decamolybdate anions. In the ammonium and thallium salts, the MoO_4 units occupy the linking sites b in Fig. 2, whereas they are situated at the a sites in MAM. The distance $Mo(3)\cdots Mo(5)$, $3\cdot 661$ (1) Å, in MAM is significantly shorter than those in the NH_4^+ [$3\cdot 700$ (1) Å] and Tl^+ salts [$3\cdot 741$ (3) Å].

Such linkage isomers have been found in the octamolybdate anions represented by [$(X)_2Mo_8-O_{26}]^{2n-4}$, where n is the formal charge of the coordinated base, X (McCarron, Whitney & Chase, 1984). MAM has the same linkage mode as those of [$H_2Mo_8O_{28}]^{6-} \equiv [(HO)_2Mo_8O_{26}]^{6-}$, [$(HCO)_2Mo_8-O_{28}]^{6-} \equiv [(HCOO)_2Mo_8O_{26}]^{6-}$, [$Mo_8O_{27}]_n^{6-} \equiv [O_{2/2}-Mo_8O_{26}]_n^{6-}$ and [$(C_5H_5N)_2Mo_8O_{26}]^{4-}$ (Isobe, Marumo, Yamase & Ikawa, 1978; Adams, Klemperer & Liu, 1979; Boschen, Buss & Krebs, 1974; McCarron, Whitney & Chase, 1984).

The crystal structure viewed along the c axis is shown in Fig. 3. The decamolybdate anions are connected by N—H$\cdots$O hydrogen bonds. All the N—H groups of the methylammonium cations and the terminal O atoms of the MoO_4 units participate in the three-dimensional hydrogen-bonding scheme.

The crystals of MAM turn red on exposure to UV light but the color does not fade away in the dark. On the other hand, photochromism was observed in crystals of $(C_3H_9N)_6[H_2Mo_8O_{28}]$ (Yamase & Ikawa, 1977). The coloration of these crystals is due to the formation of the photoreduced Mo^V site in the lattice (Yamase, 1978). Based on the fact that the structure of the octamolybdate unit in MAM is the same as that in [$H_2Mo_8O_{28}]^{6-}$, the reason the red color of the

photoreduced MAM is conserved in the dark may be the stabilization of the Mo^V site due to the linkage of the MoO_4 tetrahedra at the corners of the Mo_8O_{28} unit.

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Structure of Dichloro({(1R)-[(2S)-2-(diphenylphosphino)-1-ferrocenyl]ethyl}-dimethylamine-N,P)palladium(II) Deuterochloroform Solvate

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Abstract. [$PdCl_2(C_{26}H_{28}FeNP)].2CDCl_3$, $M_r = 859\cdot 39$, monoclinic, $P2_1$, $a = 9\cdot 9811$ (12), $b = 19\cdot 329$ (2), $c = 10\cdot 013$ (2) Å, $\beta = 114\cdot 78$ (1)°, $V = 1753\cdot 9$ (6) Å^3, $Z = 2$, $D_x = 1\cdot 627$ g cm^{-3}, $\lambda(Cu\ K\alpha) = 1\cdot 54184$ Å, $\mu = 133\cdot 29$ cm^{-1}, $F(000) = 856$, $T = 294$ K, $R = 0\cdot 079$ for 2258 observed reflections. The chelating ligand is bonded to $PdCl_2$ by N and P, resulting in a slightly distorted square-planar Pd^{II} complex. The absolute configuration of the disubstituted ferrocene is S and that of the α-C atom is R. The Cl—Pd—Cl angle is small [$86\cdot 4$ (3)°], a feature that is considered advantageous in stereoselective cross-coupling of organometallic reagents.

