Cyclopalladation to form Planar Tridentate [N–C–N]$^-$ Intramolecular Co-ordination Systems involving Pyridine Donor Groups, including Ligand Synthesis and *X*-Ray Structural * Studies

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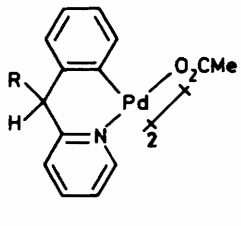
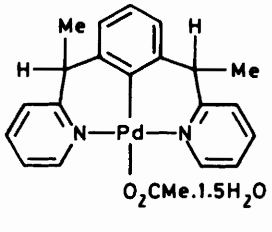
Reaction of palladium(II) acetate with 1,3-bis[1-(pyridin-2-yl)ethyl]benzene and 1,3-bis(2-pyridinecarbonyl)benzene results in cyclopalladation and formation of 2,6-bis[1-(pyridin-2-yl)ethyl]phenyl and 2,6-bis(2-pyridinecarbonyl)phenyl complexes [Pd{$(NC_5H_4CHMe)_2C_6H_3$}(O_2CMe)]·1.5H_2O (**1**) and [Pd{$(NC_5H_4CO)_2C_6H_3$}(O_2CMe)] (**4**), respectively. *X*-Ray crystallographic studies reveal square-planar co-ordination and unidentate acetate groups, with tridentate [N–C–N]$^-$ intramolecular co-ordination involving two six-membered $\overline{PdNC_3C}$ palladocycle rings. Proton n.m.r. spectra of complex (**1**) and its chloro-derivative [Pd{$(NC_5H_4CHMe)_2C_6H_3$}Cl] (**2**) indicate the presence of *meso* and *rac* diastereoisomers, but the crystal of (**1**) used for *X*-ray study contained the *meso* form only [monoclinic, space group *C*2/*c* with $a = 26.08(1)$, $b = 11.093(6)$, $c = 15.846(7)$ Å, $\beta = 116.19(3)°$, and $Z = 8$; $R = 0.042$ for 2 909 'observed' reflections]. Crystals of (**4**) contain two molecules in the asymmetric unit, with the molecules having different conformations of the tridentate ligand [monoclinic, space group *Pc* with $a = 11.373(6)$, $b = 10.925(6)$, $c = 15.640(10)$ Å, $\beta = 116.98(4)°$, $Z = 4$; $R = 0.043$ (both chiralities) for 2 677 'observed' reflections]. Syntheses of the new ligands are described.

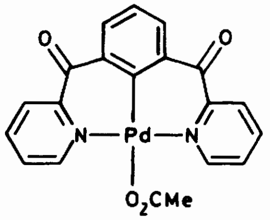
Cyclopalladation occurs readily on reaction of palladium(II) acetate with 2-benzylpyridine[1] and the closely related 2-diphenylmethylpyridine[2] to form [{Pd[$NC_5H_4CH(R)C_6H_4$](μ-O_2CMe)}$_2$] (R = H or Ph), but the presence of additional pyridine groups in the poly(pyridin-2-yl)methanes $(py)_2PhCH$ and $(py)_3PhC$ results in formation of *N*,*N'*-bidentate co-ordination complexes rather than cyclopalladation products.[2] We report here the synthesis, and reactivity toward palladium(II) acetate, of related ligands containing two pyridine groups, 1,3-bis[1-(pyridin-2-yl)ethyl]benzene and 1,3-bis(2-pyridinecarbonyl)benzene; simple molecular models indicate that cyclometallation is more likely for these than for $(py)_2PhCH$ and $(py)_3PhC$ since *N*,*N'* co-ordination without metallation should result in strained structures with a short $Pd \cdots H_{ortho}$ interaction. Cyclopalladation is found to occur readily, giving new intramolecular [N–C–N]$^-$ systems, as shown, and confirmed by *X*-ray structural determinations for *meso*-[Pd{$(NC_5H_4CHMe)_2C_6H_3$}(O_2CMe)]·1.5H_2O (**1**) and [Pd{$(NC_5H_4CO)_2C_6H_3$}(O_2CMe)] (**4**).



R = H or Ph



(**1**)



(**4**)

Results and Discussion

Synthesis and Characterization of Ligands and Complexes.— Both ligands were synthesized from 1,3-diacetylbenzene, $(MeCO)_2C_6H_4$, as shown below, by reaction with 2-lithiopyridine to form $[NC_5H_4C(OH)Me]_2C_6H_4$ [equation (1)], followed by dehydration of the alcohol to form the alkene $(NC_5H_4CCH_2)_2C_6H_4$ [equation (2)], which yields the ligands on hydrogenation [equation (3)] or ozonolysis [equation (4)].

$$(MeCO)_2C_6H_4 \xrightarrow[(ii)\ H_2O]{(i)\ 2Li(C_5H_4N)} [NC_5H_4C(OH)Me]_2C_6H_4 \quad (1)$$

$$[NC_5H_4C(OH)Me]_2C_6H_4 \xrightarrow[(ii)\ NaHCO_3]{(i)\ MeCO_2H,H_2SO_4} (NC_5H_4CCH_2)_2C_6H_4 \quad (2)$$

$$(NC_5H_4CCH_2)_2C_6H_4 \xrightarrow{H_2,Pd} (NC_5H_4CHMe)_2C_6H_4 \quad (3)$$

$$(NC_5H_4CCH_2)_2C_6H_4 \xrightarrow[(ii)\ Me_2S]{(i)\ O_3} (NC_5H_4CO)_2C_6H_4 \quad (4)$$

On heating solutions of palladium(II) acetate and $(NC_5H_4CHMe)_2C_6H_4$ or $(NC_5H_4CO)_2C_6H_4$ on a steam-bath, cyclometallated complexes (**1**) and (**4**) were obtained, and

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* (Acetato-*O*){*meso*-2,6-bis[1-(pyridin-2-yl)ethyl]phenyl-*C*,*N*,*N'*}palladium(II) sesquihydrate and (acetato-*O*)[2,6-bis(2-pyridinecarbonyl)-phenyl-*C*,*N*,*N'*]palladium(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: mmHg ≈ 133 Pa.

