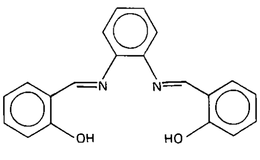
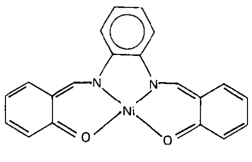
The non-planar free-ligand molecule (Pahor, Calligaris, Delise, Dodic, Nardin & Randaccio, 1976) on coordination to Ni assumes a more planar form. The whole molecule is planar to within 0·27 Å. The two Schiff-base moieties containing O(1), N(1), C(8), C(9), C(10), C(11), C(12), C(13), C(14), and O(2), N(2), C(1), C(2), C(3), C(4), C(5), C(6), C(7), which in themselves are planar [deviations from plane being 0·032 (8) and 0·042 (10) Å] are inclined at 11·5 (3)° to each other, forming a shallow umbrella form as reported in other similar structures.

Comparison of bond lengths observed in free and Ni-coordinated ligands shows no significant variation except in O—C and C—C [C(3)—C(4) and C(13)—C(14)] shortening and lengthening respectively. If it is assumed that the free ligand has predominantly the enamine structure (1*a*), on coordination to Ni the contribution from the ketamine structure (1*b*) increases as observed in the Co complex. The other C—C lengths are less affected. The phenyl rings are all planar to within about 0·021 Å. The root-mean-square deviation of the fitted atoms from the plane of all the non-hydrogen atoms is 0·1365 Å.



(1*a*)



(1*b*)

There are no short contacts observed in the structure and the packing in the unit cell is determined solely by van der Waals forces.

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Structure of *trans*(*P*,*N*)-Bis(μ-pyridyl-C^2,*N*)-bis[chloro(triphenylphosphine)palladium(II)],* $[Pd_2Cl_2(C_5H_4N)_2\{P(C_6H_5)_3\}_2]$

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Abstract. $M_r = 964{\cdot}5$, monoclinic, $P2_1/c$, $a = 10{\cdot}460$ (5), $b = 32{\cdot}751$ (25), $c = 13{\cdot}020$ (10) Å, $\beta = 108{\cdot}12$ (5)°, $V = 4239$ (5) Å^3, $Z = 4$, $D_m = 1{\cdot}56$ (2), $D_x = 1{\cdot}511$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 10{\cdot}678$ cm^{-1}, $F(000) = 1936$, $T = 292$ K, $R = 0{\cdot}075$ for 2424 unique observed reflections. The two palladium atoms lie in the line of intersection of the two pyridyl planes with average Pd—C bond lengths 1·99 Å and average Pd—N bond lengths 2·06 Å. The central six-membered ring assumes a boat conformation. Each palladium atom is bonded in a square-planar configuration.

Introduction. This crystal structure was undertaken to determine the conformation of the molecule, which was originally assumed to contain chlorine-bridged palladium atoms with pyridyl and triphenylphosphine ligands.

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* *a*,*f*-Dichloro-di-μ-(pyridyl-C^2,*N*)-*b*,*e*-bis(triphenylphosphine)dipalladium(II).

Experimental. Density measured by flotation. Crystal dimensions $0{\cdot}11 \times 0{\cdot}10 \times 0{\cdot}18$ mm, modified Picker FACS-I diffractometer. Lattice parameters determined from centered positions of 50 reflections in range $13 < 2\theta < 33°$. Integrated intensities of 4937 independent reflections with $\sin\theta/\lambda < 0{\cdot}59$ Å^{-1}, $0 < h < 10$, $0 < k < 38$, $-12 < l < 14$, measured in θ–2θ scan mode. Intensities of three standard reflections measured after those of every 47 normal reflections showed no systematic trends. The standard deviation of the intensity of a reflection, I, was calculated from the counting statistics of the individual counts associated with its observation with an additional contribution derived from the extent to which the scatter in the intensities of the standard reflections exceeded that expected from counting statistics. The standard deviation in the structure amplitude, $\sigma(F)$, is given by $\sigma(F) = [I + \sigma(I)]^{1/2} - (I)^{1/2}$ and the weight of a reflection, $w(F)$, is given by $w(F) = [\sigma(F)]^{-2}$.

