (8.0 Hz), CH_2.
[i] Signals of C_7H_8 moiety: 6.36 dd (5.3, 2.9 Hz), 6.23 dd (5.3, 2.9 Hz), =CH; 3.23 br, 2.96 br, CHC=; 2.60 d (6.0 Hz), C*H*C(O)Me; 2.28 dd (6.0, 2.3 Hz), PdCH; 1.75 d (9.3 Hz), 1.48 d (9.3 Hz), CH_2.

(Section 2). Crystals of **6** and **7** suitable for X-ray structural determinations were obtained from dichloromethane/hexane (vide infra). The methylpalladium compounds **3** and **4** both show characteristic Pd–Me resonances at about 1 ppm in the ^{1}H NMR spectrum and about 0 ppm in the ^{13}C NMR spectrum. Formation of the acylpalladium complexes **6** and **7** is clear from the shift of the methyl resonance from about 1 ppm to 2.63 ppm (^{1}H NMR) and about 0 ppm to about 35 ppm (^{13}C NMR), the CO resonance at about 230 ppm (^{13}C NMR) and the observation of a CO stretching frequency at about 1700 cm^{-1} in the IR spectrum. Since the α-diimine ligands in the

Table 3
^{13}C NMR data for compounds **1**–**10**[a]

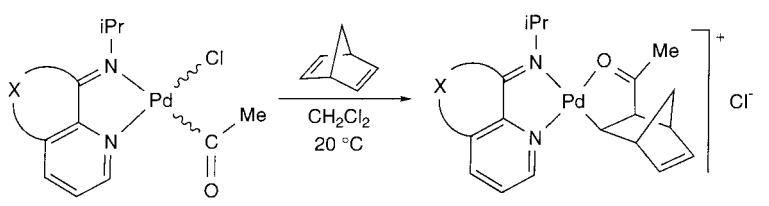
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	other signals
1b	146.3	119.5	130.2	136.8	158.8	145.2	98.0	–	32.7	45.2	22.5	–
2b	145.5	121.6	134.3	132.0	150.0	138.9	95.3	21.4	27.7	43.3	22.1	–
trans-**3**[b,c]	146.5	128.3	136.5	141.4	n.o.	n.o.	29.4	–	25.8	57.6	22.4	−0.6, Pd–Me
trans-**4**[c]	147.2	127.5	139.6	140.8	154.7	166.1	29.4	22.1	29.4	54.8	22.3	4.6, Pd–Me
trans-**6**[c]	148.0	128.3	136.1	143.3	172.8	158.9	27.9	–	25.3	56.5	22.1	225.4, C(O)Me; 35.3, C(O)Me
trans-**7**[c]	149.5	128.2	140.1	140.6	152.2	165.7	29.2	22.4	29.2	54.3	22.7	231.8, C(O)Me; 36.1, C(O)Me
8a[d]	149.4	128.2	140.7	130.2	156.3	162.4	–	–	–	62.4	22.1	238.1, C(O)Me; 27.8, C(O)Me
8b[e]	150.1	128.9	140.7	129.1	155.8	161.6	–	–	–	61.5	21.9	238.4, C(O)Me; 27.4, C(O)Me
9a[f]	148.3	130.4	139.1	145.5	161.9	176.6	30.0	–	26.1	56.2	28.7	238.1, C(O)Me; 22.7, C(O)Me
9b[g]	147.9	129.5	138.0	144.5	161.2	175.8	28.9	–	25.0	55.8	27.7	237.6, C(O)Me; 21.8, C(O)Me
10a[h]	148.4	128.8	141.2	141.8	153.4	166.9	28.3	21.1	28.3	52.8	21.3, 21	238.2, C(O)Me; 27.9, C(O)Me
10b[i]	148.5	128.5	141.2	141.4	153.5	166.8	28.4	21.2	28.4	52.8	21.2, 21	238.3, C(O)Me; 27.7, C(O)Me