Table 1. Characterization data for the complexes

Complex	Analysis[a] (%) C	H	N	$M^{a,b}$	^{1}H N.m.r.[c]
(1) $[Pd\{(NC_5H_4CHMe)_2C_6H_3\}(O_2CMe)]^d$	58.4 (58.4)	5.2 (4.9)	5.7 (6.2)	479 (453)	9.04 [*ca.* **0.6**, *d*(*br*), *meso*-H(6), $J(H^5H^6)$ 5.5], 8.97 [*ca.* **0.9**, *d*, *rac*-H(6), $J(H^5H^6)$ 6.9], 8.92 [**0.6**, *d*(*br*), *meso*-H(6), $J(H^5H^6)$ *ca.* 5.5], 7.77—7.68 [**2**, *m*, H(4)], 7.43 [**2**, *m*, H(3)], 7.23—7.15 [**2**, *m*, H(5)], 7.03—6.91 (**3**, *m*, C_6H_3), 5.01 [**0.6**, *q*, *meso*-CH(ax), *J*(CH,Me) *ca.* 6.8], 4.34 [**1.4**, *q*, *rac*- and *meso*-CH(eq), *J*(CH,Me) *ca.* 7.2], 2.23 [**4.3**, *d*, *rac*- and *meso*-Me(ax), *J*(CH,Me) *ca.* 7.2], 2.04 (**3**, *s*, O_2CMe), 1.83 [**1.7**, *d*(*br*), *meso*-Me(eq), *J*(CH,Me) 6.8][e]
(2) $[Pd\{(NC_5H_4CHMe)_2C_6H_3\}Cl]$	55.8 (56.0)	4.4 (4.5)	6.5[f] (6.5)	413 (427)	9.47 [**0.9**, *d*, *rac*-H(6), $J(H^5H^6)$ 4.4], 9.39 [**1.1**, *m*(*br*), *meso*-H(6)], 7.70 [**2**, *m*, H(4)], 7.43 [**2**, *m*, H(3)], 7.18 [**2**, *m*, H(5)], 6.98 (**3**, *m*, C_6H_3), 5.03 [**0.6**, *q*(*br*), *meso*-CH(ax), *J*(CH,Me) *ca.* 7], 4.35 [1.4, *q*(*br*), *rac*- and *meso*-CH(eq), *J*(CH,Me) *ca.* 7], 2.31 [**4.3**, *m*(*br*), *rac*- and *meso*-Me(ax), *J*(CH,Me) *ca.* 7], 1.84 [**1.7**, *d*(*br*), *meso*-Me(eq), *J*(CH,Me) *ca.* 7][e,g]
(3) $[Pd\{(NC_5H_4CHMe)_2C_6H_3\}(H_2O)][BF_4]\cdot 0.5H_2O$	47.2 (47.3)	4.4 (4.4)	5.5 (5.5)		*h*
(4) $[Pd\{(NC_5H_4CO)_2C_6H_3\}(O_2CMe)]$	52.9 (53.1)	3.1 (3.1)	6.2 (6.2)	465 (452)	9.14 [**2**, *dd*, H(6), $J(H^5H^6)$ 5.7, $J(H^4H^6)$ 1.4], 8.28 [**2**, *d*, H(3,5) (C_6H_3), $J(H^3H^4 \equiv H^{4,5})$ 7.8], 8.08 [**2**, *m*, H(4)(py), $J(H^3H^4) \approx J(H^4H^5)$ 7.7, $J(H^4H^6)$ 1.4], 7.92 [**2**, *dd*, H(3)(py), $J(H^3H^4)$ 7.7, $J(H^3H^5)$ 1.2], 7.57 [**2**, *m*, H(5)(py), $J(H^4H^5)$ 7.7, $J(H^5H^6)$, 5.7, $J(H^3H^5)$ 1.2], 7.34 [**1**, *t*, H(4)(C_6H_3), $J(H^3H^4;H^4H^5)$ 7.8], 1.99 (**3**, *s*, O_2CMe)

[a] Calculated values are given in parentheses. [b] Osmometrically, *ca.* 3×10^{-2} mol dm^{-3} at 37 °C. [c] In $CDCl_3$; chemical shifts (δ) are in p.p.m. from $SiMe_4$, *J* values in Hz. Tabulated as chemical shift, **relative intensity**, *multiplicity*, assignment. [d] Air-dried crystals of the sesquihydrate were used for *X*-ray structural analysis. [e] COSY spectra used to assist with assignment of multiplets. [f] Cl 8.2 (8.3%). [g] See Figure 3. Multiplet at δ 9.39 assigned as 9.40 [*d*(*br*)] and 9.38 [*d*(*br*)]; multiplet at 2.31 assigned as 2.32 (*d*) and 2.30 (*d*). [h] Insufficiently soluble.

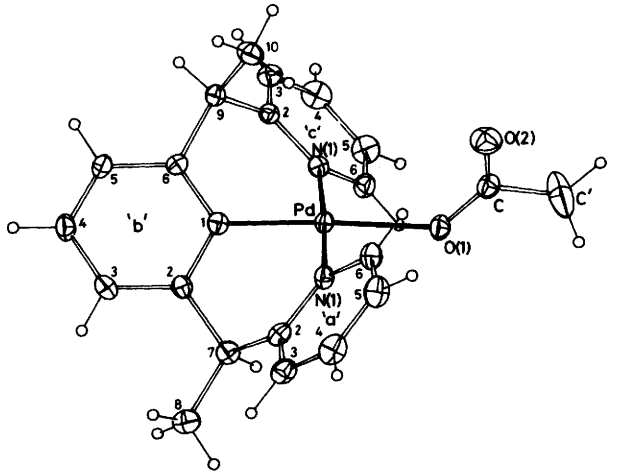

Figure 1. A molecule of $[Pd\{meso\text{-}(NC_5H_4CHMe)_2C_6H_3\}(O_2CMe)]$ in the crystal of complex (1). Hydrogen atoms are shown with an arbitrary radius of 0.1 Å, 20% thermal ellipsoids for the non-hydrogen atoms

characterized by microanalysis, osmometric molecular-weight determination, i.r. and ^{1}H n.m.r. spectroscopy (Table 1). Chloro (**2**) and aqua tetrafluoroborate (**3**) derivatives of (**1**) were obtained to assist with interpretation of i.r. and n.m.r. spectra. Although crystallographic studies of (**1**) show it to be a sesquihydrate (see below), the crystals became opaque on drying over P_2O_5 in a vacuum prior to microanalysis, and i.r. spectra are consistent with dehydration.

