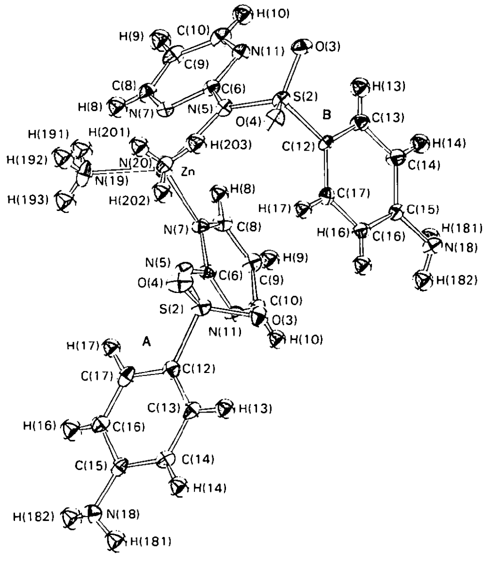

Fig. 1. Perspective view of a molecule of the title compound.

C—C distance is 1·385 Å, scatter ±0·007 Å in *A*; 1·391 Å, scatter ±0·015 Å in *B*; individual atom-position errors are ±0·006 to 0·007 Å.

The biggest differences in bond distances between ligand *A* and ligand *B* occur in the N(5)—S(2) bond distance, 0·041 Å longer in ligand *B* which is complexed to Zn at N(5); in N(5)—C(6), which is 0·022 Å longer in ligand *B*; and in N(11)—C(10), which is 0·16 Å longer in ligand *A* where the pyrimidine ring is complexed at N(7). It also should be pointed out that it is the N(5)—C(6) distance in the complexes which shows the greatest change from the bond distances observed in the uncomplexed pyrimidine structures already reported. The N(5)—C(6) bond distance is significantly shorter in the complexed ligand *A*. The S(2)—C(12) distances are significantly longer in the complexes as compared to the uncomplexed ligands, and the C(6)—N(7) and C(6)—N(11) pyrimidine bond distances also appear to be lengthened in the complexes.

The rather small differences in bond distances observed between ligands *A* and *B* may be due, in part, to the fact that although they might be characterized as ligand *A* coordinated at a pyrimidine N atom and ligand *B* coordinated at the imido N atom, the pyrimidine N(7) in ligand *B* is also 2·406 Å from the Zn atom and may also be involved in the coordination. [The imido N(5) atom in ligand *A* at 2·729 Å from the Zn atom is probably too far away to be involved significantly in bonding. It is interesting to note, however, that the combination of the distances 2·078 and 2·729 Å in ligand *A* and 2·166 and 2·406 Å in ligand *B* each combine to produce almost the same total bonding as judged from Pauling's (1947) bond order–bond-length relationship as the Zn atom bonds to the NH_3 groups.]

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Dichloro[(4*S*,7*R*)-7,8,8-trimethyl-2-(2-pyridyl)-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazole]palladium(II), $C_{16}H_{19}Cl_2N_3Pd$

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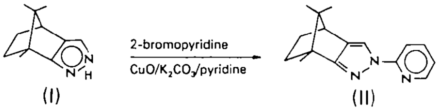
(*Received* 18 *May* 1983; *accepted* 3 *August* 1983)

Abstract. $M_r = 430·66$, orthorhombic, $P2_12_12_1$, $a = 13·154$ (2), $b = 15·394$ (4), $c = 8·402$ (2) Å, $V = 1701·4$ Å^3, $Z = 4$, $D_m = 1·66$ (1), $D_x = 1·68$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 13·8$ cm^{-1}, $F(000) = 864$, $T = 293$ K. Final $R = 0·035$ for 1659 observed reflections. The pyrazole and pyridine rings are both planar

and inclined by only 5·3 (4)° to one another. Comparison of the molecular geometry with literature data indicates little steric resistance to coordination by the ligand.