[a] Recorded at 75.48 MHz in $CDCl_3$ at 0°C, unless noted otherwise. See Table 2 for the adopted numbering scheme (n.o. = not observed).
[b] Recorded in CD_2Cl_2.
[c] Signals of the *cis* isomer were not observed.
[d] Signals of C_7H_8 moiety: 136.0, 133.6, =CH; 61.4, *C*HC(O)Me; 48.4, 47.7, *C*HC=; 46.9, PdCH; 45.6, CH_2.
[e] Signals of C_7H_8 moiety: 135.1, 132.5, =CH; 62.3, *C*HC(O)Me; 48.5, 47.8, 46.6, PdCH and *C*HC=; 45.3, CH_2.
[f] Signals of C_7H_8 moiety: 136.3, 134.5, =CH; 63.1, *C*HC(O)Me; 49.0, PdCH; 48.6, 46.1, *C*HC=; 46.4, CH_2.
[g] Signals of C_7H_8 moiety: 134.2, 132.2, =CH; 62.1, *C*HC(O)Me; 48.3, PdCH; 47.9, 44.6, *C*HC=; 45.6, CH_2.
[h] Signals of C_7H_8 moiety: 136.1, 133.5, =CH; 62.2, *C*HC(O)Me; 48.6, PdCH; 48.0, 47.8, *C*HC=; 45.5, CH_2.
[i] Signals of C_7H_8 moiety: 136.0, 133.4, =CH; 62.2, *C*HC(O)Me; 48.6, PdCH; 47.9, *C*HC=; 45.4, CH_2.

complexes **3**, **4**, **6** and **7** contain two different donor nitrogen atoms, two isomers are possible, which are *cis* and *trans* relative to the position of the methyl or acyl ligand and the imino nitrogen atom of the α-diimine ligand on the palladium centre. The most sensitive resonance for the assignment is that of proton H_1 adjacent to the nitrogen of the pyridine, which exhibits a large downfield shift for the *cis* isomer due to the strongly deshielding *cis* positioned chloride ligand [28,49]. For example, the H_1 resonance for *cis*-**4** appears at 9.10 ppm, whereas the one for *trans*-**4** appears at 8.47 ppm. Complexes **3**, **4**, **6** and **7** exist in a *cis*:*trans* ratio of 1:49, 1:10, 1:25, and 1:5, respectively, as derived from the ^{1}H NMR integrals. The ^{1}H and ^{13}C NMR spectra of these complexes show sharp signals, indicating that *cis*–*trans* isomerization does not occur on the NMR time scale.

In order to investigate the relative complexation strength of the α-diimine ligands **1a** and **2a** in the acylpalladium complexes **6** and **7**, respectively, competition experiments were carried out. Addition of an equimolar amount of free **1** to a solution of complex **7** in $CDCl_3$ at 20°C resulted in a mixture of complexes **6** and **7** and the free ligands **1** and **2** in a ratio **6**:**7** (= **2**:**1**) = 1:9. A mixture with the same **6**:**7** ratio was obtained upon addition of an equimolar amount of free **2** to a solution of complex **6**. Similar competition experiments with free **1** and the acylpalladium complex Pd(C(O)Me)Cl(*i*Pr–PyCa) (**5**) (*i*Pr–PyCa = 2-(*N*-2-propanecarbaldimino)pyridine) or free *i*Pr–PyCa and complex **6** resulted in a mixture of complexes **5** and **6** in a ratio **5**:**6** = 2:1. Addition of free **2** to complex **5** or addition of free *i*Pr–PyCa to complex **7** led to a mixture of complexes **5** and **7** in a ratio **5**:**7** = 1:5.

Reaction of the acylpalladium complexes **5**–**7** with norbornadiene led to insertion of the alkene into the acyl–palladium bond and formation of the novel alkylpalladium complexes [Pd(C_7H_8C(O)Me)(*i*Pr–PyCa)]Cl (**8a**), [Pd(C_7H_8C(O)Me)(DPIA)]Cl (**9a**) and [Pd(C_7H_8C(O)Me)(DQIA)]Cl (**10a**), respectively (Eq. (4)). The analogous complexes [Pd(C_7H_8C(O)Me)(*i*Pr–PyCa)] SO_3CF_3 (**8b**), [Pd(C_7H_8C(O)Me)(DPIA)]SO_3CF_3 (**9b**) and [Pd(C_7H_8C(O)Me)(DQIA)]SO_3CF_3 (**10b**) have been obtained by the reaction of **8a**–**10a** with one equivalent of $AgSO_3CF_3$.