I.r. spectra of the complexes differ from those of the free ligands, with (**1**) and (**4**) showing $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ separated by 212 and 216 cm^{-1}, respectively, consistent[3] with unidentate acetate co-ordination. Complex (**3**) exhibits $\nu(H_2O)$ and $\nu(BF_4^-)$ absorptions and (**4**) has $\nu(C{=}O)$ at 1 660 cm^{-1}, unchanged from that of the free ligand. The ^{1}H n.m.r. spectrum of (**4**) is readily interpretable, with the resonances of all protons resolved (Table 1), *e.g.* the palladated ring exhibits a triplet for H(4) and a doublet for H(3,5). The spectra of (**1**) and (**2**) are complex, involving *meso* and *rac* diastereoisomers, and are discussed after presentation of the *X*-ray crystallographic results.

Structures of $[Pd\{meso\text{-}(NC_5H_4CHMe)_2C_6H_3\}(O_2CMe)]\cdot 1.5H_2O$ (**1**) *and* $[Pd\{(NC_5H_4CO)_2C_6H_3\}(O_2CMe)]$ (**4**).—Molecules of (**1**) and (**4**) are shown in Figures 1 and 2, with details of the molecular geometry given in Table 2. When projected normal to the co-ordination plane, both structures resemble the tridentate pyridine-donor analogue $[Pd\{meso\text{-}(NC_5H_4CMePh)_2C_5H_3N\}(O_2CMe)]^+$ shown in ref. 2; the atom-numbering scheme has been chosen to facilitate comparison, and the methyl groups at C(7) and C(9) in (**1**) are in similar orientations to those in the pyridine analogue. The six-membered $\overline{PdNC_3C}$ palladocycle rings are in the boat conformation.

The crystal of (**1**) examined contains the *meso* diastereoisomer of the ligand, with neighbouring molecules related by centres of symmetry (space group *C*2/*c*). The molecule shown in Figure 1

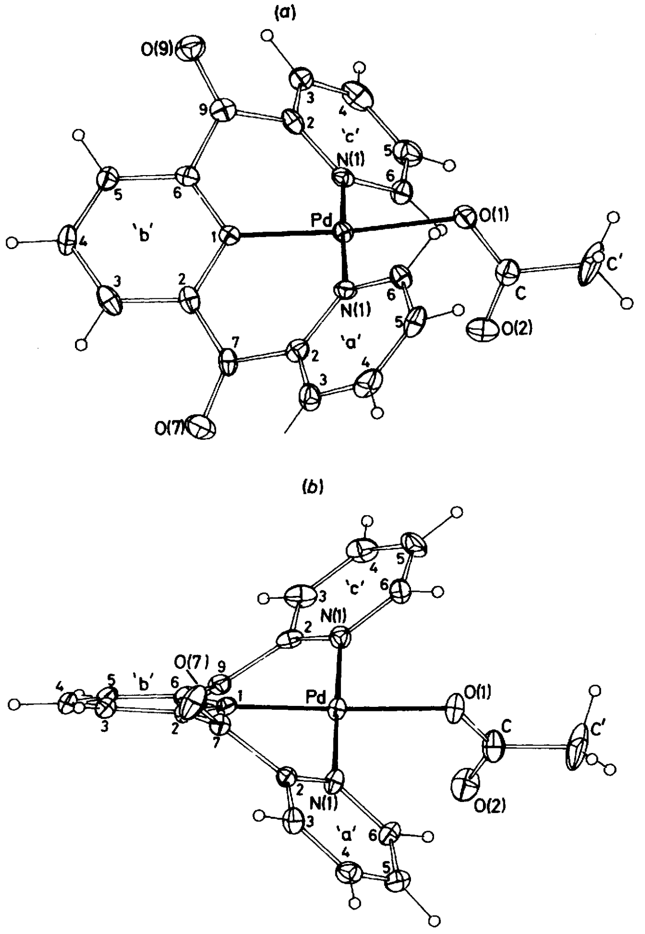

Figure 2. The molecular structure of $[Pd\{(NC_5H_4CO)_2C_6H_3\}(O_2CMe)]$ (4), showing (*a*) molecule 1 and (*b*) molecule 2, using projections to illustrate the relationship in conformation between complex (1) and molecule 1 of (4)

has *R* and *S* chirality for C(7) and C(9), respectively. Complex (4) has two molecules in the asymmetric unit of space group *Pc*, exhibiting different ligand conformations (Figure 2). The cell is related to the *C*2/*c* array of (1), with molecules 1 and 2 showing conformations of '$[(NC_5H_4CO)_2C_6H_3]PdO$' similar to the inversion-related '$[(NC_5H_4CHMe)_2C_6H_3]PdO$' moieties of (1).

Both structures have unidentate acetate co-ordination, with $Pd\cdots O(2)$ 3.493(5), 3.048(9), and 3.105(10) Å for (1), and molecules 1 and 2 of (4), respectively. The square-planar '$PdCN_2O$' kernels in (1) and (4) have bond angles close to 90°, and donor atoms alternating above and below the calculated mean planes, with the maximum deviation of −0.092 Å found for C(b1) in molecule 1 of (4) (Table 2).

The donor rings are planar, and the Pd atoms deviate 0.00—0.35 Å from the projected mean planes of the rings (Table 2). The rings form large dihedral angles with the co-ordination plane, 32.7—47.0°, with the dihedral angles for (1) within 3° of those for the tridentate pyridine analogue $[Pd\{$*meso*-$(NC_5H_4CMePh)_2C_5H_3N\}(O_2CMe)]^+$.

The carbonyl groups, 'C_3O,' of (4) are substantially planar [χ^2 about atoms 7 and 9 respectively being 9.2, 16.0 (molecule 1) and 9.4, 15.5 (molecule 2)]. The groups are not coplanar with adjacent rings, forming dihedral angles of 27.2 and 34.4 for the group between rings a and b of molecule 1, 36.2 and 31.6 (rings b and c, molecule 1), 31.5 and 36.9 (rings a and b, molecule 2), 34.3 and 29.7° (rings b and c, molecule 2).

