Tetrakis(1,2-diaminoethane)dibromodiplatinum(II,IV) Tetraperchlorate and Bis(1,2-diaminopropane)platinum(II)bis(1,2-diaminopropane)diiodoplatinum(IV) Tetraiodide: Three-Dimensionally-Ordered and Three-Dimensionally-Disordered Wolffram's Salt Analogues

By H. Endres, H. J. Keller, R. Martin and U. Traeger

Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg 1, Federal Republic of Germany

and M. Novotny

Stanford University, Physics Department, Stanford, California 94305, USA

Abstract

$[Pt(C_2H_8N_2)_2][Pt(C_2H_8N_2)_2Br_2](ClO_4)_4$ (1) crystallizes in the orthorhombic space group *I*222, $a = 9.658$ (4), $b = 10.940$ (4), $c = 13.550$ (3) Å, $Z = 2$. $[Pt(C_3H_{10}N_2)_2][Pt(C_3H_{10}N_2)_2I_2]I_4$ (2) crystallizes in the orthorhombic space group *Pmnm*, $a = 5.770$ (2), $b = 7.299$ (4), $c = 19.981$ (5) Å, $Z = 2$. The two structures were solved by Patterson and Fourier methods from diffractometer data and refined by least squares to $R = 0.064$ for 720 independent reflections for (1) and to $R = 0.087$ for 954 independent reflections for (2). In contrast to other Wolffram's salts, neither rotating-crystal nor oscillation photographs of (1) and (2) showed evidence for a one-dimensional superstructure along the $Pt^{IV}-X\cdots Pt^{II}$ chain. Compound (1) is a Wolffram's salt analogue with a repeat distance of two Pt–Pt separations, originating from the ClO_4^- positions. In (2), halide and ligand atoms are statistically disordered in all three dimensions. The two different $Pt^{IV}-X\cdots Pt^{II}$ distances along the chains are 2.71 (2) and 2.76 (2) Å in (1) and 2.995 (2) and 2.815 (2) Å in (2).

Introduction

Crystals of Wolffram's red salt and its analogues contain linear chains of halide-bridged platinum ions in the two different oxidation states, Pt^{II} and Pt^{IV} (Craven & Hall, 1961; Ryan & Rundle, 1961; Wallén, Brosset & Vannerberg, 1962; Brown & Hall, 1976; Bekaroglu, Breer, Endres, Keller & Nam Gung, 1977; Breer, Endres, Keller & Martin, 1978; Yamashita, Matsumoto & Kida, 1978; El Sharif, Endres, Keller, Martin & Traeger, 1978; Endres, Keller, Martin, Nam Gung & Traeger, 1979; Matsumoto, Yamashita & Kida, 1979). In the classification scheme for

mixed-valence solids proposed by Robin & Day (1967), these compounds could be grouped in class II (Day, 1977) if the $Pt^{IV}-X\cdots Pt^{II}$ distances along the chains alternate. The pattern has been found so far in all of these compounds. This structural classification agrees well with the physical properties of these materials (Breer, Endres, Keller & Martin, 1978; Day, 1975, 1977; Interrante, Browall & Bundy, 1974, and references therein; Clark, Franks & Trumble, 1976; Interrante & Bundy, 1977).

Further structural investigations on these linear-chain mixed-valence systems were carried out in this laboratory with the aim of answering two questions:

(i) Are there any compounds with non-alternating Pt–*X*–Pt distances? Such a compound would contain Pt in a formal oxidation state of III.

(ii) Of what type are the three-dimensional interactions in these 'one-dimensional' materials?

Here we report the X-ray structure and optical-reflectivity data of two more Wolffram's salt analogues, both showing only slight distortions from an equidistant Pt–*X*–Pt chain.

Experimental

Preparation of compounds

$[Pten_2][Pten_2Br_2](ClO_4)_4$ (1) was prepared as described earlier (Bekaroglu, Breer, Endres, Keller & Nam Gung, 1977). Instead of the green needles, which were found recently to crystallize in a monoclinic space group (Bekaroglu, Breer, Endres, Keller & Nam Gung, 1977), the platelets with a greenish lustre were used for the investigation described here. They turned out to be orthorhombic.

