ELSEVIER

Journal of Organometallic Chemistry 564 (1998) 29–35

Journal of Organometallic Chemistry

Trans-4,5-bis(2-pyridyl)norbornane: a bidentate nitrogen ligand with a potentially large bite angle[1]

Johannes G.P. Delis [a,*], Marco Rep [a], Mirko Kranenburg [a], Kees Vrieze [a], Piet W.N.M. van Leeuwen [a], Nora Veldman [b], Anthony L. Spek [b]

[a] *Institute of Molecular Chemistry, J.H. van't Hoff Research Instituut, Universiteit van Amsterdam, Nieuwe Achtergracht 166, NL-1018 WV Amsterdam, The Netherlands*

[b] *Bijvoet Center for Biomolecular Research, Vakgroep Kristal- en Structuurchemie, Universiteit Utrecht, Padualaan 8, NL-3584 CH Utrecht, The Netherlands*

Received 1 January 1998; received in revised form 28 April 1998

Abstract

The coordination chemistry of the new chiral bidentate nitrogen ligand *trans*-4,5-bis(2-pyridyl)norbornane (Renorpy) towards palladium has been studied. The novel complexes (Renorpy)Pd(η^2-alkene) (η^2-alkene = maleic anhydride, tetracyanoethylene), (Renorpy)Pd(Me)Cl and (Renorpy)Pd(C(O)Me)Cl have been synthesized. Molecular modeling calculations gave a 'natural' bite angle for the Renorpy ligand of 115.5°. Single crystal X-ray analyses of the complex (Renorpy)Pd(Me)Cl showed that the bite angle of the ligand in this complex is significantly smaller (93.7(2)°) than the 'natural' one, which is caused by the electronic preference of palladium. To accommodate this smaller bite angle the palladium atom moves out of the pyridyl planes.

Keywords: *Trans*-4,5-bis(2-pyridyl)norbornane; Bidentate; Bite angle

1. Introduction

Carbonylation of transition-metal bonds is an important step in many transition metal-catalyzed processes [1–3] like hydroformylation [4] and copolymerization of CO and alkenes [5,6]. The mechanism of the carbonylation reaction has been studied both experimentally [7–13] and theoretically [14–17]. From these studies it may be concluded that the mechanism involves coordination of CO to the metal center, followed by isomerization to bring CO and the hydrocarbyl group in mutual *cis* positions, and migration of the hydrocarbyl group to the coordinated CO molecule [9–13].

From experimental studies carried out in our laboratory it appeared that the choice of the ligands is a very important factor in determining the rate of the carbonylation reaction [18]. The rate of CO insertion into the Pd–C bond of the complexes (P⌒P)Pd(Me)Cl is strongly influenced by the number of carbon atoms in the bridge of the diphosphine ligand $Ph_2P(CH_2)_nPPh_2$. The half lives of the CO-insertion decrease in the range $n = 2 > 3 > 4$, which can be explained by an increase of the flexibility and an increase of the bite angle P–Pd–P of the ligands. These findings were supported by ab initio calculations on the carbonylation of the Pt–CH_3 bond in the model complex $Pt(CH_3)F(CO)(PH_3)$ [19], which showed that migration of the methyl group in the transition state was energetically favored by simultaneous enlargement of the F–Pt–P angle θ (see Scheme 1).

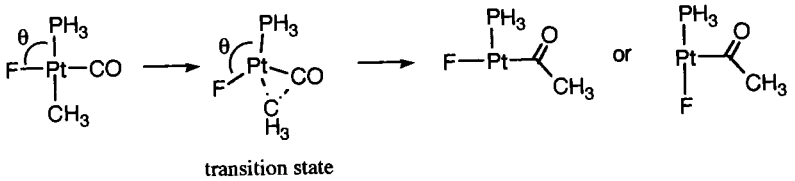
Bidentate ligands with the potential to accommodate large bite angles may therefore lead to higher rates of CO-insertion.

The bidentate nitrogen ligands we have used so far in carbonylation reactions comprise both flexible and rigid ligands, but they all have small bite angles in the range 75–85° [20–23]. We were interested what influence bidentate nitrogen ligands with potentially large bite

* Corresponding author.

[1] NIOK publication no. 98-03-06.

0022-328X/98/$19.00
PII S0022-328X(98)00632-9



Scheme 1. Methyl migration with enlargement of the F-Pt-P angle θ.

