of an adjacent layer, producing a polymeric structure. The water molecule stabilizes the crystal structure, however, by participation in five separate hydrogen bonds. It acts as an acceptor in a hydrogen bond from N(2) in the parent ligand, and from N(3) of an adjacent thiosemicarbazide. One of the water H atoms participates in a single donor bond to Cl(1) of a symmetry-related neighbor, and the other takes part in a bifurcated donation to Cl(1) and Cl(2) of two other neighbors. Details are shown in Fig. 3.

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A Tetrahedrally Surrounded Nickel(II) Complex: The Structure of Dichloro[2-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine-*N*,*P*]nickel(II)

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Abstract. [$NiCl_2(C_{21}H_{22}NP)$], $M_r = 449{\cdot}01$, triclinic, $P\bar{1}$, $a = 10{\cdot}220\ (8)$, $b = 13{\cdot}820\ (20)$, $c = 16{\cdot}550\ (2)$ Å, $\alpha = 76{\cdot}48\ (7)$, $\beta = 73{\cdot}49\ (4)$, $\gamma = 76{\cdot}84\ (8)°$, $V = 2146\ (4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}390$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54184$ Å, $\mu = 41{\cdot}34$ cm^{-1}, $F(000) = 928$, $T = 298$ K, $R = 0{\cdot}0485$ for 5090 observed reflections. The asymmetric unit consists of two independent molecules which show only minor differences in the corresponding bond distances and angles, but significant differences in some of the torsion angles of the six-membered metalla ring which has a boat conformation. The Ni^{II} atoms are tetrahedrally surrounded by two Cl atoms, one P and one N atom.

Introduction. The catalytic activity of nickel–phosphine complexes in the cross-coupling of Grignard reagents with aryl and alkenyl halides was reported by Corriu & Masse (1972) and Tamao, Sumitani & Kumada (1972). Since then a wide variety of nickel and palladium catalysts have been developed and some of them have been found to be very successful in cross-coupling reactions (Jolly, 1982). In recent years, asymmetrical cross-coupling with a chiral transition-metal catalyst has become very popular. Recently we reported the crystal structure of a chiral Pd catalyst: dichloro({(1*R*)-[(2*S*)-2-(diphenylphosphino)-1-ferrocenyl]-ethyl}-dimethylamine-*N*,*P*)palladium(II), $PdCl_2$(ppfa) (van der Steen & Kanters, 1986), the synthesis of which is described by Hayashi, Konishi, Fukushima, Mise, Kagotani, Tajika & Kumada (1982). All attempts to isolate the corresponding nickel complex $NiCl_2$(ppfa), however, failed. Since the stereoselectivity of $PdCl_2$(ppfa) and the *in situ* prepared $NiCl_2$(ppfa) catalysts in the cross-coupling of 1-phenylethylmagnesium chloride with vinyl bromide was found to be comparable (Hayashi, Konishi, Fukushima, Mise, Kagotani, Tajika & Kumada, 1982), the authors assumed that the nickel and palladium species were structurally analogous.

We now report the crystal structure of a nickel catalyst with the achiral bidentate ligand 2-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine (ppba) which is comparable to the ppfa ligand.

Experimental. A blue needle-shaped crystal (dimensions 1·0 × 0·1 × 0·1 mm approximately) was used for data collection on an Enraf–Nonius CAD-4F diffractometer with Ni-filtered Cu *Kα* radiation. The lattice parameters were derived from least-squares fitting of four alternative settings of 12 reflections ($7\cdot0 < \theta < 19\cdot2°$) with the 'set 4' method of de Boer & Duisenberg (1984). Intensity data of 8137 unique reflections, of which 5090 were considered observed with $I \geq 2\cdot5\sigma(I)$, were collected within one half of the reflection sphere: $0 \leq h \leq 12$, $-16 \leq k \leq 16$, $-20 \leq l \leq 20$; $2\theta_{\max} = 140°$. Scan mode ω–2θ, with $\Delta\omega = (0\cdot50 + 0\cdot15\tan\theta)°$. During data collection two standard reflections (220 and 022), measured every hour, showed no significant variation. The intensities were corrected for Lorentz and polarization effects.

The space group was assumed to be $P\bar{1}$, which was confirmed by the results of the refinement. The structure was solved by Patterson techniques followed by tangent expansion (*SHELX*84; Sheldrick, 1984). After isotropic positional refinement ($R = 0\cdot123$) an empirical absorption correction was applied with the *DIFABS* program (Walker & Stuart, 1983), resulting in $R = 0\cdot106$; min. and max. absorption corrections were 0·82 and 1·55 respectively.