Structure solved by Patterson methods and refined on $|F|$ by least squares using 2424 reflections for which $I > 3\sigma(I)$ or $F > 6{\cdot}46\sigma(F)$. The least-squares refinement showed that the weights calculated in this way were biased to overemphasize the very strong reflections. However, the trend in the magnitudes of $|F_o| - |F_c|$ for these reflections did not suggest that they were significantly affected by secondary extinction. The weighting scheme was modified to $w(F) = [\sigma^2(F) + 5 \times 10^{-6}\,|F|^2]^{-1}$ to remove the bias toward the strong reflections. Palladium, phosphorus and chlorine atoms refined anisotropically and all carbon and nitrogen atoms refined isotropically. Corrections for anomalous dispersion for these atoms from *International Tables for X-ray Crystallography* (1974). Hydrogen atoms not considered in refinement. Maximum excursion in residual electron density corresponded to $\rho = 0{\cdot}75$ e Å^{-3}. Final values of R, wR, S and $(\Delta/\sigma)_{\max}$ 0·075, 0·080, 2·36 and 0·05, respectively. *XRAY76* system of programs (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) used for all major calculations.

Discussion. Final positional parameters and isotropic or equivalent isotropic temperature factors are given in Table 1.* Important bond lengths and bond angles and the atom labeling are given in Fig. 1. The carbon atoms in Ph_1 to Ph_6 are numbered C(29) to C(34), C(35) to C(40), C(41) to C(46), C(11) to C(16), C(17) to C(22) and C(23) to C(28), respectively. Fig. 2 shows a stereoview of the molecule. The correct identification of the nitrogen atoms in the pyridyl rings is supported by consistent temperature factors in refinement, slightly shorter bond lengths to carbon than for carbon–carbon bonds and the necessity to satisfy valence conditions on the palladium atoms. Furthermore, elemental analysis gave 55·9%C, 3·9%H and 2·8%N by weight compared to the expected formula weights of 51·6%C, 3·6%H and 2·6%N.

The pyridyl rings bridge the palladium atoms instead of chlorine atoms and a chlorine atom and a triphenylphosphine group are bonded to each palladium atom. The central portion of the molecule is a