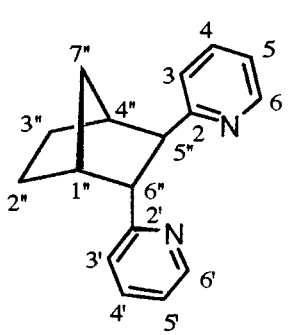
angles would have on the rate of CO insertion into Pd–C bonds. Recently, we synthesized the chiral ligand *trans*-4,5-bis(2-pyridyl)norbornene (Norpy), which has the potential to coordinate with a large bite angle as shown by molecular mechanics (calc. $\beta_n = 117.5°$) and the angle found in the Pd(0) complex (Norpy) Pd(TCNE) (N–Pd–N = 99.49(15)°) [24]. Synthesis of Pd(II) complexes containing this ligand, however, appeared to be difficult owing to the presence of the olefinic donor group, which prompted us to prepare the ligand *trans*-4,5-bis(2-pyridyl)norbornane (Renorpy) and to study the coordination chemistry of this ligand in Pd(0) and Pd(II) complexes.

2. Experimental

2.1. Material and apparatus

All manipulations have been carried out in an atmosphere of purified, dry nitrogen using standard Schlenk techniques. Solvents were dried and stored under nitrogen. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AMX 300 and DRX 300 (300.13 and 75.48 MHz, respectively). Elemental analyses were carried out by Dornis u. Kolbe Mikroanalytisches Laboratorium, Mühlheim a.d. Ruhr, Germany. Mass spectrometry was carried out on a JEOL JMS SX/SX102A four sector mass spectrometer coupled to a JEOL MS-MP 7000 data system. IR spectra were recorded on a Bio-Rad FTS-7. Synthesis of the compounds $Pd(dba)_2$ [25] (dba = dibenzylideneacetone), (COD)Pd(Me)Cl [26] (COD = *cis*,*cis*-1,5-cyclooctadiene) and *trans*-4,5-bis(2-pyridyl)norbornene (Norpy) [24] has been described before.

Atom labeling schemes for the ligand Renorpy is as follows:



2.2. Synthesis of trans-4,5-bis(2-pyridyl)norbornane (Renorpy) (**1**)

A mixture of Norpy (1 g, 4.0 mmol) and Rh(-$PPh_3)_3$Br (190 mg, 0.2 mmol) dissolved in toluene was put under an atmosphere of hydrogen and was stirred at room temperature for 8 h. The solvent was removed under vacuum and the residue was brought on a column packed with neutral Al_2O_3. Elution with a mixture of hexane/diethyl ether (1/1) provided the product, which was recrystallized from a solution of the product hexane yielding 870 mg (3.5 mmol, 87%) of the product. ^{1}H-NMR data (300 MHz, $CDCl_3$) δ: 8.56 (d, $^3J = 5.6$ Hz, 2H, H6;H6′), 7.54 (t, $^3J = 8.8$ Hz, 2H, H4;H4′), 7.24 (d, $^3J = 7.5$ Hz, 2H, H3;H3′), 7.06 (d, $^3J = 7.4$ Hz, 2H, H5;H5′), 3.94 (t, $^3J = 4.6$ Hz, 1H, H6″), 3.62 (d, $^3J = 6.4$ Hz, 1H, H5″), 2.73 (s, 1H, H4″), 2.56 (d, $^3J = 3.8$ Hz, 1H, H1″), 2.08 (d, $^3J = 9.1$ Hz, 1H, H7″), 1.64 (m, 2H, H3″), 1.40 (m, 1H, H7″), 1.35 (m, 2H, H2″). ^{13}C-NMR data (75.48 MHz, $CDCl_3$) δ: 165.8, 162.8 (C2;C2′), 149.3 (C6;C6′), 136.6, 136.3 (C4;C4′), 123.9, 123.3, 121.4 (C3;C3′;C5;C5′), 54.9, 52.2 (C5″;C6″), 45.2, 43.8 (C1″;C4″), 38.8, 31.0, 23.7 (C2″;C3″;C7″). EI MS Found (Calc. for $C_{17}H_{18}N_2$): 250 (250).

2.3. General procedure for synthesis of the complexes (N⌒N)Pd(η^2-alkene) [N⌒N = Renorpy (**2**); η^2-alkene = maleic anhydride (**a**), tetracyanoethylene (**b**)]

The compounds $Pd(dba)_2$ (0.200 g, 0.35 mmol), tetracyanoethylene (0.049 g, 0.38 mmol) or maleic anhydride (0.038 g, 0.38 mmol) and Renorpy (0.096 g, 0.38 mmol) were dissolved in 30 ml of toluene. The reaction mixture was stirred for 1 h during which a yellow solution was formed. The solvent was concentrated to 3 ml after which 30 ml of cold diethyl ether was added. The formed crystalline material was collected by centrifugation and washed with 10 ml of cold diethyl ether. The product was dried in vacuo.