X = H, H (**5**), $(CH_2)_2$ (**6**), $(CH_2)_3$ (**7**) X = H, H (**8a**), $(CH_2)_2$ (**9a**), $(CH_2)_3$ (**10a**)

(4)

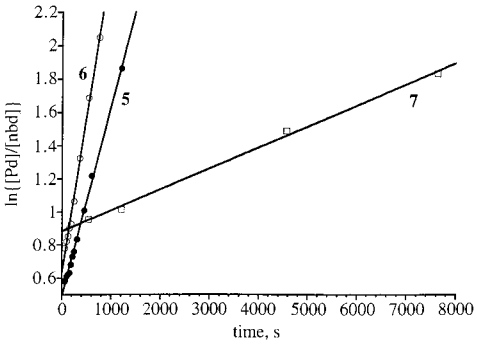


Fig. 2. Second-order plot of the reactions of complexes Pd(C(O)Me)Cl(N–N) (N–N = *i*Pr–PyCa (**5**), DPIA (**6**), DQIA (**7**)) with norbornadiene. Conditions: chloroform solvent; 20°C.

Complexes **8**–**10** were isolated and characterized by ^{1}H NMR, ^{13}C NMR (Tables 2 and 3, respectively), IR, and mass spectroscopy (Section 2). Unfortunately, no correct analytical data could be obtained for complexes **8a**–**10a**, as these complexes have only limited stability in the solid state as well as in solution. Complexes **8a**–**10a** decompose in chloroform at 20°C within 1 h, resulting in the formation of palladium black and the β-hydrogen elimination product 2-acetyl[2.2.1]bicyclohepta-2,5-diene [35]. In contrast, the analogous trifluoromethanesulfonate complexes **8b**–**10b** were stable in the solid state as well as in solution for several days. No correct analytical data could be obtained for **8b**–**10b**, most probably due to the presence of small amounts of $AgSO_3CF_3$. Formation of **8a**–**10a** is clear from the well defined pattern of the inserted norbornadiene moiety in the ^{1}H and ^{13}C NMR spectra. The expected syn–exo addition of the alkene can be concluded from the coupling constants $J_{CHC(O)Me,\ PdCH}$ which are approximately 6 Hz [50]. The low CO stretching frequency at about 1605 cm^{-1} and the high resonance of about 238 ppm for the acyl group indicate coordination of the acyl group to the palladium centre forming a five-membered palladacycle [14,22,23,31,38,50,51]. The high equivalent conductances for **8a**–**10a**, which are in the range 18–21 Ω^{-1} cm^2 mol^{-1} in dichloromethane at 20°C, compared with equivalent conductances of about 0.1 Ω^{-1} cm^2 mol^{-1} for the neutral precursors **5**–**7** are also in agreement with an ionic structure. In spite of the acyl coordination, the chemical shift difference between the resonances of the olefinic protons in the acetylnorbornene in the ^{1}H NMR spectra amounts to only 0.1 ppm in the present compounds. It has been suggested that a relatively large difference of about 0.5 ppm is also characteristic of a C,O-coordinated acetylnorbornene moiety [22,35,38].

In contrast to **3**, **4**, **6**, and **7**, complexes **8**–**10** exist as one isomer, as can be concluded from one set of resonances in the ^{1}H and ^{13}C NMR spectra. NOE experiments performed to elucidate the configuration of **8**–**10** revealed a close proximity of the protons H_1 and Pd–C*H*, indicating that the norbornene moiety is *cis*-positioned with respect to the pyridine fragment of the bidentate nitrogen ligand (see Eq. (4)).