Table 2. Co-ordination geometry for the palladium atoms in $[Pd\{(NC_5H_4CHMe)_2C_6H_3\}(O_2CMe)]\cdot1.5H_2O$ (1) and $[Pd\{(NC_5H_4CO)_2C_6H_3\}(O_2CMe)]$ (4); distances in Å, angles in °

		(4)	
	(1)	Molecule 1	Molecule 2
Pd–C(b1)	1.950(6)	1.963(11)	1.964(11)
Pd–N(a1)	2.036(5)	2.033(9)	2.030(10)
Pd–N(c1)	2.050(5)	2.031(9)	2.027(10)
Pd–O(1)	2.127(4)	2.137(8)	2.090(8)
C(b1)–Pd–N(a1)	88.5(2)	91.3(4)	89.2(4)
C(b1)–Pd–N(c1)	88.4(2)	89.7(4)	91.1(4)
N(a1)–Pd–O(1)	93.4(2)	88.6(3)	89.5(4)
N(c1)–Pd–O(1)	89.7(2)	90.5(3)	90.2(4)
C(b1)–Pd–O(1)	174.9(3)	173.7(5)	176.0(5)
N(a1)–Pd–N(c1)	176.9(2)	178.0(4)	179.4(4)
Pd–C(b1)–C(b2)	118.8(4)	120.3(9)	123.4(9)
Pd–C(b1)–C(b6)	121.7(3)	121.0(9)	120.2(9)
Pd–N(a1)–C(a2)	121.8(4)	122.2(9)	124.0(7)
Pd–N(a1)–C(a6)	118.2(3)	120.3(8)	117.1(9)
Pd–N(c1)–C(c2)	121.9(4)	123.3(7)	123.4(9)
Pd–N(c1)–C(c6)	117.2(4)	117.3(8)	118.8(9)
Pd–O(1)–C	131.3(5)	117(1)	120(1)
Deviations (Å) of atoms from the 'CN_2O' plane[a]			
Pd	0.036	0.038	−0.028
N(a1)	0.042	0.069	−0.036
C(b1)	−0.063	−0.092	0.049
N(c1)	0.038	0.070	−0.037
O(1)	−0.032	−0.055	0.028
Deviations (Å) of Pd from the 'C_5N' and 'C_6' mean planes of the rings			
Ring a	0.065	0.35	0.25
Ring b	0.025	0.00	0.03
Ring c	0.045	0.20	0.25

The mean planes have χ^2 153, 104, and 26.6 for complex (1) and molecules 1 and 2 of (4), respectively. [b] For complex (1) the mean planes of rings a, b, and c have χ^2 2.3, 9.2, and 19.0, respectively, and form dihedral angles of 47.0, 39.4, and 38.6° with the 'CN_2O' plane. Similarly, for molecule 1 of (4), the mean planes have χ^2 2.5, 2.6, and 7.0 and form dihedral angles 33.9, 35.5, and 42.5°; the mean planes for molecule 2 have χ^2 2.2, 10.7, and 1.5 and form dihedral angles 38.3, 33.7, and 32.7°.

^{1}H *N.M.R. Spectra of Complexes* (1) *and* (2).—The spectra of (1) and (2) exhibit more resonances than expected for the presence of the *meso* diastereoisomer found in the crystal of (1) examined by *X*-ray diffraction, *e.g.* (2) shows multiplets for H(3)—H(5) (py rings), H(b4), and H(b3,b5), but three resonances for H(6)(py) and methyl protons with (apparently) two resonances for the methine protons (Figure 3). The spectra are most readily accounted for as resulting from the presence of both *meso* and *rac* diastereoisomers.

Examination of Figures 1 and 4(*i*) indicates, assuming free rotation of co-ordinated acetate in solution, the presence of two methine environments in the *meso* form, H(7)(ax) (*i.e.* axial orientation in the $\overline{PdNC_3C}$ palladocycle, and near Pd) and H(9)(eq) (equatorial), two methyl environments, Me(8)(eq) and Me(10)(ax), two pyridine environments, H(a6)(Me) (on the same side of the '$PdCN_2O$' plane as a methyl group) and H(c6)(H) (on the same side as a methine group), and H(b3) differs from H(b5). In solution, conformational changes may allow the interconversion $(i) \rightleftharpoons (ii)$, *e.g.* H(7)(ax) to H(7)(eq). Similarly, the *rac* form may exist in conformations (*iii*) and/or (*iv*), although in this case the conformers are expected to have different stabilities and thus only one may be present. Structural studies suggest that (*iii*) may be preferred, since square-planar

Table 3. Non-hydrogen atom co-ordinates for $[Pd\{(NC_5H_4CHMe)_2C_6H_3\}(O_2CMe)]\cdot1.5H_2O$ (**1**)

Atom	*x*	*y*	*z*
Pd	0.850 62(2)	0.601 85(4)	0.865 66(3)
Tridentate ligand			
N(a1)	0.818 4(2)	0.718 2(4)	0.755 1(3)
C(a2)	0.766 8(3)	0.699 5(6)	0.680 3(4)
C(a3)	0.746 2(3)	0.784 5(5)	0.607 8(4)
C(a4)	0.778 0(3)	0.885 7(7)	0.613 4(5)
C(a5)	0.829 9(3)	0.902 6(7)	0.687 9(5)
C(a6)	0.849 1(3)	0.816 8(6)	0.758 0(4)
C(b1)	0.827 8(2)	0.468 9(5)	0.776 0(4)
C(b2)	0.774 7(2)	0.476 1(5)	0.694 6(4)
C(b3)	0.758 6(2)	0.380 7(6)	0.630 4(4)
C(b4)	0.793 6(3)	0.281 8(6)	0.643 7(4)
C(b5)	0.845 0(3)	0.274 6(5)	0.725 6(4)
C(b6)	0.861 8(2)	0.367 7(5)	0.790 2(4)
N(c1)	0.882 3(2)	0.477 2(4)	0.972 0(3)
C(c2)	0.911 0(2)	0.378 2(5)	0.966 5(4)
C(c3)	0.933 7(3)	0.299 7(6)	1.043 1(4)
C(c4)	0.923 6(3)	0.317 6(7)	1.118 6(4)
C(c5)	0.893 4(3)	0.416 8(7)	1.123 2(4)
Atom	*x*	*y*	*z*
Tridentate ligand			
C(c6)	0.872 3(3)	0.495 7(6)	1.046 3(4)
C(7)	0.736 3(2)	0.584 4(6)	0.683 2(4)
C(8)	0.676 6(3)	0.576 2(6)	0.604 6(4)
C(9)	0.919 5(2)	0.356 9(5)	0.879 3(4)
C(10)	0.964 5(7)	0.439 7(7)	0.873 6(4)
Acetate			
C	0.913 3(3)	0.802 5(6)	1.008 9(4)
O(1)	0.869 9(2)	0.741 5(4)	0.967 2(3)
O(2)	0.952 0(2)	0.823 0(5)	0.986 3(3)
C	0.918 1(4)	0.863 3(9)	1.095 9(6)
Solvent molecules			
O(1)	0.038 5(2)	0.978 9(6)	0.121 0(4)
O(2)	0	0.903 1(8)	$\frac{3}{4}$

Table 4. Non-hydrogen atom co-ordinates for $[Pd\{(NC_5H_4CO)_2C_6H_3\}(O_2CMe)]$ (**4**)