2.3.1. (Renorpy)Pd(maleic anhydride) (**2a**)

Yield: 120 mg, 0.26 mmol, 76%. ^{1}H-NMR data (300 MHz, $CDCl_3$) δ: 8.87, 8.51 (d, $^3J = 5.2$ Hz, 2H, H6;H6′), 7.74, 7.72 (dt, $^3J = 8.0$ Hz, $^3J = 1.8$ Hz, 2H, H4; H4′), 7.42, 7.28 (d, $^3J = 6.9$ Hz, 2H, H3;H3′), 7.20,

7.20 (dt, $^3J = 6.7$ Hz, 2H, H5;H5′), 4.44 (d, $^3J = 5.6$ Hz, 1H, H6″), 2.93 (d, $^3J = 6.2$ Hz, 1H, H5″), 2.93 (s, 1H, H4″), 2.81 (d, $^3J = 3.7$ Hz, 1H, H1″), 1.93, 1.70 (d, $^3J = 8.9$ Hz, 2H, H7″), 1.80–1.23 (m, 4H, H2″;H3″), 3.86 (s, 2H, $CH=_{ma}$). IR ν(C=N) (KBr): 1787, 1718 cm^{-1}.

*2.3.2. (Renorpy)Pd(tetracyanoethylene) (**2b**)*

Yield: 86 mg, 0.18 mmol, 51%. ^{1}H-NMR data (300 MHz, $CDCl_3$) δ: 9.01, 8.70 (d, $^3J = 5.4$ Hz, 2H, H6;H6′), 7.87 (t, $^3J = 7.8$ Hz, 2H, H4;H4′), 7.53, 7.45 (d, $^3J = 8.8$ Hz, 2H, H3;H3′), 7.37 (t, $^3J = 6.3$ Hz, 2H, H5;H5′), 4.74 (d, $^3J = 6.5$ Hz, 1H, H6″), 3.01–2.91 (m, 3H, H1″;H4″;H5″), 1.93, 1.78 (d, $^3J = 10.4$ Hz, 2H, H7″), 1.94–1.23 (m, 4H, H2″;H3″). FAB MS Found (Calc. for $C_{23}H_{19}N_6Pd-CN$): 459 (459). IR ν(C=N) (KBr): 2202 cm^{-1}.

*2.4. Synthesis of (Renorpy)Pd(Me)Cl (**3**)*

The complex (COD)Pd(Me)Cl (100 mg, 0.37 mmol) and Renorpy (109 mg, 0.43 mmol) were dissolved in dichloromethane (20 ml). The volume of the reaction mixture was reduced after 15 min and hexane (30 ml) was added. The crystalline material was collected by centrifugation and washed twice with cold diethyl ether (20 ml). Yield: 61 mg, 0.15 mmol, 40%. ^{1}H-NMR data (300 MHz, $CDCl_3$) δ: 9.47, 8.51 (dd, $^3J = 6.3$ Hz, $^4J = 2.0$ Hz, 2H, H6;H6′), 7.77, 7.62 (dt, $^3J = 7.8$ Hz, $^4J = 1.8$ Hz, 2H, H4;H4′), 7.28–7.13 (m, 3H, H3;H3′;H5), 7.37 (d, $^3J = 7.9$ Hz, 1H, H5′), 5.90 (d, $^3J = 7.3$ Hz, 1H, H6″), 2.94 (s, 1H, H4″), 2.87 (s, 1H, H1″), 2.78 (d, $^3J = 7.0$ Hz, 1H, H5″), 1.96, 1.74 (d, $^3J = 10.1$ Hz, H7″), 1.85–1.40 (m, 4H, H2″;H3″), 0.87 (s, 3H, Pd–CH_3). ^{13}C-NMR data (75.48 MHz, $CDCl_3$) δ: 167.9, 161.2 (C2;C2′), 153.6, 152.3 (C6; C6′), 138.0, 136.6 (H4;H4′), 123.5, 122.9, 121.6, 119.7 (C3;C3′; C5;C5′), 57.6, 52.8 (C5″;C6″), 41.3, 40.9 (C1″;C4″), 39.4, 31.3, 22.8 (C2″;C3″;C7″), −2.6 (Pd–CH_3). FAB MS Found (Calc. for $C_{18}H_{21}ON_2Pd$): 371 (371).