3.2. Kinetics

A comparison of the reactivity of the acylpalladium compounds **5**–**7** toward norbornadiene was obtained by monitoring the disappearance of the norbornadiene and the C(O)Me resonances in the ^{1}H NMR spectra, which did not show the presence of any intermediate in the temperature range of -80 to $+20$°C. Plotting In{[Pd]/[nbd]} vs. time resulted in straight lines (Fig. 2), which indicates that the reactions follow second-order kinetics. The second-order rate constants *k*, which were calculated from the slopes of these plots [3], are 0.14(1), 0.21(1), and 0.011(1) s^{-1} M^{-1} for the reaction of norbornadiene with complex **5**, **6**, and **7**, respectively. In order to study the kinetics more extensively, the reactions were followed spectrophotometrically under pseudo-first-order conditions, i.e., by employing a large excess of norbornadiene over acylpalladium complex. Unfortunately, using dichloromethane or acetonitrile as solvent, no isosbestic points were obtained, which indicates that the reactions are unselective under these conditions. For this reason, a detailed kinetic study was not carried out.

[3] The second-order rate constants *k* were calculated by using the equation $k = \mathrm{tg}\,\alpha / \{[Pd]_0 - [nbd]_0\}$, with $\mathrm{tg}\,\alpha$ = slope of second-order plot; $[Pd]_0$ = concentration of acylpalladium complex at $t = 0$ s; $[nbd]_0$ = concentration of norbornadiene at $t = 0$ s.

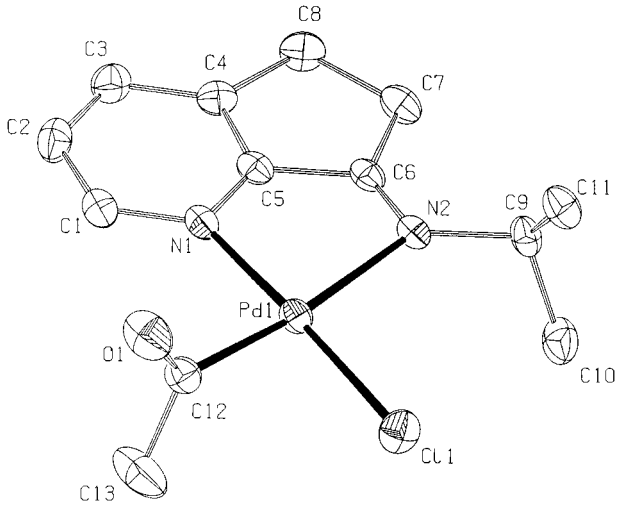


Fig. 3. ORTEP drawing (50% probability level) and adopted numbering scheme of Pd(C(O)Cl)(DPIA) (**6**). Hydrogen atoms have been omitted for clarity.

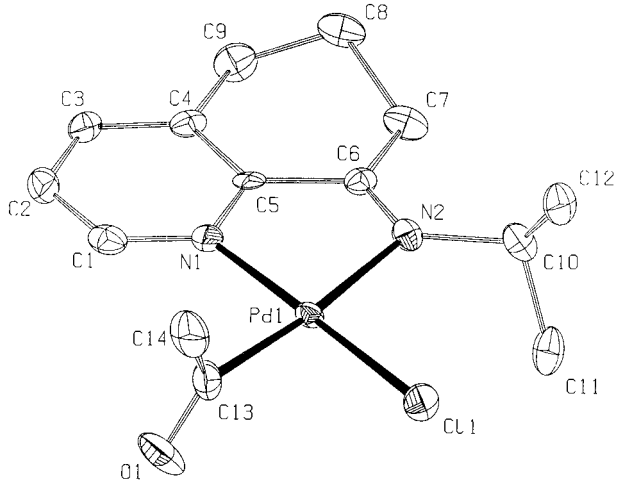


Fig. 4. ORTEP drawing (50% probability level) and adopted numbering scheme of Pd(C(O)Cl)(DQIA) (**7**). Hydrogen atoms have been omitted for clarity.