All H atoms were introduced on calculated positions (C—H = 1·0 Å). Two-block full-matrix refinement on *F*, including overall scale factor, positional and anisotropic thermal parameters of the non-H atoms and an overall isotropic thermal parameter for the H atoms, resulted in $R = 0\cdot0485$ and $wR = 0\cdot0565$, where $w = 1\cdot9364/[\sigma^2(F) + 0\cdot000398(F_o)^2]$. The overall thermal parameter for the H atoms refined to 0·098 (6) Å^2. $\Delta/\sigma = 0\cdot003$ (av.) and 0·012 (max.). Final residual electron density $-0\cdot22 < \Delta\rho < 0\cdot55$ e Å^{-3}.

The scattering factors for the non-H atoms were taken from Cromer & Mann (1968), those for the H atoms from Stewart, Davidson & Simpson (1965); anomalous-dispersion factors were taken from Cromer & Liberman (1970). The calculations were performed with *SHELX*76 (refinement) (Sheldrick, 1976) and the *EUCLID* package (geometry and illustrations) (Spek, 1982).

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*
Molecule (I)				
Ni(1)	0·24595 (7)	0·01638 (5)	0·27993 (4)	0·0532 (3)
Cl(11)	0·2561 (1)	−0·0709 (1)	0·40953 (7)	0·0790 (5)
Cl(12)	0·2137 (2)	−0·0488 (1)	0·17919 (9)	0·0940 (5)
P(1)	0·4369 (1)	0·0944 (1)	0·2198 (1)	0·0403 (3)
N(1)	0·1020 (4)	0·1470 (3)	0·2859 (2)	0·066 (1)
C(1)	0·1643 (5)	0·2399 (4)	0·2674 (3)	0·065 (2)
C(11)	0·0094 (5)	0·1600 (5)	0·2280 (4)	0·102 (3)
C(12)	0·0146 (6)	0·1407 (5)	0·3761 (3)	0·105 (3)
C(111)	0·5887 (4)	0·0246 (3)	0·1568 (2)	0·046 (1)
C(112)	0·7223 (4)	0·0204 (3)	0·1653 (3)	0·053 (2)
C(113)	0·8361 (5)	−0·0340 (3)	0·1155 (3)	0·063 (2)
C(114)	0·8178 (5)	−0·0824 (4)	0·0575 (3)	0·071 (2)
C(115)	0·6870 (6)	−0·0797 (4)	0·0488 (3)	0·079 (2)
C(116)	0·5729 (5)	−0·0265 (4)	0·0985 (3)	0·064 (2)
C(121)	0·5038 (4)	0·1444 (3)	0·2893 (2)	0·037 (1)
C(122)	0·4899 (4)	0·0973 (3)	0·3740 (2)	0·047 (1)
C(123)	0·5509 (4)	0·1287 (3)	0·4259 (3)	0·056 (2)
C(124)	0·6249 (4)	0·2067 (3)	0·3946 (3)	0·053 (2)
C(125)	0·6368 (4)	0·2547 (3)	0·3107 (3)	0·052 (1)
C(126)	0·5778 (4)	0·2246 (3)	0·2576 (2)	0·047 (1)
C(131)	0·3784 (4)	0·2057 (3)	0·1462 (2)	0·047 (2)
C(132)	0·2488 (5)	0·2635 (3)	0·1766 (3)	0·054 (2)
C(133)	0·2023 (6)	0·3484 (4)	0·1208 (4)	0·079 (2)
C(134)	0·2777 (8)	0·3747 (5)	0·0399 (4)	0·093 (3)
C(135)	0·4051 (7)	0·3183 (5)	0·0106 (3)	0·088 (2)
C(136)	0·4559 (5)	0·2326 (4)	0·0638 (3)	0·066 (2)
Molecule (II)				
Ni(2)	0·24174 (8)	0·46192 (5)	0·70647 (4)	0·0516 (3)
Cl(21)	0·2543 (1)	0·5116 (1)	0·82222 (7)	0·0774 (5)
Cl(22)	0·2599 (2)	0·5674 (1)	0·58320 (8)	0·0861 (5)
P(2)	0·0448 (1)	0·3915 (1)	0·7367 (1)	0·0421 (3)
N(2)	0·3833 (4)	0·3328 (3)	0·6859 (2)	0·064 (1)
C(2)	0·3212 (5)	0·2394 (3)	0·7209 (3)	0·060 (2)
C(21)	0·4519 (6)	0·3351 (4)	0·5936 (3)	0·092 (2)
C(22)	0·4911 (6)	0·3238 (5)	0·7329 (4)	0·112 (3)
C(211)	−0·1006 (4)	0·4732 (3)	0·6997 (2)	0·048 (1)
C(212)	−0·2339 (4)	0·4853 (3)	0·7511 (3)	0·058 (2)
C(213)	−0·3410 (5)	0·5468 (4)	0·7179 (3)	0·071 (2)
C(214)	−0·3154 (6)	0·5945 (4)	0·6344 (3)	0·080 (2)
C(215)	−0·1843 (6)	0·5859 (4)	0·5828 (3)	0·088 (2)
C(216)	−0·0765 (5)	0·5253 (4)	0·6154 (3)	0·073 (2)
C(221)	−0·0292 (4)	0·3350 (3)	0·8469 (2)	0·042 (1)
C(222)	−0·0200 (4)	0·3739 (3)	0·9143 (2)	0·055 (2)
C(223)	−0·0844 (5)	0·3355 (4)	0·9979 (3)	0·066 (2)
C(224)	−0·1559 (5)	0·2573 (4)	1·0136 (3)	0·068 (2)
C(225)	−0·1636 (5)	0·2165 (4)	0·9473 (3)	0·062 (2)
C(226)	−0·1020 (4)	0·2554 (3)	0·8636 (3)	0·054 (2)
C(231)	0·0914 (4)	0·2874 (3)	0·6775 (2)	0·046 (1)
C(232)	0·2210 (4)	0·2265 (3)	0·6746 (2)	0·050 (1)
C(233)	0·2561 (6)	0·1466 (3)	0·6297 (3)	0·069 (2)
C(234)	0·1659 (6)	0·1281 (4)	0·5901 (3)	0·085 (2)
C(235)	0·0384 (6)	0·1880 (4)	0·5935 (3)	0·080 (2)
C(236)	0·0011 (5)	0·2673 (4)	0·6371 (3)	0·064 (2)