*2.5. Synthesis of (Renorpy)Pd(acetyl)Cl (**4**)*

Carbon monoxide was bubbled through a solution of (Renorpy)Pd(Me)Cl (100 mg, 0.25 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 diethyl ether (30 ml) was added. The crystalline material (56 mg, 0.13 mmol, 52%) was collected by centrifugation and washed twice with hexane (20 ml). ^{1}H-NMR data (300 MHz, $CDCl_3$) δ: 9.25, 8.70 (d, $^3J = 5.2$ Hz, 2H, H6;H6′), 7.79, 7.61 (t, $^3J = 7.6$ Hz, 2H, H4;H4′), 7.28–7.11 (m, 3H, H3;H3′;H5), 7.44 (d, $^3J = 7.7$ Hz, 1H, H5′), 5.75 (d, $^3J = 7.1$ Hz, 1H, H6″), 2.96 (s, 1H, H4″), 2.90 (s, 1H, H1″), 2.83 (d, $^3J = 7.1$ Hz, 1H, H5″), 2.02, 1.78 (d, $^3J = 10.0$ Hz, H7″), 1.90–1.40 (m, 4H, H2″;H3″), 2.46 (s, 3H, C(O)CH_3). ^{13}C-NMR data (75.48 MHz, $CDCl_3$) δ: 167.5, 161.3 (C2;C2′), 153.5, 152.2 (C6; C6′), 139.0, 137.3 (H4;H4′), 124.0, 123.1, 122.1, 120.6 (C3;C3′;C5;-C5′), 58.6 54.4 (C5″;C6″), 42.2, 41.49 (C1″;C4″), 39.1, 32.1, 23.3 (C2″;C3″;C7″), 35.1 (C(O)CH_3), 235.1 (C(O)CH_3). FAB MS Found (Calc. for $C_{19}H_{21O}N_2Pd$): 399 (399). IR ν(C=N) (KBr): 1699 cm^{-1}.

*2.6. Crystal structure determination and refinement of (Renorpy)Pd(Me)Cl (**3**)*

A yellow, transparent, rhombus-shaped crystals was mounted on a Lindemann-glass capillary and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-Turbo diffractometer on a 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) [27] in the range $11.57 < \theta < 14.00°$. The unit-cell parameters were checked for the presence of higher lattice symmetry [28]. Crystal data and details on data collection and refinement are presented in Table 1. Data were corrected for *Lp* effects and the observed linear decay. An empirical absorption/extinction correction was applied (DIFABS [29] as implemented in PLATON) [30] (transmission range 0.378–1.000).

The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92) [31]. Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93) [32]; no observance criteria were applied during refinement. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic displacement parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms by a factor of 1.5 for the methyl hydrogen atoms and 1.2 for the other H atoms, respectively. Weights were introduced in the final refinement cycles. Neutral atom scattering factors and anomalous dispersion corrections were taken from International Tables for Crystallography [33]. Geometrical calculations and illustrations were performed with PLATON [30]. All calculations were performed on a DECstation 5000/133.

2.7. Calculation of the 'natural' bite angle of Renorpy

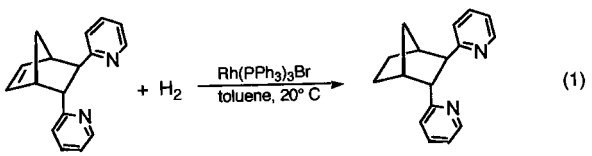
The calculations were performed using CAChe WorkSystem software [34] on an Apple Power Macintosh 950 equipped with two CAChe CXP coprocessors. The Molecular Mechanics calculations were performed using the MM2 force field [35], and the CAChe 'augmented force field' parameters. Block-diagonal Newton-

Raphson was used as optimization method. 'Natural' bite angle calculations were performed using a method similar to that described by Casey and Whiteker [36], using a Pd–N bond length of 2.120 Å. The 'natural' bite angles for Renorpy and Norpy were calculated at 115.5 and 117.5°.

3. Results and discussion

3.1. Synthesis of the ligand *trans*-4,5-bis(2-pyridyl)norbornane (Renorpy)

The bidentate nitrogen ligand *trans*-4,5-bis(2-pyridyl)norbornane (Renorpy, **1**) has been obtained by a Rh-catalyzed hydrogenation of the double bond of *trans*-4,5-bis(2-pyridyl)norbornene (Norpy) (see Eq. 1).



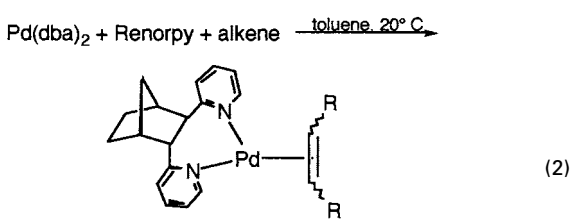
(1)

1

The ligand has been characterized by ^{1}H- and ^{13}C-NMR spectrometry and mass spectrometry. These NMR spectra show two inequivalent pyridyl groups. Renorpy is a chiral ligand analogous to the ligand Norpy. The racemic mixture, which was obtained in a high yield of 87%, was used in further reactions without separation of the enantiomers.

3.2. Synthesis of (N⌒N)Pd(η^2-alkene) complexes

The zero-valent palladium complexes (Renorpy)Pd(MA) (**2a**) and (Renorpy)Pd(TCNE) (**2b**) were readily synthesized in high yields by reaction of Pd(dba)$_2$ with Renorpy in the presence of the alkene (Eq. 2). This method has been used before for synthesis of Pd(0) complexes containing bidentate nitrogen ligands and electron-poor alkenes [23,37,38].