Table 1. *Positional and isotropic thermal parameters with e.s.d.'s*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}(Å^2)
Pd(1)	0·2416 (2)	0·6387 (1)	0·4767 (1)	0·045
Pd(2)	0·2886 (2)	0·6465 (1)	0·7281 (1)	0·043
Cl(1)	0·2832 (6)	0·5731 (1)	0·4154 (5)	0·066
Cl(2)	0·0905 (6)	0·6578 (2)	0·7774 (5)	0·065
P(1)	0·0205 (6)	0·6380 (6)	0·3805 (4)	0·043
P(2)	0·3504 (6)	0·5907 (6)	0·8340 (4)	0·038
N(1)	0·436 (2)	0·6407 (5)	0·578 (1)	0·046 (5)
N(2)	0·246 (2)	0·6987 (5)	0·635 (1)	0·046 (5)
C(1)	0·224 (2)	0·6946 (6)	0·529 (2)	0·044 (6)
C(2)	0·194 (2)	0·7296 (7)	0·457 (2)	0·060 (7)
C(3)	0·193 (2)	0·7675 (8)	0·505 (2)	0·080 (8)
C(4)	0·212 (2)	0·7722 (8)	0·616 (2)	0·072 (8)
C(5)	0·245 (2)	0·7353 (7)	0·683 (2)	0·061 (7)
C(6)	0·459 (2)	0·6443 (6)	0·688 (2)	0·043 (6)
C(7)	0·586 (2)	0·6465 (7)	0·763 (2)	0·055 (6)
C(8)	0·697 (2)	0·6461 (7)	0·721 (2)	0·062 (7)
C(9)	0·679 (2)	0·6380 (8)	0·615 (2)	0·074 (8)
C(10)	0·544 (2)	0·6367 (7)	0·543 (2)	0·064 (7)
C(11)	0·408 (2)	0·6076 (6)	0·977 (2)	0·045 (6)
C(12)	0·414 (2)	0·5781 (7)	1·061 (2)	0·060 (7)
C(13)	0·452 (2)	0·5948 (7)	1·169 (2)	0·065 (7)
C(14)	0·482 (2)	0·6343 (8)	1·186 (2)	0·082 (8)
C(15)	0·480 (3)	0·6627 (8)	1·108 (2)	0·087 (9)
C(16)	0·439 (2)	0·6492 (7)	0·996 (2)	0·055 (7)
C(17)	0·226 (2)	0·5513 (6)	0·830 (2)	0·041 (6)
C(18)	0·120 (3)	0·5623 (3)	0·865 (2)	0·091 (9)
C(19)	0·016 (3)	0·5292 (9)	0·967 (2)	0·113 (11)
C(20)	0·036 (3)	0·4908 (8)	0·836 (2)	0·074 (8)
C(21)	0·146 (3)	0·4812 (8)	0·811 (2)	0·077 (8)
C(22)	0·243 (2)	0·5114 (7)	0·805 (2)	0·073 (8)
C(23)	0·486 (2)	0·5599 (6)	0·811 (2)	0·041 (6)
C(24)	0·463 (2)	0·5487 (7)	0·701 (2)	0·057 (7)
C(25)	0·562 (2)	0·5214 (7)	0·681 (2)	0·056 (6)
C(26)	0·669 (2)	0·5072 (7)	0·763 (2)	0·072 (8)
C(27)	0·689 (2)	0·5189 (7)	0·872 (2)	0·058 (7)
C(28)	0·591 (2)	0·5447 (6)	0·896 (2)	0·046 (6)
C(29)	−0·012 (2)	0·6308 (6)	0·237 (2)	0·041 (6)
C(30)	0·098 (2)	0·6278 (6)	0·197 (2)	0·052 (6)
C(31)	0·078 (2)	0·6254 (7)	0·085 (2)	0·072 (8)
C(32)	−0·052 (3)	0·6241 (7)	0·016 (2)	0·072 (8)
C(33)	−0·166 (2)	0·6255 (6)	0·051 (2)	0·055 (6)
C(34)	−0·144 (2)	0·6301 (7)	0·165 (2)	0·066 (7)
C(35)	−0·076 (2)	0·6825 (6)	0·389 (2)	0·048 (6)
C(36)	−0·092 (2)	0·6918 (7)	0·492 (2)	0·062 (7)
C(37)	−0·159 (3)	0·7281 (9)	0·505 (2)	0·094 (9)
C(38)	−0·212 (3)	0·7547 (9)	0·416 (3)	0·124 (12)
C(39)	−0·185 (3)	0·7476 (9)	0·320 (3)	0·112 (11)
C(40)	−0·123 (3)	0·7112 (8)	0·304 (2)	0·083 (8)
C(41)	−0·071 (2)	0·5982 (6)	0·426 (2)	0·039 (6)
C(42)	0·003 (3)	0·5723 (9)	0·508 (2)	0·101 (9)
C(43)	−0·070 (3)	0·5424 (9)	0·548 (2)	0·106 (10)
C(44)	−0·203 (3)	0·5352 (8)	0·499 (2)	0·083 (9)
C(45)	−0·277 (3)	0·5604 (9)	0·424 (2)	0·090 (9)
C(46)	−0·209 (3)	0·5944 (8)	0·384 (2)	0·083 (8)

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* Lists of structure factors, anisotropic temperature factors, parameters of least-squares planes and additional details of molecular geometry have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42174 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