Table 1. *Crystal data of* (1) *and* (2)

	Compound (1)	Compound (2)
	[Pten$_2$][Pten$_2$Br$_2$](ClO$_4$)$_4$	[Pt(dapn)$_2$][Pt(dapn)$_2$I$_2$]I$_4$
M_r	1067·64	1447·8
	Orthorhombic *I*222	Orthorhombic *Pmnm*
a (Å)	9·658 (4)	5·770 (2)
b (Å)	10·940 (4)	7·299 (4)
c (Å)	13·550 (3)	19·981 (5)
V (Å^3)	1432	1684
Z	2	2
d_c (Mg m^{-3})	2·5	2·9

[Pt(dapn)$_2$][Pt(dapn)$_2$I$_2$]I$_4$ (2) was prepared from Pt(dapn)$_2$Cl$_2$ (dapn = 1,2-diaminopropane) (Bekaroglu, Breer, Endres, Keller & Nam Gung, 1977) by precipitating the Cl$^-$ with Ag$_2$O and acidifying with HI. One half of the aqueous solution of Pt(dapn)$_2$I$_2$ obtained in this way was oxidized with a solution of I$_2$ in ethanol. The Pt(dapn)$_2$I$_2$ and Pt(dapn)$_2$I$_4$ solutions were evaporated to dryness *in vacuo*. The residues were dissolved in methanol and mixed together. Adding a mixture of acetone and petroleum ether (40–60) precipitated a blue-brown powder. It was dissolved in methanol and several ml of *n*-butanol, and the solution was allowed to evaporate. Golden, shiny, dichroic, plate-like crystals of (2) formed together with a brown powder.

Rotating-crystal and Weissenberg photographs (Cu *K*α radiation) showed the symmetry and systematic extinctions, and yielded approximate lattice constants. Exact lattice constants (Table 1) were calculated by least squares (Berdesinsky & Nuber, 1966) from the θ values of 13 reflections for (1) and 26 reflections for (2), measured on a diffractometer.

Intensity measurements obtained on a Siemens diffractometer [Mo *K*α radiation, θ–2θ scans, five-value method, $2\theta \le 60°$ for (1), $2\theta \le 55°$ for (2)] yielded 720 observed independent reflections for (1) and 954 for (2). In both cases reflections with $I \le 2·58(I)$ were classified as unobserved. Intensities were corrected only for Lorentz and polarization factors. Calculations were performed on Siemens 301 (Anorganisch-Chemisches Institut, Heidelberg) and IBM 370/168 computers (Universitätsrechenzentrum, Heidelberg) with programs of the XRAY system (Stewart, Kundell & Baldwin, 1970). Scattering factors were those of Hanson, Herman, Lea & Skillman (1964).

Structure determination and refinement

(1): The systematic absences ($h + k + l = 2n + 1$) correspond to the centrosymmetric space group *Immm* and to noncentrosymmetric *Imm*2, *I*222 and *I*2$_1$2$_1$2$_1$. The positions of Pt, Cl and Br(1) midway between the Pt sites could be found in a Patterson synthesis. N and C atoms were located from Fourier maps. Difference

maps were necessary to find the O atoms. Only the refinement in *I*222 was successful.