(2)

alkene = maleic anhydride (**a**), tetracyanoethylene (**b**)

The products have been characterized by ^{1}H-, ^{13}C- and ^{1}H-Cosy-NMR spectrometry, mass spectrometry or elemental analysis. The chemical shift for the olefinic protons of the maleic anhydride of complex **2a** is 3.86 ppm in the ^{1}H-NMR spectrum, which is 3 ppm lower than that of free maleic anhydride. Such a shift to lower ppm value is normal for Pd(η^2-alkene) complexes [37,38]. Only one signal is observed for these olefinic protons in spite of the local C_s-symmetry of maleic anhydride and the C_1-symmetry of the ligand.

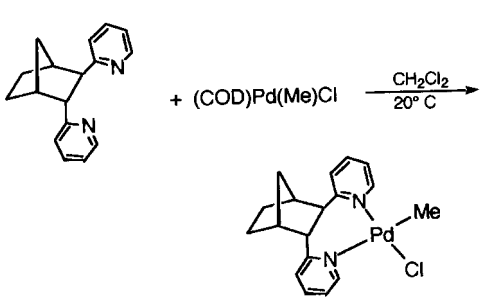
Table 1
Crystal and refinement data for (Renorpy)Pd(Me)Cl (**3**)

Crystal data	
Chemical formula	$C_{18}H_{21}ClN_2Pd \cdot CH_2Cl_2$
Molecular weight	492.18
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a (Å)	10.8440(15)
b (Å)	16.338(2)
c (Å)	12.720(2)
β (°)	117.790(11)
V (Å^3)	1993.7(5)
$D_{calc.}$ (g·cm^{-3})	1.640
Z	4
$F(000)$	992
μ (cm^{-1})	13.4
Crystal size (mm)	$0.13 \times 0.13 \times 0.33$
Data collection	
T (K)	150
Wavelength (Å)	0.71073 (Mo–K$_\alpha$) (graphite monochromator)
Data set (*hkl* range)	−7–14, 0–21, −16–14
DIFABS correlation range	0.378–1.000
Refinement	
Final R^a	0.0623 [2899 $F_o > 4\sigma(F_o)$]
Final wR_2^b	0.1562
w^{-1c}	$\sigma^2(F^2)+(0.0731P)^2+1.3344P$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.001, 0.000
Largest difference peak and hole (e Å^{-3})	0.99 (near Pd), -1.36

[a] $R = \Sigma(\|F_o\|-\|F_c\|)/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{0.5}$. [c] $P = (\max(F_o^2, 0)+2F_c^2)/3$.

3.3. Synthesis of (Renorpy)Pd(Me)Cl (3)

The complex (Renorpy)Pd(Me)Cl (**3**) has been synthesized (see Eq. 3) in a reaction of the ligand Renorpy with (COD)Pd(Me)Cl (COD = *Z*,*Z*-1,5-cyclooctadiene) similar to the syntheses of other L$_2$Pd(Me)Cl complexes containing P⌒P [18], P⌒N [39], N⌒N ligands [20–23] and terdentate nitrogen ligands [26,40,41].



(3)

3

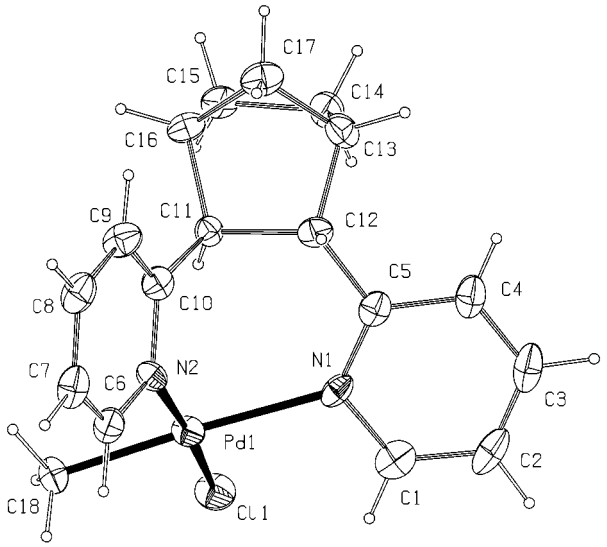


Fig. 1. An ORTEP plot at 50% probability level of complex (Renorpy)Pd(Me)Cl (**3**) (CH_2Cl_2 not shown).

Remarkably, quantitative formation of complex **3** occurs in the case of Renorpy, while several uncharacterizable products were obtained in the case of Norpy. This unexpected behavior of the latter ligand might be explained by the double bond of the norbornene fragment, which might give rise to formation of several products by insertion into the Pd–Me bond.