*3.3. Single crystal X-ray structures of Pd(C(O)Me)Cl(DPIA) (**6**) and Pd(C(O)Me)Cl(DQIA) (**7**)*

The molecular structures of Pd(C(O)Me)Cl(DPIA) (**6**) and Pd(C(O)Me)Cl(DQIA) (**7**) are presented in Figs. 3 and 4, respectively. Bond distances and selected bond angles are reported in Tables 4 and 5, respectively. The complexes

Table 4
Selected bond distances (Å) for Pd(C(O)Me)Cl(DPIA) (**6**) and Pd(C(O)Me)Cl(DQIA) (**7**) (with estimated standard deviations in parentheses)

6		**7**	
Pd(1)–Cl(1)	2.3275(10)	Pd(1)–Cl(1)	2.3305(19)
Pd(1)–N(1)	2.081(2)	Pd(1)–N(1)	2.066(6)
Pd(1)–N(2)	2.275(2)	Pd(1)–N(2)	2.202(6)
Pd(1)–C(12)	1.945(3)	Pd(1)–C(13)	1.946(8)
O(1)–C(12)	1.189(3)	O(1)–C(13)	1.214(11)
N(1)–C(1)	1.351(3)	N(1)–C(1)	1.330(10)
N(1)–C(5)	1.336(3)	N(1)–C(5)	1.375(9)
N(2)–C(6)	1.267(3)	N(2)–C(6)	1.268(9)
N(2)–C(9)	1.480(3)	N(2)–C(10)	1.489(11)
C(5)–C(6)	1.466(3)	C(5)–C(6)	1.484(10)
C(12)–C(13)	1.499(5)	C(13)–C(14)	1.481(12)

Table 5
Selected bond angles (°) for Pd(C(O)Me)Cl(DPIA) (**6**) and Pd(C(O)Me)Cl(DQIA) (**7**) (with estimated standard deviations in parentheses)

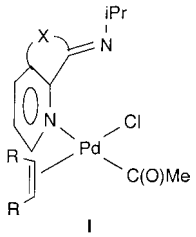
6		**7**	
Cl(1)–Pd(1)–N(2)	101.46(6)	Cl(1)–Pd(1)–N(2)	104.36(16)
Cl(1)–Pd(1)–C(12)	86.05(8)	Cl(1)–Pd(1)–C(13)	83.8(2)
N(1)–Pd(1)–N(2)	79.14(9)	N(1)–Pd(1)–N(2)	77.2(2)
N(1)–Pd(1)–C(12)	93.45(10)	N(1)–Pd(1)–C(13)	94.6(3)
Pd(1)–N(1)–C(1)	133.10(19)	Pd(1)–N(1)–C(1)	127.0(5)
Pd(1)–N(1)–C(5)	111.52(17)	Pd(1)–N(1)–C(5)	115.1(5)
Pd(1)–N(2)–C(6)	108.59(17)	Pd(1)–N(2)–C(6)	114.7(5)
Pd(1)–N(2)–C(9)	131.59(17)	Pd(1)–N(2)–C(10)	124.4(4)
Pd(1)–C(12)–O(1)	121.5(2)	Pd(1)–C(13)–O(1)	120.7(6)
Pd(1)–C(12)–C(13)	115.8(2)	Pd(1)–C(13)–C(14)	115.6(6)
O(1)–C(12)–C(13)	122.6(3)	O(1)–C(13)–C(14)	123.7(8)

6 and **7** both show the expected square planar arrangement of the α-diimine, acyl, and chloride ligand around the palladium centre. The acyl ligands are positioned *cis* with regard to N(1) and *trans* to N(2), thus, the *trans* isomers are formed. It is interesting to note that only the *trans* isomers have been found in the crystals, while in solution both isomers are present (vide supra). The bite angles of the α-diimine ligands in complexes **6** and **7** are comparable (79.14(8)° and 77.2(2)°, respectively) and are almost similar to that of *i*Pr–PyCa (which is the flexible analogue of DPIA and DQIA) in Pd(C(O)Me)(*i*Pr–PyCa) (**5**) (78.1(1)°) [28]. The palladium–nitrogen distances are in the range of those observed for other palladium complexes bearing α-diimine ligands (2.01–2.28 Å) [23,24,27,28,32,48,52–56] and are somewhat longer for **6** as compared to those of **7**. The longer Pd–N(2) bonds as compared to the Pd–N(1) bonds are in agreement with the larger *trans* influence of the acyl group. The backbones of the α-diimine ligands are very close to planarity as appears from the torsion angle N(1)–C(5)–C(6)–N(2) of −1.4(4)° for **6** and −0.4(10)° for **7** and the torsion angle C(4)–C(5)–C(6)–C(7) of −2.8(3)° for **6** and −4.8(11)° for **7**. The almost perpendicular position of the acyl group with respect to the palladium coordination plane (83.1(3)° for **6** and 78.3(9)° for **7**) is a common feature in square planar acylpalladium compounds [27,28,30].