	Molecule 1			Molecule 2		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Pd	1*	1.033 18(8)	0*	0.565 34(11)	0.641 32(9)	0.055 88(8)
Tridentate ligand						
N(a1)	0.874 1(9)	1.171 8(9)	−0.071 0(7)	0.449 7(9)	0.791 7(10)	0.003 6(7)
C(a2)	0.748 7(12)	1.177 7(12)	−0.079 8(8)	0.462 4(11)	0.892 0(11)	0.053 7(8)
C(a3)	0.675 2(12)	1.282 5(12)	−0.111 9(10)	0.372 8(12)	0.982 8(12)	0.020 0(9)
C(a4)	0.723 0(14)	1.380 3(13)	−0.138 4(11)	0.265 6(12)	0.977 1(13)	−0.067 4(9)
C(a5)	0.846 9(14)	1.373 1(12)	−0.131 5(10)	0.252 5(11)	0.876 7(14)	−0.122 1(9)
C(a6)	0.916 8(11)	1.268 4(11)	−0.099 4(9)	0.346 4(11)	0.782 6(13)	−0.084 4(8)
C(b1)	0.857 3(11)	0.912 3(11)	−0.055 6(7)	0.718 1(11)	0.748 9(11)	0.124 0(8)
C(b2)	0.725 7(11)	0.944 2(12)	−0.074 4(8)	0.710 0(11)	0.861 7(12)	0.161 2(8)
C(b3)	0.628 2(12)	0.855 3(14)	−0.112 4(9)	0.818 9(13)	0.937 0(12)	0.212 4(9)
C(b4)	0.652 8(13)	0.738 2(12)	−0.135 1(10)	0.939 9(12)	0.901 6(14)	0.219 5(9)
C(b5)	0.779 2(12)	0.712 1(12)	−0.118 9(9)	0.953 6(12)	0.791 4(14)	0.183 5(9)
C(b6)	0.881 3(11)	0.795 6(12)	−0.077 9(8)	0.847 0(11)	0.711 5(12)	0.138 6(8)
N(c1)	1.127 3(9)	0.897 8(9)	0.075 4(7)	0.680 2(10)	0.490 6(9)	0.106 7(7)
C(c2)	1.129 1(11)	0.787 1(12)	0.038 1(9)	0.806 8(13)	0.482 2(12)	0.116 3(8)
C(c3)	1.228 3(12)	0.703 4(11)	0.087 2(10)	0.871 6(14)	0.374 5(13)	0.138 9(10)
C(c4)	1.322 4(13)	0.727 6(15)	0.177 6(11)	0.814 9(14)	0.269 7(13)	0.152 1(10)
C(c5)	1.319 1(13)	0.840 0(15)	0.215 5(10)	0.688 5(15)	0.274 4(13)	0.145 8(10)
C(c6)	1.223 7(12)	0.926 3(12)	0.162 9(8)	0.626 1(13)	0.387 5(13)	0.120 9(10)
C(7)	0.690 2(12)	1.064 6(11)	−0.059 3(9)	0.582 8(12)	0.910 5(12)	0.148 9(9)
O(7)	0.596 2(9)	1.083 2(9)	−0.041 8(8)	0.572 9(9)	0.978 7(10)	0.206 7(7)
C(9)	1.015 8(13)	0.748 6(12)	−0.053 4(9)	0.875 1(12)	0.595 3(13)	0.108 8(9)
O(9)	1.030 3(9)	0.669 3(9)	−0.102 7(7)	0.964 2(9)	0.577 3(9)	0.086 4(8)
Acetate						
C	1.177 0(12)	1.227 7(12)	0.118 1(9)	0.373 3(13)	0.475 7(13)	−0.088 5(11)
C	1.274 8(21)	1.327 8(17)	0.139 5(12)	0.246 2(18)	0.406 3(22)	−0.134 0(14)
O(1)	1.159 0(8)	1.161 5(8)	0.047 0(6)	0.397 9(8)	0.530 7(8)	−0.009 9(6)
O(2)	1.118 2(9)	1.214 0(9)	0.166 1(7)	0.442 8(9)	0.484 0(10)	−0.129 6(7)

* Defines origin.

complexes of related poly(pyridin-2-yl)methanes, $(py)_2(R)CH$, adopt structures with axial R in $[Pd\{(py)_2(R)CH\}_2]^{2+}$ (R = py)[4] and $[AuMe_2\{(py)_2(R)CH\}]^+$ (R = py or Ph).[5] Preference for axial orientation of R may result from close proximity of R to adjacent hydrogen atoms on aromatic rings when in an equatorial orientation [Figure 4(*iv*), and illustrated also by C(8) only in Figure 1], and thus the *rac* forms of (**1**) and (**2**) may be static with conformation (*iii*).

For the chloro-derivative (**2**) the ^1H n.m.r. spectrum exhibits non-integral relative intensities for the H(6), methine, and methyl resonances (Figure 3), and may be accounted for as resulting from a *ca.* 3:4 ratio of a static *rac* form, probably (*iii*),

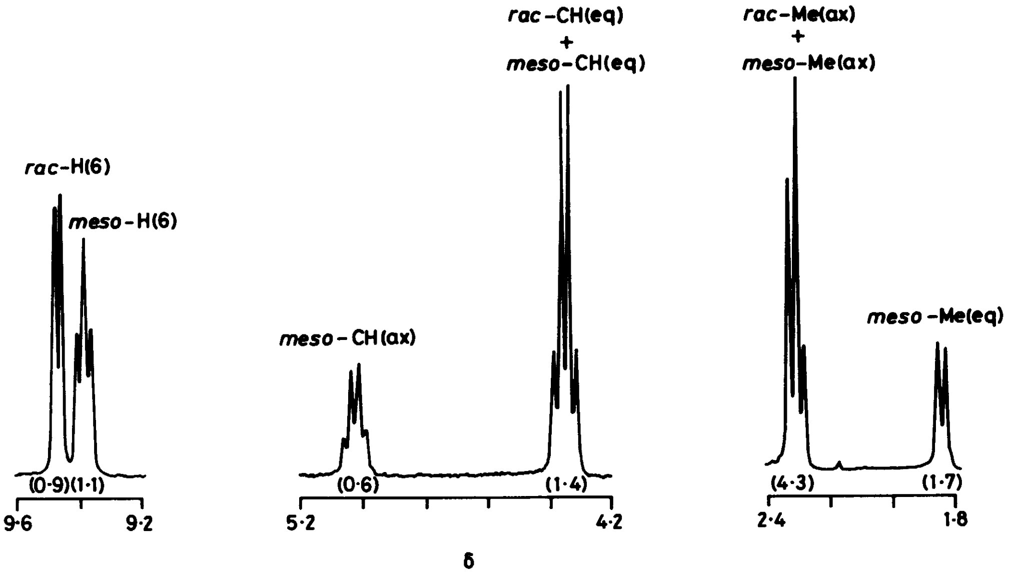

Figure 3. Parts of the ^{1}H n.m.r. spectrum of $[\text{Pd}\{(\text{NC}_5\text{H}_4\text{CHMe})_2\text{C}_6\text{H}_3\}\text{Cl}]$ (2), illustrating the relative integration and assignments for H(6)(pyridine), methine, and methyl protons, where the conformation (*iii*) (Figure 4) is assumed for the *rac* form