Introduction. As part of a study involving the synthesis of new optically active bidentate ligands for use as chiral auxiliaries in asymmetric organic synthesis, the ligand (II) was prepared by Ullmann condensation (Khan & Polya, 1970) of (I) (Jacquier & Maury, 1967) with 2-bromopyridine. In order to assess the steric requirements of this ligand the title palladium complex was prepared [from ligand (II) and $PdCl_2$ in 2*M* HCl] for single-crystal X-ray analysis since the literature contains useful comparative data in the form of structural parameters for palladium complexes with sterically encumbered ligands.



Experimental. Orange crystal, 0·3 × 0·1 × 0·1 mm, from water–ethanol–acetone. D_m by flotation (aqueous zinc bromide solution). Nicolet *R*3*m* automated four-circle diffractometer, graphite-monochromated Mo *Kα*. Lattice parameters from 22 reflections in range $30 < 2\theta < 35°$; space group $P2_12_12_1$ from systematic absences. $\theta/2\theta$ scans, $2\theta_{\max} = 56°$. Standard reflections (no change) 200, 040, 002. 2380 reflections measured, 1659 with $I > 3\sigma(I)$ used in refinement, *h* 0–17, *k* 0–19, *l* 0–11. Empirical absorption corrections (transmission factor 1·36–1·47) applied. Coordinates of Pd obtained from Patterson calculations, 21 non-H atoms from two sequential difference Fourier maps. Blocked-cascade least-squares refinement, all non-H's anisotropic, H atoms included in calculated positions with isotropic thermal parameters equal to isotropic equivalent of their carrier atoms (C—H 0·96 Å); 199 parameters refined. $R = 0{\cdot}035$, $wR = 0{\cdot}031$, $w = [\sigma^2(F) + 0{\cdot}00008F^2]^{-1}$; $S = 1{\cdot}52$. $(\Delta/\sigma)_{\max} = 0{\cdot}49$ [C(8) *z* coordinate]. $\Delta\rho = -0{\cdot}4$–$0{\cdot}5$ e Å^{-3}. Pd scattering factors from Cromer & Mann (1968), anomalous-dispersion corrections from Cromer & Liberman (1970). *SHELXTL* (Sheldrick, 1981) for structure determination, refinement, geometry calculations and diagram.

Discussion. Positional parameters and equivalent isotropic thermal parameters for the non-H atoms are listed in Table 1.* Bond lengths and angles are in Table 2. Fig. 1 shows a perspective view of the complex and includes the atom labelling.

Table 1. *Atom coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å² ×10³) *with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}*
Pd	8723 (1)	1067 (1)	6432 (1)	47 (1)
Cl(1)	8768 (2)	2263 (1)	4858 (2)	74 (1)
Cl(2)	9437 (2)	292 (2)	4420 (2)	94 (1)
N(1)	8112 (3)	1643 (3)	8398 (6)	42 (1)
N(2)	8278 (4)	1106 (3)	9716 (5)	45 (2)
N(1′)	8790 (4)	50 (3)	7959 (5)	43 (2)
C(2′)	8572 (5)	254 (4)	9487 (7)	43 (2)
C(3′)	8673 (5)	−338 (4)	10709 (8)	54 (2)
C(4′)	9019 (5)	−1151 (5)	10346 (10)	65 (3)
C(5′)	9215 (5)	−1369 (4)	8793 (10)	68 (3)
C(6′)	9094 (5)	−768 (4)	7627 (9)	63 (3)
C(3)	8046 (4)	1527 (4)	11109 (7)	47 (2)
C(3a)	7704 (4)	2316 (4)	10702 (7)	47 (2)
C(4)	7359 (5)	3196 (4)	11282 (9)	58 (2)
C(5)	8279 (5)	3792 (4)	10948 (10)	73 (3)
C(6)	8324 (5)	3841 (4)	9108 (10)	69 (3)
C(7)	7414 (4)	3268 (4)	8538 (9)	53 (2)
C(7a)	7747 (4)	2371 (4)	9017 (7)	45 (2)
C(8)	6630 (5)	3452 (4)	9919 (9)	56 (2)
C(7*m*)	7040 (6)	3448 (5)	6846 (9)	77 (3)
C(8*a*)	6245 (6)	4398 (4)	9992 (10)	87 (3)
C(8*s*)	5692 (5)	2859 (4)	9803 (10)	73 (3)