4. Discussion

The new bidentate nitrogen ligands (5,6-dihydro-[1]pyrindin-7-ylidene)-isopropylamine (DPIA, **1a**) and 6,7-dihydro-5*H*-quinolin-8-ylidene)-isopropylamine (DQIA, **2a**) can easily be synthesized from the corresponding pyridine–ketones in a condensation reaction with isopropylamine. In the pure form as well as in solution the α-diimines **1a** and **2a** are in equilibrium with the more favourable tautomeric pyridine–enamine forms **1b** and **2b**, respectively. A similar preference for an imine–enamine form has been observed for 1,2-bis(isopropylimino)cyclohexane and has been attributed to a combination of a greater stability of an exocyclic double bond and the formation of an intramolecular hydrogen bridge between the amine and the imine nitrogen atoms [48]. The observed high N–H stretching frequency at about 3390 cm^{-1} in the IR spectra of **1** and **2**, however, points to the absence of an internally bridging N–H fragment and thus, the enhanced stability of the pyridine–enamines **1b** and **2b** as compared to the pyridine–imines **1a** and **2a** is probably caused by a greater stability of an endocyclic carbon–carbon double bond as compared to an exocyclic carbon–nitrogen double bond [48].

The compounds **1a** and **2a** reacted with Pd(Me)Cl(COD) to form in high yields methylpalladium complexes from which the corresponding acylpalladium complexes can be prepared quantitatively by stirring a solution under a CO atmosphere for several minutes. Interestingly, the *trans* configuration is apparently the most favourable configuration for the methyl- and acylpalladium complexes **3**, **4**, **6**, and **7**, while the opposite has been observed for the complexes Pd(R)Cl(*i*Pr–PyCa) (R = Me, C(O)Me) [28] and Pt(Me)Cl(*i*Pr–PyCa) [57], in which the pyridine and imine fragment of the α-diimine ligand are, in contrast to **1a** and **2a**, non-bridged. These results can be explained by comparing the molecular structures of **6** and **7** with that of Pd(C(O)Me)Cl(*i*Pr–PyCa) (**5**) [28]. An important difference between the molecular structure of **6**/**7** and **5** involves the methyl groups of the isopropyl moiety of the α-diimine ligand. In the case of **5**, the methyl groups were found to be pointing away from the *cis* positioned ligand. However, the sterically demanding bridge between the pyridine and imine fragment of the α-diimine ligand in **6** and **7** forces the isopropyl substituent in a conformation in which the methyl groups are in the neighbourhood of the *cis* positioned ligand. A configuration in which the acyl ligand, which can be considered to be sterically more demanding than the chloride



I

Fig. 5. Structure of species I, a possible intermediate in the reaction of acylpalladium complexes **5**–**7** with norbornadiene.

ligand [4], is positioned *trans* to the sterically demanding isopropyl–imine moiety will thus be most favourable. Thus, the *trans* isomer will be the most favourable configuration, as was inferred from the ^{1}H NMR data of **3**, **4**, **6**, and **7** (vide supra).

The *cis*:*trans* ratio increases in the order **3** < **6** < **4** < **7**. The fact that the acylpalladium complexes have a higher *cis*:*trans* ratio as compared to the corresponding methylpalladium complexes can be attributed to the almost perpendicular position of the acyl group with respect to the palladium coordination plane. In this conformation, the acyl group is sterically less demanding than the methyl group and is sterically less constrained by the bulk of the two methyl groups of the isopropyl group.