Complex **3** has been characterized by ^{1}H- and ^{13}C-NMR spectroscopy, mass spectroscopy and an X-ray structure determination. An interesting observation in the ^{1}H-NMR spectrum is that of the two possible *cis*/*trans* isomers of complex **3**, one isomer is formed in 95% yield. In this isomer the steric repulsion between the methyl group and the coordinated pyridyl ring *cis* to this group might be less than in the other isomer. The signal of the methyl protons can be observed at 0.87 ppm, which is as expected for a palladium–methyl complex containing a bidentate nitrogen ligand [20–22].

3.4. Molecular structure of (Renorpy)Pd(Me)Cl (3)

The molecular structure and adopted numbering scheme are presented in Fig. 1 and bond distances and selected bond angles are collected in Tables 2 and 3.

This structure displays a square-planar surrounding of the palladium atom by a bidentate coordinated Renorpy ligand, the chloride atom and by the carbon atom of the methyl group. The Pd–N(1) distance of 2.226(6) Å is longer than the Pd–N(2) distance of 2.027(5) Å, since the methyl group has a larger *trans* influence than the chloride [42]. The Pd–Cl distance of 2.313(2) Å is as expected [21–23], while the distance Pd–C(18) of 2.046(7) Å is relatively long as compared to those of other Pd–Me complexes containing bidentate nitrogen ligands (around 2.010 Å) [21]. The bite angle N(1)–Pd–N(2) of the ligand Renorpy (93.7(2)°) is significantly smaller than that of the ligand Norpy in the zero-valent complex (Norpy)Pd(TCNE) (99.49(15)°), albeit much larger than those of other palladium complexes containing bidentate nitrogen ligands like bis(*p*-anisylimino)acenaphthene (Ar-BIAN), 2-(N-R-carbaldimino)pyridine (R-PyCa) and 2,2′-bipyridine (bpy) (bite angles around 78°) [20,21,43]. Also the bite angle of the ligand Renorpy is significantly smaller than the calculated natural bite angle of 115.5°, which is caused by the electronic preference of the palladium(II) centre. One way for the Renorpy ligand to adopt bite angles that are smaller than the designed 'natural' bite angle is to move the palladium out of the pyridyl planes. Indeed, in the crystal structure the palladium atom is not coordinated in the plane of the pyridyl groups, which is illustrated by the angles C(8)–N(2)–Pd(1) = 171.8(3)° and C(3)–N(1)–Pd(1) = 169.1(3)°. We have observed this phenomenon before in the complex (Norpy)Pd(TCNE) in which the analogous angles are 167.7(3) and 164.6(3)° [24]. In this case the bite angle (99.45(15)° is also much smaller than the natural one (117.5°).

Table 2
Bond distances (Å) for (Renorpy)Pd(Me)Cl (**3**) (with estimated S.D. in parentheses)

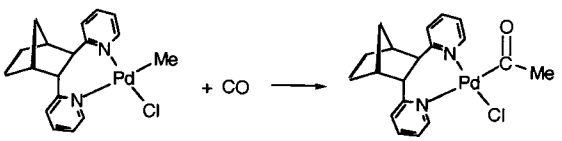
Pd(1)–Cl(1)	2.313(2)	C(7)–C(8)	1.365(10)
Pd(1)–N(1)	2.226(6)	C(8)–C(9)	1.379(10)
Pd(1)–N(2)	2.027(5)	C(9)–C(10)	1.385(11)
Pd(1)–C(18)	2.046(7)	C(10)–C(11)	1.511(8)
N(1)–C(1)	1.349(8)	C(11)–C(12)	1.558(10)
N(1)–C(5)	1.351(9)	C(11)–C(16)	1.540(8)
N(2)–C(6)	1.349(8)	C(12)–C(13)	1.544(9)
N(2)–C(10)	1.354(8)	C(13)–C(14)	1.524(12)
C(1)–C(2)	1.377(10)	C(13)–C(17)	1.520(10)
C(2)–C(3)	1.357(12)	C(14)–C(15)	1.550(10)
C(3)–C(4)	1.373(11)	C(15)–C(16)	1.542(9)
C(4)–C(5)	1.391(10)	C(16)–C(17)	1.546(12)
C(5)–C(12)	1.512(9)	Cl(2)–C(19)	1.782(14)
C(6)–C(7)	1.360(10)	Cl(3)–C(19)	1.750(14)

Table 3
Selected bond angles (°) for (Renorpy)Pd(Me)Cl (**3**) (with estimated S.D. in parentheses)