Introduction. In recent years there has been considerable interest in stereoselective catalysts for a variety of

reactions. One way of achieving this type of catalysis is the use of a coordinated ligand which possesses one or more chiral centres in order to form a coordination sphere, only allowing specific reactions around the metal. One such ligand is {1-[2-(diphenylphosphino)-ferrocenyl]ethyl}dimethylamine (II) (ppfa) which possesses a chiral centre at the amine-substituted C atom and planar chirality of the disubstituted ferrocene and can be prepared as either optical isomer (Batelle, Bau, Gokel, Oyakawa & Ugi, 1972). A crystal-structure determination established that (+)-ppfa has the (S,R)-configuration (Einstein & Willis, 1980). [(diene)Rh($\pm$)-(ppfa)]$^+X^-$ [diene = 8,9,10-trinorbornadiene (nbd) or cyclooctadiene (cod); $X^- = ClO_4^-$, BF_4^- or PF_6^-] have been applied for the specific hydrogenation of α-acetamidocinnamic acid, giving high optical yields of R [with (+)-(ppfa)] and S [with (−)-(ppfa)] products (Cullen & Yeh, 1977). Now we report the crystal structure of (ppfa)PdCl$_2$.2CDCl$_3$ (I) in which the Pd atom is coordinated by N and P.

Experimental. Crystals obtained from the Department of Organic Chemistry, University of Utrecht, The Netherlands, crystallized from a deuterochloroform solution, used for NMR experiments. Because the crystals were air-sensitive, they were sealed under nitrogen in a capillary tube. Red crystal, 0·78 × 0·14 × 0·35 mm, Enraf–Nonius CAD-4F diffractometer, Ni-filtered Cu $K\alpha$ radiation, $\omega/2\theta$ scan with $\omega = (1\cdot50 + 0\cdot15\tan\theta)°$. Lattice parameters from 14 reflections (θ range 6·7–18·9°), 3443 intensities measured with $2\theta_{max} = 140°$; $0 \le h \le 12, -23 \le k \le 0$, $-12 \le l \le 12$, 2258 reflections with $I > 2\cdot5\sigma(I)$ considered observed. Standard reflections 200 and 0$\bar{2}$1 every 50 reflections (1% variation). Empirical absorption correction with *DIFABS* (Walker & Stuart, 1983) applied. Structure solved with Patterson method, which revealed positions of heavy atoms [Pd, Fe, P, Cl(1) and Cl(2)]. Subsequent difference Fourier synthesis revealed positions of remaining non-H atoms. At this stage a number of peaks showed the presence of two disordered chloroform molecules. The molecules were disordered over several positions; for each Cl atom, three maxima (approximate spacing 0·75 Å) could be assigned. Refinement of the site-occupation factors resulted in 0·72 (2), 0·150 (10) and 0·130 (13) for the first, and 0·73 (2), 0·155 (11) and 0·115 (9) for the second solvent molecule. Non-methyl H atoms placed at calculated positions and assigned isotropic temperature factors of their carrier atoms. Remaining H atoms located from difference maps and included in refinement, with fixed isotropic thermal parameters of their carrier atoms. Temperature factors of methyl C atoms kept isotropic in refinement. Anisotropic, weighted blocked full-matrix refinement on F gave $R = 0\cdot079$, $wR = 0\cdot084$, $w = [\sigma^2(F_o) + 0\cdot002314 F_o^2]^{-1}$ and $S = 3\cdot27$. The relatively high disagreement factor is