* $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

Discussion. The asymmetric part of the structure consists of two independent molecules of the title compound. The atomic coordinates and isotropic thermal parameters are listed in Table 1, bond distances, angles and selected torsion angles of the metalla ring are listed in Table 2.* A perspective view

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and internal geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44294 (56 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å), *angles* (°) *and selected torsion angles* (°) *for labelled atoms of molecule* (I) *and their counterparts in molecule* (II)

	Molecule (I)	Molecule (II)
Ni(1)—Cl(11)	2·219 (4)	2·225 (4)
Ni(1)—Cl(12)	2·202 (4)	2·200 (4)
Ni(1)—P(1)	2·305 (4)	2·310 (4)
Ni(1)—N(1)	2·055 (5)	2·055 (5)
P(1)—C(111)	1·815 (5)	1·813 (5)
P(1)—C(121)	1·817 (5)	1·824 (4)
P(1)—C(131)	1·824 (5)	1·827 (5)
N(1)—C(1)	1·492 (7)	1·490 (6)
N(1)—C(11)	1·484 (7)	1·485 (6)
N(1)—C(12)	1·500 (6)	1·488 (8)
C(1)—C(132)	1·507 (7)	1·504 (7)
Cl(11)—Ni(1)—Cl(12)	123·3 (1)	120·1 (1)
Cl(11)—Ni(1)—P(1)	110·2 (1)	109·9 (1)
Cl(11)—Ni(1)—N(1)	111·7 (1)	110·4 (1)
Cl(12)—Ni(1)—P(1)	107·0 (1)	109·5 (1)
Cl(12)—Ni(1)—N(1)	105·1 (1)	107·4 (1)
P(1)—Ni(1)—N(1)	96·2 (2)	97·0 (2)
Ni(1)—P(1)—C(111)	117·3 (2)	115·6 (2)
Ni(1)—P(1)—C(121)	118·3 (2)	119·3 (2)
Ni(1)—P(1)—C(131)	104·7 (2)	106·3 (2)
C(111)—P(1)—C(121)	104·7 (2)	104·9 (2)
C(111)—P(1)—C(131)	106·3 (2)	104·8 (2)
C(121)—P(1)—C(131)	104·3 (2)	104·6 (2)
Ni(1)—N(1)—C(1)	113·6 (3)	112·7 (3)
Ni(1)—N(1)—C(11)	112·1 (3)	112·0 (3)
Ni(1)—N(1)—C(12)	107·9 (3)	108·3 (3)
C(1)—N(1)—C(11)	109·0 (4)	109·1 (4)
C(1)—N(1)—C(12)	105·8 (4)	105·8 (4)
C(11)—N(1)—C(12)	108·2 (4)	108·6 (4)
N(1)—C(1)—C(132)	113·8 (4)	114·8 (4)
P(1)—C(111)—C(112)	122·0 (3)	123·0 (3)
P(1)—C(111)—C(116)	119·5 (4)	118·3 (3)
P(1)—C(121)—C(122)	119·0 (3)	120·3 (3)
P(1)—C(121)—C(126)	121·5 (3)	120·2 (3)
P(1)—C(131)—C(132)	117·0 (3)	118·1 (3)
P(1)—C(131)—C(136)	122·3 (4)	121·9 (4)
C(1)—C(132)—C(131)	122·4 (4)	123·3 (4)
C(1)—C(132)—C(133)	119·9 (5)	118·7 (4)
Ni(1)—P(1)—C(131)—C(132)	45·0 (4)	40·4 (3)
P(1)—C(131)—C(132)—C(1)	3·8 (6)	2·8 (5)
C(131)—C(132)—C(1)—N(1)	−71·7 (6)	−69·4 (5)
C(132)—C(1)—N(1)—Ni(1)	65·9 (5)	69·0 (4)
C(1)—N(1)—Ni(1)—P(1)	−10·5 (3)	−17·1 (3)
N(1)—Ni(1)—P(1)—C(131)	−36·7 (2)	−29·0 (2)