Br was shifted away from its central position between Pt(1) and Pt(2) and the *y* parameter was left free to adjust. The ClO$_4^-$ ion and the ligand had to be refined separately. Least-squares refinement in *I*222 gave *R* = 0·10 with isotropic and *R* = 0·064 with anisotropic temperature factors. The ClO$_4^-$ refined badly, showing large standard deviations in the bond distances and angles. Atomic coordinates are listed in Table 2.*

(2): The systematic absences ($h0l$ with $h + l = 2n + 1$) correspond to the centrosymmetric space group *Pmnm* and to the noncentrosymmetric *Pmn*2$_1$. A Patterson synthesis yielded the positions of Pt, I(2), and I(1) exactly midway between the Pt sites. N and C atoms were located from Fourier maps. Least-squares refinement was successful in *Pmnm* with anisotropic temperature factors for Pt and I and isotropic for C and N. With I(1) midway between the Pt atoms *R* = 0·093 was obtained. The *R* factor dropped to 0·087 when I(1) was left free to adjust in the *x* direction. This drop in *R* on releasing I(1) from its constrained position was shown to be significantly better within the 0·005

---

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34773 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic coordinates* ($\times 10^3$) *of compound* (1)

	x	y	z
Pt(1)	0	0	0
Pt(2)	0	500	0
Br	0	248 (2)	0
N(1)	177 (5)	0 (4)	95 (2)
N(2)	157 (4)	500 (4)	102 (2)
C(1)	286 (6)	57 (7)	34 (5)
C(2)	297 (6)	464 (6)	54 (5)
Cl	424 (1)	755 (4)	201 (8)
O(1)	509 (14)	651 (6)	233 (5)
O(2)	304 (5)	770 (10)	211 (8)
O(3)	460 (10)	758 (9)	96 (3)
O(4)	477 (12)	855 (3)	240 (3)

Table 3. *Atomic coordinates* ($\times 10^3$) *of compound* (2)

	x	y	z
Pt	250	341·5 (2)	250
I(1)	762 (2)	342·5 (6)	250
I(2)	250	156·6 (5)	635·7 (3)
N(1)	250	148 (4)	327 (2)
N(2)	250	530 (4)	327 (1)
C(1)	203 (9)	436 (6)	106 (2)
C(2)	183 (9)	251 (7)	108 (3)
C(3)	218 (29)	145 (15)	438 (5)
C(4)	242 (46)	539 (10)	454 (3)

level of Hamilton's (1965) test. No improvement in R could be achieved with anisotropic refinement of the ligand atoms. The only effect of the calculations was poorer standard deviations in the anisotropic U_{ij} values of the C atoms than in the isotropic U values. Atomic coordinates are listed in Table 3.*

Description of the structure

Fig. 1 shows the $[Pten_2]^{2+}$ complex units as a projection on to the ac plane. The bond angles and bond distances of the two crystallographically inequivalent complex units of (1) are shown in Table 4. The bond distances and angles of the ClO_4^- counter ion are shown in Table 5. The Br atoms refined to positions which yield Pt—Br distances of 2·71 (2) and 2·76 (2) Å, which are not significantly different. Thus, within experimental error, the Br is located midway between the Pt sites. Similar arguments hold for the Pt—N distances in the two cations [Pt(1)—N(1) = 2·03 (5), Pt(2)—N(2) = 2·07 (4) Å]. This implies crystallographically different but possibly chemically equivalent Pt^{III} units, within experimental error.

Fig. 2 shows one complex unit of (2) projected on to the bc plane. The point-group symmetry of the Pt sites ($2mm$) implies a statistical disorder of the ligand atoms to fulfil the symmetry conditions. The mirror plane in the PtN_4 plane generates two sites for each C, one above and one below the plane. Therefore the C atoms have to be inserted into the calculations with an occupancy factor of 0·5. For the symmetry conditions
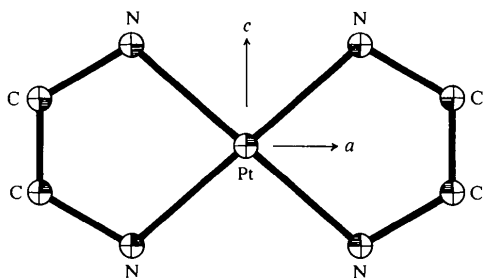
* See previous footnote.

Fig. 1. A projection of the $[Pten_2]^{2+}$ cations on to the ac plane. For numbering scheme, bond lengths and angles see Table 4. The spheres are drawn with arbitrary values for the thermal parameters.