Table 1. *Atomic coordinates and isotropic thermal parameters* (Å^2) *for* (ppfa)PdCl$_2$.2CDCl$_3$ *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}^*/U
Pd	0·0573 (2)	0·0000	0·0338 (2)	0·0489 (4)
Fe	−0·3775 (3)	−0·1559 (2)	−0·0628 (4)	0·055 (1)
Cl(1)	0·2629 (6)	−0·0383 (3)	0·0106 (7)	0·062 (2)
Cl(2)	0·1789 (8)	0·1102 (4)	0·0969 (9)	0·090 (3)
P	−0·0077 (6)	−0·1113 (3)	0·0094 (6)	0·044 (2)
N	−0·141 (2)	0·038 (1)	0·035 (2)	0·09 (1)
C(1)	−0·421 (2)	−0·174 (2)	−0·281 (3)	0·08 (1)
C(2)	−0·436 (3)	−0·233 (2)	−0·213 (3)	0·10 (1)
C(3)	−0·542 (3)	−0·228 (2)	−0·157 (3)	0·07 (1)
C(4)	−0·601 (2)	−0·159 (1)	−0·191 (3)	0·07 (1)
C(5)	−0·528 (3)	−0·127 (2)	−0·268 (3)	0·10 (1)
C(6)	−0·195 (2)	−0·180 (1)	0·122 (2)	0·066 (8)
C(7)	−0·319 (2)	−0·163 (2)	0·156 (2)	0·08 (1)
C(8)	−0·358 (3)	−0·094 (2)	0·107 (3)	0·08 (1)
C(9)	−0·263 (2)	−0·068 (1)	0·043 (2)	0·059 (8)
C(10)	−0·164 (2)	−0·127 (1)	0·049 (2)	0·060 (8)
C(11)	−0·274 (2)	0·001 (1)	−0·039 (2)	0·053 (6)
C(12)	−0·416 (2)	0·038 (1)	−0·054 (3)	0·082 (8)
C(13)	−0·107 (4)	0·052 (2)	0·192 (3)	0·12 (1)
C(14)	−0·169 (4)	0·107 (2)	−0·036 (4)	0·12 (1)
C(15)	−0·047 (3)	−0·108 (1)	−0·281 (3)	0·07 (1)
C(16)	−0·067 (4)	−0·136 (2)	−0·412 (3)	0·10 (2)
C(17)	−0·095 (4)	−0·206 (2)	−0·439 (4)	0·10 (2)
C(18)	−0·094 (4)	−0·246 (2)	−0·327 (3)	0·09 (1)
C(19)	−0·070 (3)	−0·217 (1)	−0·187 (3)	0·068 (8)
C(20)	−0·042 (2)	−0·149 (1)	−0·166 (2)	0·051 (8)
C(21)	0·235 (3)	−0·203 (1)	0·113 (3)	0·07 (1)
C(22)	0·342 (3)	−0·241 (1)	0·226 (4)	0·09 (1)
C(23)	0·356 (3)	−0·239 (2)	0·371 (4)	0·11 (2)
C(24)	0·261 (3)	−0·200 (2)	0·399 (3)	0·10 (1)
C(25)	0·147 (2)	−0·166 (1)	0·294 (2)	0·068 (8)
C(26)	0·133 (2)	−0·167 (1)	0·146 (2)	0·054 (6)
C(27)	0·491 (2)	0·0378 (9)	0·377 (2)	0·10 (1)
Cl(3)	0·430 (2)	0·072 (1)	0·501 (2)	0·146 (6)†
Cl(4)	0·618 (3)	0·093 (1)	0·357 (3)	0·21 (2)†
Cl(5)	0·569 (3)	−0·0429 (9)	0·435 (3)	0·20 (1)†
C(28)	0·158 (1)	0·0946 (7)	0·732 (2)	0·095 (9)
Cl(6)	0·289 (1)	0·1548 (7)	0·739 (2)	0·107 (4)†
Cl(7)	0·154 (2)	0·0267 (7)	0·618 (2)	0·133 (7)†
Cl(8)	−0·014 (1)	0·133 (1)	0·672 (3)	0·17 (1)†

* $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.
† Of the three disordered Cl atoms, only the ones with the highest s.o.f.'s are listed.

very probably caused by the inadequate description of the disorder of the CDCl$_3$ molecules. Max. Δ/σ 0·286 for z of C(14) (mean 0·04 for all atoms). Final difference synthesis revealed maximal electron densities of 0·8–1·2 e Å^{-3} at about 0·9–1·3 Å from Pd. The absolute configuration of (ppfa)PdCl$_2$ was assigned as dichloro({(1R)-[(2S)-2-(diphenylphosphino)-1-ferrocenyl]ethyl}dimethylamine)palladium (II) on the basis of its precursor (R,S)-ppfa. This was confirmed by refinement of the inverted model, resulting in $R = 0\cdot1022$, $wR = 0\cdot1103$. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Calculations performed with *SHELX*76, *SHELX*84 (structure determination and refinement) (Sheldrick, 1976, 1984), *DIFABS* (absorption) (Walker & Stuart, 1983) and the *EUCLID* package (illustrations and molecular geometry) (Spek, 1982) on the CDC Cyber-175 of the University of Utrecht.