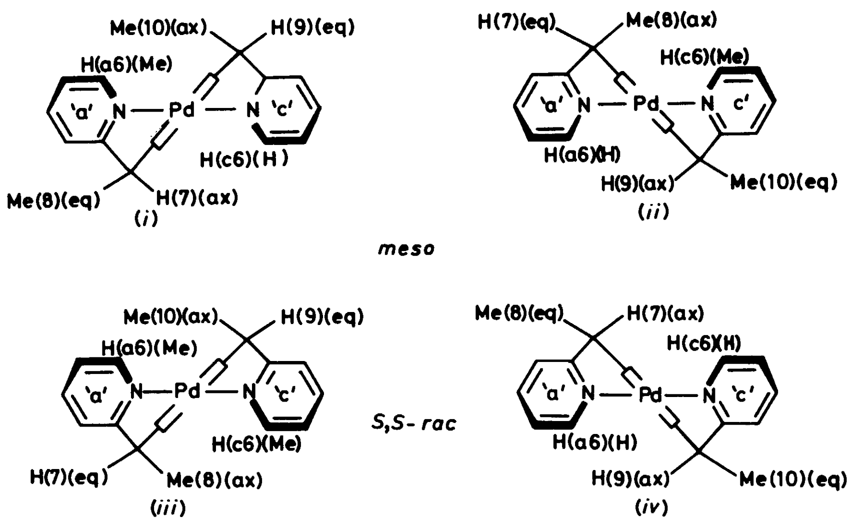

Figure 4. Conformations of $[\text{Pd}\{(\text{NC}_5\text{H}_4\text{CHMe})_2\text{C}_6\text{H}_3\}\text{X}]$ [X = O_2CMe (1) or Cl (2)] viewed along the Pd–X bond, with X omitted for clarity, showing (*i*) the *meso* conformation shown in Figure 1 for X = O_2CMe, (*ii*) the *meso* form after inversion of both $\overline{\text{PdNC}_3\text{C}}$ palladocycles, (*iii*) the *S,S-rac* form with two axial methyl groups, and (*iv*) the ring-inverted structural isomer with axial methine groups

and exchanging *meso* forms [(*i*)$\rightleftharpoons$(*ii*)], giving the assignments (see Table 1) δ 9.47 [*rac*-H(6), integration 0.9 (calc. for 3:4 ratio 0.86)], 9.40 (br d) and 9.38 (br d) [*meso*-H(6), 1.1 (1.14)], 5.03 [*meso*-CH(ax), 0.6 (0.57)], 4.35 [*rac*- and *meso*-CH(eq), coincident, 1.4 (1.43)], 2.32 (d), and 2.30 (d) [*rac*- and *meso*-Me(ax), 4.3 (4.29)], and 1.84 [*meso*-Me(eq), 1.7 (1.71)].

Chemical shifts for the axial and equatorial groups are consistent with this assignment, with axial groups further downfield from free-ligand values (*ca.* 0.7 p.p.m.) than are equatorial groups from free-ligand values (*ca.* 0.1 p.p.m.), as found for other palladium(II) complexes where downfield shifts are attributed to axial Pd ··· H interactions, *e.g.* complexes of 8-methylquinoline and benzo[*h*]quinoline.[6]

The spectra of the acetate complex (1) may be similarly interpreted (see Table 1), with the same *rac*:*meso* ratio, *ca.* 3:4. For (1) the three H(6)(py) resonances are well separated, with exchanging *meso* forms [Figure 4(*i*) and (*ii*)] giving broad doublets at δ 9.04 and 8.92, and the *rac* form giving a sharp doublet at 8.97. However, the methine CH(eq) resonances of the *rac* and *meso* forms are coincident, 4.34, as also are the Me(ax) resonances, 2.23, with *meso*-CH(ax) at 5.01 and *meso*-Me(eq) at 1.83. These assignments are supported by two-dimensional ^{1}H, ^{1}H correlation spectroscopy (COSY). Cooling solutions of (1) or (2) to −50 °C resulted in sharpening of resonances assigned to the exchanging *meso* protons.

The $[\text{N–C–N}]^-$ ligand systems described here are related to $[\text{P–C–P}]^-$ and $[\text{S–C–S}]^-$ systems, formed by palladation of $1,3\text{-}(\text{Bu}^t{}_2\text{PCH}_2)_2\text{C}_6\text{H}_4$ and $1,3\text{-}(\text{Bu}^t\text{SCH}_2)_2\text{C}_6\text{H}_4$,[7,8] and the $[\text{N–C–N}]^-$ system formed on reaction of $\text{Li}[2,6\text{-}(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]$ with metal halide substrates.[9] The new complexes described here differ from these in several respects, possessing pyridine donor groups, six-membered palladocycle rings compared with five-membered rings for the earlier complexes, the presence of a ketone functionality in the rings of (**4**), and of two asymmetric carbon atoms in complexes (**1**)—(**3**).

Experimental

Palladium(II) acetate[10] was prepared as described, diethyl ether was dried with a column of 4-Å molecular sieves followed by distillation over sodium–benzophenone and storage over sodium, 2-bromopyridine was dried over NaOH followed by distillation from CaO and storage over sieves, ethyl acetate and dichloromethane were distilled, and the solvents acetic acid, acetone, and chloroform were purified as described.[2]

Microanalyses were by the Canadian Microanalytical Service, Vancouver. I.r. spectra of thin films, Nujol or hexachlorobutadiene mulls (4 000—400 cm^{-1}) between KBr plates were measured with a Hitachi 270—30 spectrophotometer, ^{1}H n.m.r. spectra in $CDCl_3$, with a Bruker AM-300 spectrometer, and mass spectra with a VG MM 70-70F spectrometer. Molecular weights were determined in chloroform with a Knauer vapour-pressure osmometer.