Cl(1)–Pd(1)–N(1)	91.23(17)	C(12)–C(11)–C(16)	103.8(5)
Cl(1)–Pd(1)–C(18)	88.5(2)	C(5)–C(12)–C(11)	118.8(6)
N(1)–Pd(1)–N(2)	93.7(2)	C(5)–C(12)–C(13)	117.6(5)
N(2)–Pd(1)–C(18)	86.7(2)	C(11)–C(12)–C(13)	101.6(5)
Pd(1)–N(1)–C(5)	130.2(4)	C(12)–C(13)–C(14)	110.1(6)
C(1)–N(1)–C(5)	117.6(6)	C(12)–C(13)–C(17)	100.3(5)
Pd(1)–N(2)–C(10)	119.2(4)	C(13)–C(14)–C(15)	103.4(5)
C(6)–N(2)–C(10)	116.9(6)	C(14)–C(15)–C(16)	102.9(6)
N(1)–C(5)–C(12)	121.0(6)	C(11)–C(16)–C(15)	106.1(5)
N(2)–C(10)–C(11)	115.0(6)	C(11)–C(16)–C(17)	102.5(6)
C(10)–C(11)–C(12)	109.6(5)	C(13)–C(17)–C(16)	94.4(6)
C(10)–C(11)–C(16)	117.7(5)		

3.5. CO insertion into the Pd–Me bond of (Renorpy)Pd(Me)Cl (3)

When CO is bubbled through a solution of complex **3** in dichloromethane for 5 min, CO insertion occurs into the Pd–Me bond (see Eq. 4). However, the product (Renorpy)Pd(C(O)Me)Cl (**4**) has been obtained in low yield (52%), since during the reaction formation of palladium metal takes place. Because of the small N–Pd–N angle in **3** compared to the calculated natural one and the out of plane deviation of the palladium one might presume a large strain in the ligand Renorpy. The unfavorable coordination of the ligand Renorpy in complex **3** explains the extensive formation of palladium metal upon CO insertion in this complex.



(4)

3 **4**

Complex **4** has been characterized by ^{1}H- and ^{13}C-NMR spectroscopy and mass spectroscopy. Analogous to complex **3**, one of the two possible isomers of **4** has been obtained in high yield (95%) as could be elucidated from the ^{1}H-NMR spectrum. The ^{1}H-NMR spectrum of **4** is comparable with that of **3** except for the methyl signal, which is shifted from 0.87 to 2.46 ppm as expected [20–23].

Although no kinetic measurements have been carried out, we can say that the CO insertion rate of this reaction is of the same order of magnitude as that for the CO insertion in (N⌒N)Pd(Me)Cl complexes containing bidentate nitrogen ligands with a small bite angle such as bpy, *p*-An-BIAN and 1,10-phenanthroline [20,21]. The CO-insertion rate is also comparable for that in the complex (8-(2-pyridyl) quinoline)Pd(Me)Cl, in which the bidentate nitrogen ligand coordinates with a bite angle (87.7(1)°) [23]. We might conclude that the bite angle has no significant influence on the CO-insertion rate in complexes containing dipyridyl ligands. This is in contrast to diphosphine ligands [18] for which we found an increase of the insertion rate when longer, more flexible backbones were used. As yet, this phenomenon cannot be explained.

4. Supplementary material

Further details of the structure determination, including atomic coordinates, bond lengths and angles and thermal parameters for **3** can be obtained, upon request, from the Cambridge Crystallographic Data Centre or from the authors.

Acknowledgements

Professor Dr E. Drent and Dr W.P. Mul (Koninklijke/Shell-Laboratorium, Amsterdam) are acknowledged for their helpful discussions and Shell Research BV for financial support. This work was supported in part (N. Veldman and A.L. Spek) by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