Table 2. *Bond distances* (Å) *and bond angles* (°) *of* (ppfa)PdCl₂.2CDCl₃

Pd—Cl(1)	2·283 (7)	Pd—Cl(2)	2·401 (8)
Pd—P	2·231 (6)	Pd—N	2·12 (2)
Fe—C(1)	2·07 (3)	Fe—C(6)	2·03 (2)
Fe—C(2)	2·02 (3)	Fe—C(7)	2·02 (2)
Fe—C(3)	2·06 (3)	Fe—C(8)	2·02 (3)
Fe—C(4)	2·06 (3)	Fe—C(9)	2·07 (2)
Fe—C(5)	2·05 (3)	Fe—C(10)	2·03 (2)
C(1)—C(2)	1·37 (5)	C(6)—C(7)	1·45 (3)
C(2)—C(3)	1·39 (5)	C(7)—C(8)	1·42 (5)
C(3)—C(4)	1·44 (4)	C(8)—C(9)	1·44 (4)
C(4)—C(5)	1·41 (4)	C(9)—C(10)	1·49 (3)
C(5)—C(1)	1·45 (5)	C(10)—C(6)	1·37 (3)
C(15)—C(16)	1·35 (4)	C(21)—C(22)	1·40 (4)
C(16)—C(17)	1·39 (5)	C(22)—C(23)	1·40 (5)
C(17)—C(18)	1·36 (5)	C(23)—C(24)	1·33 (5)
C(18)—C(19)	1·43 (4)	C(24)—C(25)	1·35 (4)
C(19)—C(20)	1·34 (3)	C(25)—C(26)	1·43 (3)
C(20)—C(15)	1·38 (3)	C(26)—C(21)	1·38 (4)
N—C(13)	1·49 (3)	N—C(14)	1·48 (4)
C(11)—C(9)	1·55 (3)	C(11)—C(12)	1·54 (3)
C(11)—N	1·41 (3)	P—C(10)	1·79 (2)
P—C(20)	1·80 (2)	P—C(26)	1·84 (2)
Cl(1)—Pd—Cl(2)	86·4 (3)	Cl(1)—Pd—P	84·8 (2)
Cl(1)—Pd—N	174·8 (5)	Cl(2)—Pd—P	167·4 (3)
Cl(2)—Pd—N	93·5 (6)	P—Pd—N	96·1 (6)
Pd—P—C(26)	112·7 (7)	Pd—P—C(10)	112·3 (7)
Pd—P—C(20)	115·2 (7)	Pd—N—C(11)	120 (1)
Pd—N—C(13)	106 (2)	Pd—N—C(14)	107 (2)
C(10)—P—C(20)	109 (1)	C(10)—P—C(26)	101·6 (9)
C(20)—P—C(26)	105·2 (9)	C(11)—N—C(13)	113 (2)
C(11)—N—C(14)	105 (2)	C(13)—N—C(14)	105 (2)
C(2)—C(1)—C(5)	104 (3)	C(7)—C(6)—C(10)	111 (2)
C(1)—C(2)—C(3)	114 (3)	C(6)—C(7)—C(8)	106 (2)
C(2)—C(3)—C(4)	106 (3)	C(7)—C(8)—C(9)	110 (3)
C(3)—C(4)—C(5)	106 (2)	C(8)—C(9)—C(10)	105 (2)
C(1)—C(5)—C(4)	110 (3)	C(6)—C(10)—C(9)	107 (2)
P—C(10)—C(6)	131 (2)	P—C(10)—C(9)	119 (1)
C(16)—C(15)—C(20)	121 (2)	C(22)—C(21)—C(26)	117 (3)
C(15)—C(16)—C(17)	121 (3)	C(21)—C(22)—C(23)	122 (3)
C(16)—C(17)—C(18)	118 (3)	C(22)—C(23)—C(24)	118 (3)
C(17)—C(18)—C(19)	122 (3)	C(23)—C(24)—C(25)	124 (3)
C(18)—C(19)—C(20)	118 (3)	C(24)—C(25)—C(26)	119 (2)
C(15)—C(20)—C(19)	120 (2)	C(21)—C(26)—C(25)	120 (2)
P—C(20)—C(15)	121 (2)	P—C(26)—C(21)	122 (2)
P—C(20)—C(19)	119 (2)	P—C(26)—C(25)	118 (2)
C(10)—C(9)—C(11)	125 (2)	C(9)—C(11)—C(12)	108 (2)
C(8)—C(9)—C(11)	129 (2)	N—C(11)—C(9)	108 (2)
N—C(11)—C(12)	116 (2)		