with atomic numbering of molecule (I) is depicted in Fig. 1. With a few exceptions bond lengths and angles are generally as expected. The two independent molecules have very similar geometries, as is borne out by the average deviations of corresponding distances, angles and torsion angles of non-H atoms, which amount to 0·006 (5) Å, 0·8 (7) and 4 (3)° respectively. In the discussion of the geometry data referring to molecule (II) will be placed between brackets.

In the title compound Ni is coordinated by the bidentate ligand ppba and two Cl atoms. The coordination is tetrahedral as follows from the average value of 109 (9)° [109 (7)°] of the six angles subtending at Ni, and the dihedral angle of 88·7 (1)° [89·0 (1)°] between the Cl—Ni—Cl and P—Ni—N planes.

Tetrahedrally surrounded Ni^{II} complexes are relatively rare, as is shown by a search in the Cambridge Crystallographic Database that resulted in only 25 hits with tetrahedral angles within the range of 100–120° out of a total of 764 four-coordinated complexes with liganding atoms C, H, O, N, P, S, F, Cl, Br and/or I. The tetrahedral complexes are usually of the types NiX_4^{2-}, NiX_3L^-, NiX_2L_2 and $Ni(L-L)_2$ where X is a halogen, L_2 two neutral ligands or a neutral bidentate ligand, and $L-L$ a bidentate ligand which is uninegatively charged (Cotton & Wilkinson, 1976).

From the set of tetrahedral Ni^{II} compounds only two are of the type $NiCl_2L_2$: dichloro[oxydiethylenebis(diphenylphosphine)]nickel(II) [NiCl$_2$(pop)] (Green & Sacconi, 1970) and dichlorobis(acetophenone thiosemicarbazone)nickel(II) [NiCl$_2$(bat)] (Dapporto, de Munno & Tomlinson, 1984).

The overall conformation of NiCl$_2$(ppba) is chiefly governed by the metalla-ring conformation which is a slightly distorted boat as is indicated by the Cremer & Pople (1975) ring puckering parameters: $\theta = 87{\cdot}3$ (3)° [91·2 (3)°] and $\varphi = 59{\cdot}8$ (3)° [64·9 (3)°]. Though the average deviation of the endocyclic torsion angles of molecules (I) and (II) is small [4 (3)°], that of the torsion angles involving Cl atoms is significantly larger [10 (2)°].