1,3-*Bis*[1-(*pyridin*-2-*yl*)*ethyl*]*benzene*, $(NC_5H_4CHMe)_2C_6H_4$.—A deep red solution of 2-lithiopyridine was obtained on addition of 2-bromopyridine (6.27 cm^3, 64.3 mmol) in diethyl ether (30 cm^3) to a solution of phenyl-lithium [from lithium (142 mmol) and bromobenzene (64.3 mmol)] in diethyl ether (100 cm^3) at −50 °C under nitrogen. After stirring for 15 min, 1,3-diacetylbenzene (4.74 g, 29.2 mmol) in diethyl ether (30 cm^3) was added over 15 min to give a thick purple slurry. On allowing the slurry to warm to ambient temperature (2 h), water (50 cm^3) was added followed by 5 mol dm^{-3} HCl until the aqueous phase became acidic to litmus. The isolated aqueous extract was washed once with dichloromethane (20 cm^3), and made alkaline by addition of a saturated sodium hydrogencarbonate solution. The solution was extracted with dichloromethane (3 × 50 cm^3), dried over magnesium sulphate, filtered, and the solvent removed by rotary evaporation to give 1,3-*bis*[1-*hydroxy*-1-(*pyridin*-2-*yl*)*ethyl*]*benzene*, $[NC_5H_4C(OH)Me]_2C_6H_4$, as a viscous brown oil after drying under vacuum (3 h, 70 °C, 0.1 mmHg), yield 7.88 g (*ca.* 84%).

The crude alcohol was dehydrated by dissolution in a mixture of glacial acetic acid (50 cm^3) and concentrated sulphuric acid (100 cm^3) and standing for 24 h. After neutralization of the solution by addition of saturated $NaHCO_3$ solution the crude alkene 1,3-*bis*[1-(*pyridin*-2-*yl*)*ethenyl*]*benzene*, $(NC_5H_4CCH_2)_2C_6H_4$, separated as brown oily droplets and was extracted into chloroform (4 × 50 cm^3). On drying of the extract over magnesium sulphate and removal of solvent under vacuum, the very dark oil was chromatographed on a short silica column (eluant: 5% methanol in chloroform) under medium pressure to give the alkene as a pale yellow oil (4.64 g, *ca.* 66%) from the first eluant (R_f 0.25 with chloroform elution on a silica plate) prior to a red-purple band.

The alkene $(NC_5H_4CCH_2)_2C_6H_4$ was quantitatively hydrogenated (^{1}H n.m.r. estimation) in ethyl acetate (80 cm^3) over 4 h with hydrogen (60 lbf in^{-2}, *ca.* 413 700 Pa) using 5% palladium-on-charcoal as catalyst. Distillation (140—142 °C, 0.02 mmHg) gave 1,3-*bis*[1-(*pyridin*-2-*yl*)*ethyl*]*benzene*, $(NC_5H_4CHMe)_2C_6H_4$, as a very pale yellow viscous oil; $\nu_{max.}$ at 3 136s, 3 052s, 3 004s, 2 968s, 2 928s, 1 590vs, 1 570s, 1 486vs, 1 452vs, 1 370s, 1 148s, 1 044s, 994s, 892s br, 782s, 748vs, and 706vs cm^{-1}. Mass spectrum: *m*/*e* 289 (*M* + 1, 18), 288 (4), 287 (10), 183 (15), 182 (100), 181 (20), 180 (45), 167 (88), and 106 (35%). ^{1}H N.m.r.: δ 8.54 [dd, 2 H, $J(H^5H^6)$ 5.6, $J(H^4H^6)$ 1.8, H(6)(py)], 7.54 (m, 2 H), 7.26—7.19 (m, 3 H), 7.13—7.05 (m, 5 H), 4.26 [q, 2 H, *J*(CH,Me), 7.3 CH], and 1.67 [d, 6 H, *J*(CH,Me), 7.3 Hz, Me].

1,3-*Bis*(2-*pyridinecarbonyl*)*benzene*, $(NC_5H_4CO)_2C_6H_4$.—Ozonolysis of the alkene $(NC_5H_4CCH_2)_2C_6H_4$ in ethyl acetate (1% w/v) at −50 °C gave the required compound (*ca.* 82%), after reduction of the ozonide with dimethyl sulphide, as a colourless crystalline solid on recrystallization from acetone, m.p. 114—115 °C (Found: C, 74.8; H, 4.2; N, 9.7. $C_{18}H_{14}N_2O_2$ requires C, 75.0; H, 4.2; N, 9.7%); $\nu_{max.}$ at 1 668vs [ν(C=O)], 1 596m, 1 582m, 1 568m, 1 432m, 1 302s, 1 280m, 1 242m, 1 120s, 1 012s, 826m, 786m, 738s, 694vs, 662s, and 618m cm^{-1}. Mass spectrum: *m*/*e* 288 (*M*, 12), 287 (7), 286 (10), 285 (8), 210 (15), 182 (100), and 180 (3%). ^{1}H N.m.r. 8.82 [m, 1 H, $J(H^2H^4 \equiv H^2H^6)$ 1.6, H(2)(C_6H_4)], 8.73 [m, 2 H, $J(H^5H^6)$ 4.8, H(6)(py)], 8.35 [dd, 2 H, $J(H^3H^4)$ 7.8, $J(H^3H^5)$ 1.8, H(3)(py)], 8.09 [m, 2 H, $J(H^{4,6}H^5)$ 7.8, $J(H^{4,6}H^2)$ 1, H(4,6)(C_6H_4)], 7.92 [m, 2 H, $J(H^4H^3 \equiv H^4H^5)$ 7.7, $J(H^4H^6)$ 1.8, H(4)(py)], 7.64 [t, 1 H, $J(H^5H^4 \equiv H^5H^6)$ 7.7, H(5)(C_6H_4)], and 7.51 [m, 2 H, $J(H^4H^5)$ 7.6, $J(H^5H^6)$ 4.8, $J(H^3H^5)$ 1.3 Hz, H(5)(py)].