Table 3. *Deviations of atoms* (Å) *from the least-squares planes of some square-planar* Pd[II] *complexes*

Compound	(I)	(II)	(III)
Pd	−0·029 (6)	−0·056	−0·093
Cl(1)	−0·14 (1)	−0·132	−0·124
Cl(2)	0·14 (1)	0·151	0·177
P	0·148 (9)	0·161	0·199
N	−0·12 (2)	−0·124	−0·158
Fe*	−0·29 (2)		

* Atom not included in the least-squares calculation.

Discussion. Atomic coordinates and isotropic thermal parameters are listed in Table 1;* the molecular geometries in Table 2. A view of the molecule with atomic numbering is presented in Fig. 1.

The (ppfa)PdCl₂ complex is one of the few examples of square-planar complexes where both N and P are bonded to the metal, as is the case in the [(ppfa)-Rh(nbd)]⁺PF₆⁻ complex (III) (Cullen, Einstein, Huang, Willis & Yeh, 1980).

The square-planar arrangement about Pd is slightly distorted as in the [N,N-dimethyl-α-methyl-o-(butyl-phenylphosphino)benzylamine]PdCl₂ (IV) (Takenaka, Sasada, Yamamoto & Tsuji, 1977) and [(8-methyl-2-quinolylmethyl)di-*tert*-butylphosphino]PdCl₂ (V) complexes (Deeming, Rothwell, Hursthouse & Malik, 1980). The Cl(1)—Pd—P and Cl(2)—Pd—N planes have a twist angle of 6·8 (2)° [7·1° in (IV) and 8·3° in (V)]. Deviations from the least-squares planes are given in Table 3. These distortions of the square-planar arrangement are caused by repulsions, *e.g.* in (I) between Cl(2) and C(14) [Cl(2)···C(14) 3·16 Å]. The Pd—P and Pd—N distances [2·231 (6) and 2·12 (2) Å] are normal. The mutually *cis* Cl atoms have normal bond lengths: Pd—Cl(2) 2·401 (8) and Pd—Cl(1) 2·283 (7) Å. The longer bond to Cl(2) reflects the larger *trans* effect of P over N, as is also found in both (IV) and (V). The Cl—Pd—Cl angle is small [86·4 (3)°], which has also been observed in (IV) and the (dppf)PdCl₂† complex (VI) (Hayashi, Konishi, Kobori, Kumada, Higuchi & Hirotsu, 1984). This structural feature is considered advantageous in stereoselective cross-coupling of organometallic reagents. The P—Pd—N angle is large [96·1 (6)°], as in (III) and (IV). In (V) this angle is 82·3°, which is probably caused by the smaller metalla-ring size [five atoms in (V) and six in (I), (III) and (IV)].
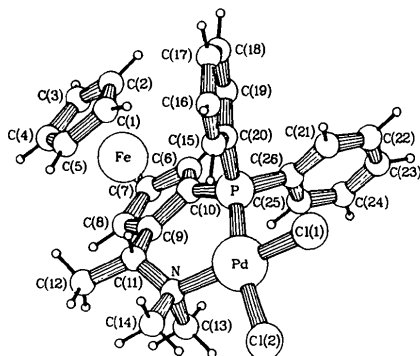

Fig. 1. A perspective view of the molecular conformation of (ppfa)PdCl₂. The disordered solvent molecules are omitted for clarity.