* U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Pd(1)–Cl(1)	2·269 (2)	Pd(1)–Cl(2)	2·272 (2)
Pd(1)–N(1)	2·039 (5)	Pd(1)–N(1′)	2·026 (5)
N(1)–N(2)	1·399 (7)	N(1)–C(7a)	1·326 (7)
N(2)–C(2′)	1·381 (8)	N(2)–C(3)	1·372 (8)
N(1′)–C(2′)	1·352 (8)	N(1′)–C(6′)	1·350 (8)
C(2′)–C(3′)	1·379 (9)	C(3′)–C(4′)	1·366 (9)
C(4′)–C(5′)	1·372 (12)	C(5′)–C(6′)	1·357 (11)
C(3)–C(3a)	1·339 (9)	C(3a)–C(4)	1·510 (9)
C(3a)–C(7a)	1·419 (9)	C(4)–C(5)	1·545 (9)
C(4)–C(8)	1·544 (10)	C(5)–C(6)	1·549 (11)
C(6)–C(7)	1·563 (9)	C(7)–C(7a)	1·504 (8)
C(7)–C(8)	1·578 (10)	C(7)–C(7*m*)	1·530 (11)
C(8)–C(8*a*)	1·543 (10)	C(8)–C(8*s*)	1·539 (9)

Cl(1)–Pd(1)–Cl(2)	88·9 (1)	Cl(1)–Pd(1)–N(1)	97·4 (1)
Cl(2)–Pd(1)–N(1)	173·5 (1)	Cl(1)–Pd(1)–N(1′)	174·6 (2)
Cl(2)–Pd(1)–N(1′)	92·7 (1)	N(1)–Pd(1)–N(1′)	80·8 (2)
Pd(1)–N(1)–N(2)	108·8 (3)	Pd(1)–N(1)–C(7a)	145·9 (4)
N(2)–N(1)–C(7a)	104·2 (5)	N(1)–N(2)–C(2′)	119·6 (5)
N(1)–N(2)–C(3)	111·2 (5)	C(2′)–N(2)–C(3)	129·1 (5)
Pd(1)–N(1′)–C(2′)	114·4 (4)	Pd(1)–N(1′)–C(6′)	127·1 (4)
C(2′)–N(1′)–C(6′)	118·4 (5)	N(2)–C(2′)–N(1′)	114·4 (5)
N(2)–C(2′)–C(3′)	123·4 (6)	N(1′)–C(2′)–C(3′)	122·2 (5)
C(2′)–C(3′)–C(4′)	118·1 (6)	C(3′)–C(4′)–C(5′)	120·0 (7)
C(4′)–C(5′)–C(6′)	119·8 (7)	N(1′)–C(6′)–C(5′)	121·4 (7)
N(2)–C(3)–C(3a)	106·6 (5)	C(3)–C(3a)–C(4)	146·3 (6)
C(3)–C(3a)–C(7a)	107·2 (5)	C(4)–C(3a)–C(7a)	106·3 (5)
C(3a)–C(4)–C(5)	103·8 (5)	C(3a)–C(4)–C(8)	100·1 (5)
C(5)–C(4)–C(8)	101·6 (6)	C(4)–C(5)–C(6)	103·9 (6)
C(5)–C(6)–C(7)	104·4 (6)	C(6)–C(7)–C(7a)	102·3 (5)
C(6)–C(7)–C(8)	100·0 (5)	C(7a)–C(7)–C(8)	99·1 (5)
C(6)–C(7)–C(7*m*)	115·4 (6)	C(7a)–C(7)–C(7*m*)	120·6 (6)
C(8)–C(7)–C(7*m*)	116·2 (5)	N(1)–C(7a)–C(3a)	110·8 (5)
N(1)–C(7a)–C(7)	141·0 (6)	C(3a)–C(7a)–C(7)	108·1 (5)
C(4)–C(8)–C(7)	95·4 (5)	C(4)–C(8)–C(8*a*)	114·5 (6)
C(7)–C(8)–C(8*a*)	114·4 (6)	C(4)–C(8)–C(8*s*)	113·2 (6)
C(7)–C(8)–C(8*s*)	111·8 (6)	C(8*a*)–C(8)–C(8*s*)	107·4 (5)