The P—Ni—N angle is small {96·2 (2)° [97·0 (2)°]}, which is probably caused by the rigidity of the bidentate ligand, whereas the Cl—Ni—Cl angle is large {123·3 (1)° [120·1 (1)°]} in accordance with observations in the aforementioned complexes NiCl$_2$(pop) and NiCl$_2$(bat): 127·1 (2) and 124·3 (2)° respectively. The Ni—Cl distances, 2·219 (4) and 2·202 (4) Å [2·225 (4) and 2·200 (4) Å], correspond well to those of NiCl$_2$(pop) and NiCl$_2$(bat) whose values average to 2·220 (4) and 2·243 (2) Å respectively. These values are consistent with the value calculated assuming covalent radii of 0·99 Å for chlorine (Bondi, 1964) and 1·21 Å for tetrahedrally coordinated Ni^{II} (Pauling, 1960).

The average C—C distance and C—C—C angle of the phenyl rings are 1·384 (3) Å [1·381 (3) Å] and 119·9 (8)° [120·0 (9)°] respectively. The three phenyl

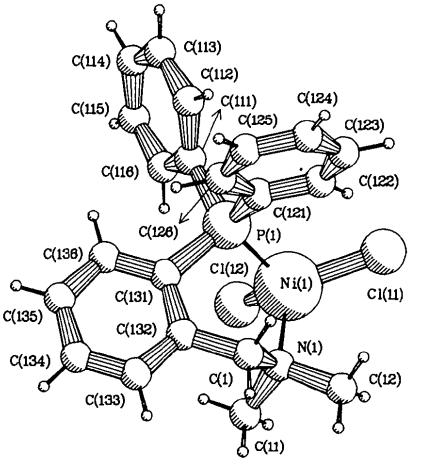

Fig. 1. Perspective view of the molecular conformation and atomic numbering of molecule (I) of the title compound. The numbering of molecule (II) can be derived from that of molecule (I) by changing the first digit of the labels into a 2.

rings are planar within 0·005 Å with interplanar angles between the free rings of 75·2 (2)° [78·4 (2)°] and between the free and the anchored rings of 74·4 (2)° [73·5 (2)°] and 85·4 (2)° [82·2 (2)°].

The shortest intermolecular contacts are between H···H (2·36 Å) C···H (2·74 Å) and Cl···H (2·75 Å).

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Structure of Trichlorobis(dimethyl sulfoxide)(1-methylbenzimidazole)rhodium(III) Dimethyl Sulfoxide Solvate

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Abstract. [$RhCl_3(C_2H_6OS)_2(C_8H_8N_2)$].$C_2H_6OS$, $M_r = 575{\cdot}82$, orthorhombic, *Pbca*, $a = 14{\cdot}088\,(3)$, $b = 15{\cdot}774\,(8)$, $c = 20{\cdot}623\,(5)$ Å, $V = 4583\,(3)$ Å^3, $Z = 8$, $D_x = 1{\cdot}669$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu = 13{\cdot}7$ cm^{-1}, $F(000) = 2336$, $T = 295$ K, $R = 0{\cdot}0440$ for 2554 observed reflections with $I > 2\sigma(I)$. The Rh atom is octahedrally coordinated by three meridional Cl atoms, two *cis* sulfur-bonded dimethyl sulfoxide molecules and an N atom of the 1-methylbenzimidazole ligand. The Rh—Cl bond [2·358 (2) Å] *trans* to dimethyl sulfoxide is significantly longer than the two mutually *trans*-positioned Rh—Cl bonds [2·340 (2), 2·341 (2) Å].

Introduction. In the course of a program aimed at the development of catalysts containing a metal centre with coordinated imidazole ligands we have synthesized the title rhodium complex (Niele, Zwikker & Nolte, 1986; Smeets, Sijbesma, Niele, Spek, Smeets & Nolte, 1987). It is the first example of a Rh^{III} complex with an *N*-bonded benzimidazole derivative as a ligand that has been characterized by X-ray methods. The title compound was obtained from a reaction of $RhCl_3$ with 1-methylbenzimidazole in dimethyl sulfoxide (Me_2SO). It resembles the crystal structure of $Rh(Me_2SO)_3Cl_3$ with the oxygen-bonded Me_2SO molecule replaced by the present 1-methylbenzimidazole ligand (Sokol & Porai-Koshits, 1975).

Experimental. Crystals were obtained by recrystallization from Me_2SO. A block-shaped transparent orange crystal 0·20 × 0·25 × 0·37 mm suitable for X-ray diffraction was sealed in a Lindemann-glass capillary to avoid loss of Me_2SO. Enraf–Nonius CAD-4F diffractometer, Zr-filtered Mo $K\alpha$ radiation, unit-cell parameters and their e.s.d.'s were derived from

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