† dppf = 1,1'-bis(diphenylphosphino)ferrocene.

Complexation with $PdCl_2$ causes ppfa to assume a conformation different from that observed in the crystal structures of the free ligand and the Rh(nbd) complex. There is a rotation of −65° about P—C(10) [−40° in (III)] and of −10° about C(9)—C(11) [−100° in (III)], compared with the free ligand. The rotation about P—C(10) brings one phenyl ring into proximity with the ferrocenyl moiety and forces this ring to be 'edge-on' to the Pd atom and the other ring to be 'face-on' [angles between the least-squares planes of the rings and of the coordination plane are 71 (1) and 88·0 (9)° respectively]. The distortion from tetrahedral geometry of C(11) is less than in (III) (probably due to the smaller metal—N and —P distance in the $PdCl_2$ complex), which causes less strain in the formation of the six-membered chelating ring. Puckering parameters $[Q = 0·63 (2)$ Å, $\theta = 105 (2)°$ and $\varphi = 64 (2)°$ for the sequence Pd—P—C(10)—C(9)—C(11)—N] indicate that the metalla-ring has a distorted boat conformation.

Bond lengths and angles are generally as expected. The Fe atom is located near the line between the centroids [Cp(i)] of the cyclopentadienyl rings [angle Cp(1)—Fe—Cp(2) = 176·6 (2)°] and lies 1·67 (8) Å beneath the plane of the unsubstituted ring and 1·64 (6) Å above the plane of the substituted ring, as is commonly observed in ferrocenyl derivatives.

In the crystal packing, the two disordered $CDCl_3$ molecules only fill the space between the (ppfa)$PdCl_2$

molecules and have weak interactions [shortest intermolecular contacts: $Cl(2)\cdots D(1) = 2·45 (2)$ and $Cl(1)\cdots D(2)(x,y,z−1) = 2·74 (2)$ Å].

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Structure of [N,N'-4-Methyl-4-azaheptane-1,7-diylbis(salicylideneiminato)]copper(II) Benzene Solvate

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Abstract. $[Cu(C_{21}H_{25}N_3O_2)].C_6H_6$, $M_r = 493·1$, monoclinic, $P2_1/a$, $a = 13·095 (3)$, $b = 16·671 (4)$, $c = 11·532 (3)$ Å, $\beta = 93·78 (4)°$, $V = 2512 (1)$ Å^3, $Z = 4$, $D_x = 1·30$ Mg m^{-3}, λ(Mo $K\alpha) = 0·7107$ Å, $\mu = 8·95$ mm^{-1}, $F(000) = 1036$, $T = 298$ K, $R = 0·073$ for 1746 unique observed reflections. The structure is similar to that of the analogous Co^{II} compound. Crystals of both compounds are monoclinic and can be obtained from benzene solutions. The Cu atom is linked to three N and to two O atoms of the ligand and the coordination geometry is distorted trigonal bipyramidal. The O(1)—Cu—O(2) angle is 145·6 (3)°, 15·8° larger than the corresponding angle in the Co complex. The Cu—N(3) distance [2·337 (9) Å] is longer than the Co—N(3) length [2·15 (1) Å]. Conversely, the other two Cu—N bond lengths [average 1·954 (8) Å] are shorter than the corresponding Co—N distances [average 2·04 (1) Å]. Again a disorder of the ligand's atoms bound to N(3) is present. The benzene molecule is almost coplanar with the equatorial coordination plane and lies in the proximity of the metal atom. An H atom belonging to the benzene molecule points towards the metal at a distance of 2·90 Å from the cation.

Introduction. Continuing structural investigations of N,N'-4-methyl-4-azaheptane-1,7-diylbis(salicylidene-iminato) (hereafter SALMeDPT)–metal complexes and their dioxygen adduct to understand the stereo-