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38788 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

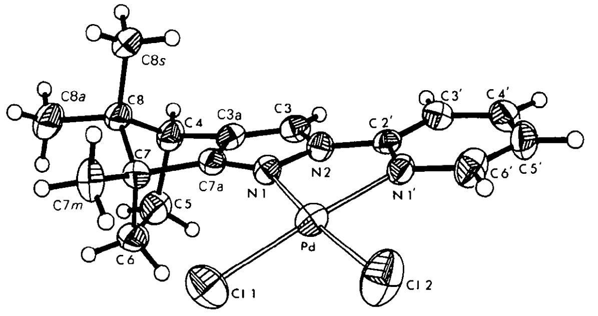

Fig. 1. Perspective view and atom labelling of the title complex. Thermal ellipsoids are drawn at the 35% probability level; H atoms with 0·15 Å radii.

The study confirms the structure of the ligand and its absolute configuration (as determined by anomalous dispersion) is consistent with that of (+)-camphor (Northolt & Palm, 1966) from which it was synthesized. The pyrazole and pyridine rings are both planar (mean deviations 0·007 and 0·010 Å respectively) and only slightly inclined [5·3 (4)°] to one another.

Coordination about Pd is essentially planar with no significant pyramidal distortion as is observed in Pd^{II} complexes with sterically encumbered ligands (Newkome, Fronczek, Gupta, Puckett, Pantaleo & Kiefer, 1982). Indeed the N(1), N(1′), Pd and Cl(2) atoms are coplanar (mean deviation 0·004 Å) with Cl(1) slightly displaced [0·188 (2) Å] from the plane, probably due to a weak C(7*m*)methyl···Cl(1) interaction. Also, the Pd—N bonds [2·039 (5) and 2·026 (5) Å] show no significant lengthening due to steric interactions as is the case with more bulky ligands (Deeming, Rothwell, Hursthouse & Backer-Dirks, 1979; Newkome *et al.*, 1982). Indeed the parameters defined by Newkome *et al.* (1982) to describe molecular distortions in such square-planar complexes [out-of-plane distortions: $d_1 = 0{\cdot}203\ (2)$, $d_2 = 0{\cdot}025\ (2)$ Å; ring tilts: $\beta_1 = 9{\cdot}3\ (2)$, $\beta_2 = 6{\cdot}0\ (2)$; ring coplanarity distortions: $\gamma_1 = 5{\cdot}8\ (5)$, $\gamma_2 = 1{\cdot}7\ (5)°$] are all considerably less than those observed in dichloro(6-methyl-2,2′-bipyridine)palladium(II).

In conclusion, the chiral ligand (II) appears to offer little steric resistance to coordination and hence it and related ligands currently under study should prove useful chiral auxiliaries in synthesis.

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Acta Cryst. (1983). C**39**, 1625–1628

5,10,15,20-Tetraphenylporphyrin–Bis(trifluoroacetic acid)–Dioxouranium(VI) Trifluoroacetate, $C_{44}H_{30}N_4.2C_2HF_3O_2.[UO_2][C_2F_3O_2]_2$

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Abstract. $M_r = 1339$, monoclinic, Pc, $a = 9{\cdot}593\ (8)$, $b = 17{\cdot}481\ (4)$, $c = 15{\cdot}816\ (9)$ Å, $\beta = 97{\cdot}3\ (2)°$, $Z = 2$, $V = 2631\ (7)$ Å^3, $D_x = 1{\cdot}69$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 9{\cdot}85$ mm^{-1}, $T = 233\ (5)$ K, $F(000) = 1304$, final $R = 0{\cdot}068$ for 3417 observed reflections. The structural features generate a pseudosymmetry which renders the interpretation of the Fourier synthesis and refinement of the structure difficult. The uranyl group has no direct contact with the tetraphenylporphyrin (TPP) but presents a pentacoordination in the equatorial plane with five O atoms belonging to four trifluoroacetate groups. Hydrogen bonds connect the TPP and the bridging trifluoroacetic acid molecules (Htfa).

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