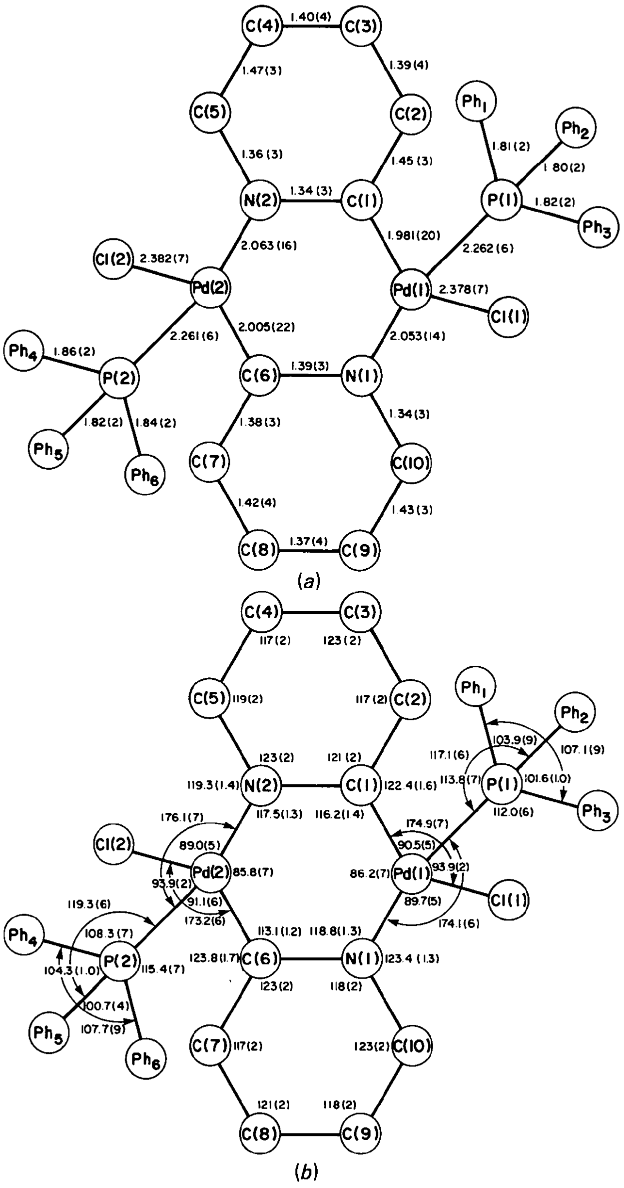

Fig. 1. Geometry and atom labeling, (*a*) bond lengths (Å), (*b*) bond angles (°).

six-membered ring [Pd(1), N(1), C(6), Pd(2), N(2), C(1)] in a boat conformation. The molecule contains a local pseudo twofold rotation axis about the center of this ring. The two palladium atoms lie at the intersection of the planes of the two pyridyl rings so that the molecule is folded about the palladium–palladium vector with a fold angle of 97·4 (1)°. The Pd(1)—Pd(2) distance is 3·165 (3) Å, which is slightly longer than that normally assumed for bonded Pd=Pd bonds (2·61–2·98 Å, Brown, Brown & Hawthorne, 1981). Each palladium atom is bonded in a square-planar configuration. The boat conformation of the central ring tilts these planes with respect to each other.

The bromine analog of the molecule has been reported by Nakatsu, Kinoshita, Kanda, Isobe, Nakamura & Kawaguchi (1980). The geometry of the molecule is similar to that reported here. The greater electronegativity and smaller size of the chlorine atoms are consistent with the observation that in the chlorine compound the carbon, nitrogen and phosphorus atoms show shorter bond lengths to the palladium atoms than in the bromine compound. In spite of the similarity in the geometry of the two molecules they pack quite differently. The bromine analog is triclinic, space group $P\bar{1}$, $Z = 2$. In the chlorine compound the Pd—C bond lengths (average 1·99 Å) and the Pd—Cl bond lengths (average 2·380 Å) are both among the shorter values for recently reported ranges (2·00 to 2·04 Å for Pd—C bonds and 2·40 to 2·45 Å for Pd—Cl bonds in the same configuration, Brown *et al.*, 1981). Also the Pd—N bond lengths (average 2·06 Å) and the Pd—P bond lengths (average 2·262 Å) are relatively short (2·07 to 2·15 Å for Pd—N bonds and 2·30 to 2·35 Å for Pd—P bonds, Brown *et al.*, 1981).

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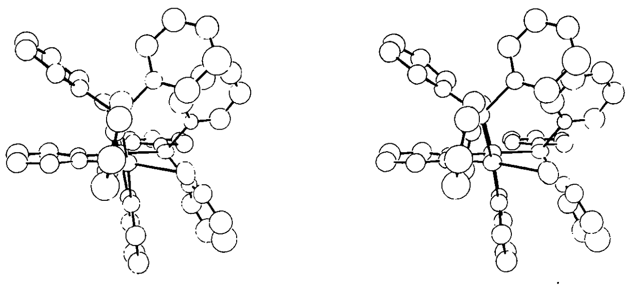

Fig. 2. Stereoscopic view of the molecule.

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