From the results of the competition experiments with the α-diimine ligands **1a**, **2a**, and *i*Pr–PyCa, which is the flexible analogue of **1a** and **2a**, interesting information about the relative complexation strength was obtained. Firstly, these experiments indicate that ligand **2a** in complex **7** is coordinated much more strongly to the palladium than the α-diimine ligand **1a** in complex **6**. The weaker coordination of **1a** is also reflected by the longer nitrogen–palladium distances and the larger deviation of the angles Pd(1)–N(1)–C(1) and Pd(1)–N(2)–imino–carbon from the ideal 120° for **6** as compared to those in **7**. Secondly, it can be deduced that the complexation strength of *i*Pr–PyCa lies in between those of ligands **1a** and **2a**; the complexation strength of the α-diimine ligands increases in the order **1a** < *i*Pr–PyCa ≪ **2a**. Interestingly, this order in complexation strength of the α-diimine ligands is exactly opposite to the reactivity of the corresponding acylpalladium complexes toward norbornadiene, which decreases for Pd(C(O)Me)Cl(N–N) in the order N–N = **1a** > *i*Pr–PyCa ≫ **2a**. One may surmise that this indicates that insertion of norbornadiene may occur via intermediates from which the α-diimine ligand is completely dissociated. However, a mechanism via complete α-diimine ligand dissociation cannot account for the following facts:

1. During the reaction no trace of free α-diimine ligand is observed in the ^{1}H NMR spectra;
2. No palladium black formation is observed during the reaction, whereas intermediates of the type Pd(C(O)Me)Cl(solvent)$_2$ can be expected to be highly unstable and to decompose very easily;
3. The reactions follow second-order kinetics, whereas a mechanism via dissociation of α-diimine ligand would result in non-second-order kinetics.

A more conceivable intermediate I, which does account for these observations, contains a unidentate coordinated α-diimine ligand, in which the nitrogen atom of the most sterically demanding part of the ligand, i.e., the imino–nitrogen atom (vide supra), is dissociated (Fig. 5). In the case of complexes containing the flexible bidentate nitrogen ligand *i*Pr–PyCa, i.e., complex **5**, the dissociated nitrogen atom may be turned away from the palladium centre. However, for complexes containing a rigid bidentate nitrogen ligand, i.e., complexes **6** and **7**, the dissociated nitrogen atom is forced to remain in the vicinity of the palladium centre. Coordination in a unidentate fashion has been observed earlier for palladium complexes containing both flexible [30,39] and rigid [38,58–60] bidentate nitrogen ligands. A mechanism via intermediates in which the α-diimine ligand is coordinated in a unidentate fashion also accounts for the fact that the insertion rate decreases in the order **6** > **5** ≫ **7**, i.e., the insertion rate decreases with the increasing complexation strength of the α-diimine ligand. It is also in line with earlier studies of CO [28], alkene [31], and allene [39] insertion reactions in acylpalladium complexes containing both flexible and rigid bidentate nitrogen ligands, which were also proposed to proceed via intermediates, containing a unidentate coordinated bidentate nitrogen ligand. Unfortunately, unselective reactions of complexes **5**–**7** with norbornadiene under pseudo-first-order conditions prevented a detailed kinetic study of these reactions. For this reason, the exact mechanism of formation of species I from the starting complexes **5**–**7** and formation of the products **8a**–**10a** from species I remain unclear.

[4] The fact that for methyl- and acylpalladium complexes, which contain the 6-substituted ligand *i*Pr-6-Me-PyCa, only the *cis* isomers were observed, whereas complexes containing *t*Bu–PyCa occur exclusively in the *trans* form [28], indicates that in this type of complexes a chloride ligand is sterically less demanding than an acyl ligand.

5. Conclusion

The novel rigid α-diimines DPIA and DQIA coordinate to palladium in the expected bidentate fashion. From the crystal data of **6** and **7**, it can be concluded that DPIA and DQIA coordinate with comparable bite angles. Methyl- and acylpalladium complexes containing DPIA and DQIA were reactive toward CO and norbornadiene, respectively. The increase of the reactivity of acylpalladium complexes toward norbornadiene upon decrease of the complexation strength of the α-diimine ligand indicates that insertion predominantly occurs via unidentate coordination of the α-diimine ligand.

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