References

[1] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, California, 1987.
[2] A. Yamamoto, Organotransition Metal Chemistry, Wiley, New York, 1986.
[3] I. Wender, P. Pino, Organic Synthesis via Metal Carbonyls, vol. 2, Wiley, New York, 1977.
[4] J.A. Moulijn, P.W.N.M. van Leeuwen, R.A. van Santen, Catalysis: An Integrated Approach to Homogeneous Heterogeneous and Industrial Catalysis, Elsevier, Amsterdam, 1993.
[5] E. Drent, J.A.M. van Broekhoven, M.J. Doyle, J. Organomet. Chem. 417 (1991) 235.
[6] E. Drent, P.H.M. Budzelaar, Chem. Rev. 96 (1996) 663.
[7] P.E. Garrou, R.F. Heck, J. Am. Chem. Soc. 98 (1976) 4115.
[8] G.K. Anderson, R.J. Cross, Acc. Chem. Res. 17 (1984) 67.
[9] R.J. Mawby, F. Basolo, R.G. Pearson, J. Am. Chem. Soc. 86 (1964) 5043.
[10] K. Noack, F. Calderazzo, J. Organomet. Chem. 10 (1967) 101.
[11] T.C. Flood, J.E. Jensen, J.A. Statler, J. Am. Chem. Soc. 103 (1981) 4410.
[12] P.W.N.M. van Leeuwen, C.F. Roobeek, H. van der Heijden, J. Am. Chem. Soc. 116 (1994) 12117.
[13] P.W.N.M. van Leeuwen, K.F. Roobeek, Rec. Trav. Chim. Pays. Bas 114 (1995) 73.
[14] H. Berke, R. Hoffmann, J. Am. Chem. Soc. 100 (1978) 7224.
[15] N. Koga, K. Morokuma, J. Am. Chem. Soc. 108 (1986) 6136.
[16] N. Koga, K. Morokuma, Chem. Rev. 91 (1991) 823.
[17] H.J. Calhorda, J.M. Brown, N.A. Cooley, Organometallics 10 (1991) 1431.
[18] G.P.C.M. Dekker, C.J. Elsevier, K. Vrieze, P.W.N.M. van Leeuwen, Organometallics 11 (1992) 1598.
[19] S. Sakaki, K. Kitaura, K. Morokuma, K. Ohkubo, J. Am. Chem. Soc. 105 (1983) 2280.
[20] R. van Asselt, E.E.C.G. Gielens, R.E. Rülke, K. Vrieze, C.J. Elsevier, J. Am. Chem. Soc. 116 (1994) 977.
[21] R.E. Rülke, J.G.P. Delis, A.M. Groot, et al., J. Organomet. Chem. 508 (1996) 109.
[22] J.G.P. Delis, P.W.N.M. van Leeuwen, K. Vrieze, N. Veldman, A.L. Spek, J. Fraanje, K. Goubitz, J. Organomet. Chem. 514 (1996) 125.
[23] J.G.P. Delis, M. Rep, R.E. Rülke, P.W.N.M. van Leeuwen, K. Vrieze, N. Veldman, A.L. Spek, Inorg. Chim. Acta 250 (1996) 87.
[24] M. Kranenburg, J.G.P. Delis, P.C.J. Kamer, et al., J. Chem. Soc. Dalton Trans. (1997) 1839.
[25] M.F. Rettig, P.M. Maitlis, Inorg. Synth. 17 (1977) 134.
[26] R.E. Rülke, J.M. Ernsting, A.L. Spek, C.J. Elsevier, P.W.N.M. van Leeuwen, K. Vrieze, Inorg. Chem. 32 (1993) 5769.
[27] J.L. de Boer, A.J.M. Duisenberg, Acta Crystallogr. A 40 (1984) C410.

[28] A.L. Spek, J. Appl. Crystallogr. 21 (1988) 578.
[29] N. Walker, D. Stuart, Acta Crystallogr. A 39 (1983) 158.
[30] A.L. Spek, Acta Crystallogr. A 46 (1990) C34.
[31] P.T. Beurskens, G. Admiraal, G. Beurskens, et al., The DIRDIF Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.
[32] G.M. Sheldrick, SHELXL-93, Program for crystal structure refinement, University of Göttingen, Germany, 1993.
[33] A.J.C. Wilson, International Tables for Crystallography, vol. C, Kluwer Academic, Dordrecht, 1992.
[34] CAChe Scientific Inc., CAChe WorkSystem version 3.7, 18700 NW Walker Road, Building 92-01, Beaverton, OR 97006, USA.
[35] U. Burkert, N.L. Allinger, Molecular Mechanics, Am. Chem. Soc., Washington, DC, 1982.
[36] C.P. Casey, G.T. Whiteker, Isr. J. Chem. 30 (1990) 299.
[37] R. van Asselt, C.J. Elsevier, W.J.J. Smeets, A.L. Spek, Inorg. Chem. 33 (1994) 1521.
[38] R.A. Klein, P. Witte, R. van Belzen, J. Fraanje, K. Goubitz, M. Naman, H. Schenk, J.M. Ernsting, C.J. Elsevier, Eur. J. Inorg. Chem. (1998) 319.
[39] G.P.C.M. Dekker, A. Buijs, C.J. Elsevier, et al., Organometallics 11 (1992) 1937.
[40] R.E. Rülke, I.M. Han, C.J. Elsevier, et al., Inorg. Chim. Acta 169 (1990) 5.
[41] R.E. Rülke, V.E. Kaasjager, D. Kliphuis, C.J. Elsevier, P.W.N.M. van Leeuwen, K. Vrieze, K. Goubitz, Organometallics 15 (1996) 668.
[42] T.G. Appleton, H.C. Clark, L.E. Manzer, Coord. Chem. Rev. 10 (1973) 335.
[43] B.A. Markies, D. Kruis, M.H.P. Rietveld, et al., J. Am. Chem. Soc. 117 (1995) 5263.