(*Acetato*-O){2,6-*bis*[1-(*pyridin*-2-*yl*)*ethyl*]*phenyl*-C,N,N′}-*palladium*(II), $[Pd\{(NC_5H_4CHMe)_2C_6H_3\}(O_2CMe)]$ (**1**).—A solution of palladium(II) acetate (0.595 g, 2.65 mmol) and $(NC_5H_4CHMe)_2C_6H_4$ (0.642 g, 2.23 mmol) in glacial acetic acid (40 cm^3) was heated on a steam-bath for 12 h, filtered while hot, and most of the solvent removed in a vacuum to give a brown oil. The oil was dissolved in chloroform (40 cm^3) and treated with a saturated solution of Na_2CO_3. The organic phase was isolated, dried over magnesium sulphate, filtered, and reduced to dryness to give a pale brown foam. Column chromatography on silica (eluant: 5% methanol in chloroform) with medium pressure gave the product (R_f 0.24 with the same solvent on a silica plate) as a near colourless foam on removal of solvent. Addition of acetone (5 cm^3) gave an initial crop of colourless crystals, with a further crop obtained on exposure to diethyl ether vapour in a sealed chamber (0.711 g, 1.57 mmol, 71%), m.p. *ca.* 240 °C (decomp.); $\nu_{max.}$ at 1 596s br (CO_2), 1 568m, br, 1 482m, 1 428m, 1 384s br (CO_2), 1 328m, 1 156m, 814m, 776m, 758s, 730s, and 666s cm^{-1}.

(*Chloro*){2,6-*bis*[1-(*pyridin*-2-*yl*)*ethyl*]*phenyl*-C,N,N′}-*palladium*(II), $[Pd\{(NC_5H_4CHMe)_2C_6H_3\}Cl]$ (**2**).—A white flocculent suspension formed on addition of sodium chloride (0.119 g, 2.04 mmol) to a stirred suspension of complex (**1**) (0.614 g, 1.36 mmol) in acetone (16 cm^3) and water (8 cm^3). After stirring for 2 h the colourless microcrystalline product was collected, washed with water, and dried under vacuum over P_2O_5 (yield 0.534 g, 1.24 mmol, 91%), m.p. >250 °C; $\nu_{max.}$ at 1 602m, 1 564w, 1 480m, 1 430m br, 1 280w, 1 246w, 1 158m, 814m, 784m, 776m, 760s, 598w, 564w, 542w, and 510w cm^{-1}.

(*Aqua*){2,6-*bis*[1-(*pyridin*-2-*yl*)*ethyl*]*phenyl*-C,N,N′}-*palladium*(II) *Tetrafluoroborate Hemihydrate*, $[Pd\{(NC_5H_4CHMe)_2C_6H_3\}(H_2O)][BF_4]\cdot 0.5H_2O$ (**3**).—Silver tetrafluoroborate (0.211 g, 1.08 mmol) in water (5 cm^3) was added to a suspension of complex (**2**) (0.472 g, 1.10 mmol) in acetone (15 cm^3) and stirred for 6 h. After removal of AgCl the filtrate was slowly evaporated in a draught to give colourless flocculent crystals, which were collected and recrystallized from acetone (yield 0.393 g, 0.77 mmol, 72%), m.p. 167—168 °C; $\nu_{max.}$ at 3 500vs vbr (H_2O), 1 642m br, 1 608s, 1 574w, 1 484m, 1 458m, 1 064vs vbr (BF_4), 812m, 788m, 778m, 760s, and 732s cm^{-1}.

(*Acetato*-O)[2,6-*bis*(2-*pyridinecarbonyl*)*phenyl*-C,N,N′]-*palladium*(II), $[Pd\{(NC_5H_4CO)_2C_6H_3\}(O_2CMe)]$ (**4**).—This complex was obtained from palladium(II) acetate and $(NC_5H_4CO)_2C_6H_4$ in glacial acetic acid as described for (**1**), but chromatographic purification was not needed, recrystallization from dichloromethane–acetone giving (**4**) as a pale yellow crystalline solid (72%), m.p. >250 °C; $\nu_{max.}$ at 1 660s (CO), 1 616s, 1 590s (CO_2), 1 442m, 1 374m (CO_2), 1 280m, 1 242m, 1 156m, 832m, 754s, 716s, and 666s cm^{-1}.

Crystallography.—For each complex a unique data set measured at 295 K with a preset $2\theta_{max.}$ limit (determined by the extent of the data) was measured using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ—θ scan mode with monochromatic Mo-K_α radiation ($\lambda = 0.710\,69$ Å), yielding N independent reflections, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the basically 9 × 9 block-diagonal least-squares refinement after absorption correction, and solution of the structures by the heavy-atom method. Complex (**1**) is formulated as a sesquihydrate on the basis of refinement of difference-map artefacts; the half molecule of water lies on a two-fold axis and is fully weighted. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (x, y, z, U_{iso}) for hydrogen atoms were included at estimated values, although the locations of these atoms were indicated in difference maps. Neutral complex scattering factors were used;[11] computation with the XTAL 83 program system was implemented[12] by S. R. Hall on a Perkin-Elmer 3240 computer.

Crystals of (**1**) were obtained as described above and crystals of (**4**) were obtained by dissolution of the complex in 1:1 dichloromethane–acetone followed by diffusion of diethyl ether vapour in a sealed chamber.

Crystal data. (**1**), $C_{22}H_{25}N_2O_{3.5}Pd$, $M = 479.9$, monoclinic, space group $C2/c$ (C^6_{2h}, no. 15), $a = 26.08(1)$, $b = 11.093(6)$, $c = 15.846(7)$ Å, $\beta = 116.19(3)°$, $U = 4\,113(3)$ Å^3, $Z = 8$, $D_c = 1.55$ g cm^{-3}, $F(000) = 1\,960$. Specimen: 0.20 × 0.13 × 0.28 mm, μ(Mo-K_α) = 8.7 cm^{-1}, $A^*_{min.,max.} = 1.11$, 1.22 (analytical correction), $2\theta_{max.} = 55°$, $N = 4\,483$, $N_o = 2\,909$, $R = 0.042$, $R' = 0.041$ [statistical weights; (**4**) also].

(**4**), $C_{20}H_{14}N_2O_4Pd$, $M = 452.8$, monoclinic, space group Pc(C^2_s, no. 7), $a = 11.373(6)$, $b = 10.925(6)$, $c = 15.640(10)$ Å, $\beta = 116.98(4)°$, $U = 1\,732(1)$ Å^3, $Z = 4$, $D_c = 1.74$ g cm^{-3}, $F(000) = 904$. Specimen: 0.08 × 0.40 × 0.13 mm, μ(Mo-K_α) = 10.3 cm^{-1}, $A^*_{min.,max.} = 1.08$, 1.17 (Gaussian correction), $2\theta_{max.} = 50°$, $N = 3\,078$, $N_o = 2\,677$, $R = 0.043$, $R' = 0.048$ (both chiralities).

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