Table 4. *Bond lengths* (Å) *and bond angles* (°) *of the* $[Pten_2]^{2+}$ *cations of compound* (1)

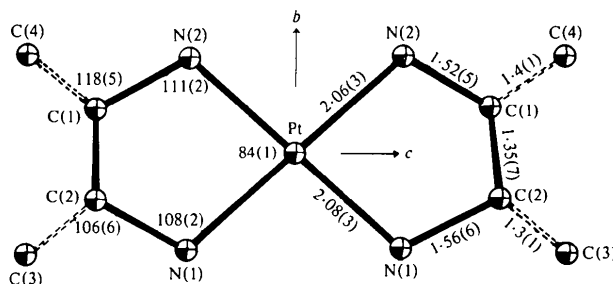|			
Pt(1)—N(1)	2·03 (5)	N(1)—Pt(1)—N(1)	78 (2)
N(1)—C(1)	1·48 (8)	Pt(1)—N(1)—C(1)	104 (4)
C(1)—C(1)	1·55 (9)	N(1)—C(1)—C(1)	113 (2)
Pt(2)—N(2)	2·07 (4)	N(2)—Pt(2)—N(2)	84 (1)
N(2)—C(2)	1·54 (7)	Pt(2)—N(2)—C(2)	111 (3)
C(2)—C(2)	1·67 (9)	N(2)—C(2)—C(2)	105 (4)

Fig. 2. A projection of the $[Pt(dapn)_2]^{2+}$ cation on to the bc plane with the numbering scheme, bond lengths (Å) and bond angles (°). The four possible orientations of the methyl group of the statistically disordered ligand are indicated by dotted lines. The spheres are drawn with arbitrary values for the thermal parameters.

Table 5. *Bond lengths* (Å) *and bond angles* (°) *of the* ClO_4^- *ion of compound* (1)

Cl—O(1)	1·46 (4)	O(1)—Cl—O(2)	120 (3)
Cl—O(2)	1·23 (3)	O(1)—Cl—O(3)	104 (3)
Cl—O(3)	1·49 (3)	O(1)—Cl—O(4)	109 (4)
Cl—O(4)	1·35 (4)	O(2)—Cl—O(3)	108 (3)
		O(2)—Cl—O(4)	107 (4)
		O(3)—Cl—O(4)	105 (2)

it would be sufficient to locate one methyl group (and its mirror image generated by the mirror plane parallel to the PtN_4 plane) on each side of the complex, cis to each other. However, a difference Fourier synthesis showed prominent maxima at the two other possible methyl sites. Insertion of C with an occupancy factor of $\frac{1}{4}$ at each site lowered R by 0·001. The additional methyl sites are indicated by dotted bonds in Fig. 2. Two half-occupied I positions in the strand are found and result in Pt—I separations of 2·815 (2) and 2·995 (2) Å, respectively.

Discussion and comparison with other Wolffram's salt analogues

Usually Wolffram's salt analogues show a one-dimensional superstructure along the $M—X \cdots M$ chains. The true repeat distance along the chain comprises two metal—metal separations, but adjacent chains are disordered such that the distribution of Pt^{II} and Pt^{IV} over the Pt sites is random. Thus a repeat distance of only one metal—metal separation is found for the three-dimensional structure, and the one-dimensional superstructure reveals itself as diffuse sheets midway between the planes of the Bragg reflections. In $[Pten_2]$-$[Pten_2Br_2](ClO_4)_4$ (1), normal though weak Bragg reflections occur instead of diffuse sheets. This means full three-dimensional order with a repeat distance of two metal—metal separations along the chains. The only other Wolffram's salt analogues with this exceptional

three-dimensional ordering are the Cl and the Cl,en analogues of (1) (Bekaroglu, Breer, Endres, Keller & Nam Gung, 1977; Matsumoto, Yamashita & Kida, 1978). The structure of (1) makes it evident that only the perchlorate ions contribute markedly to the reflections with $k = 2n + 1$, for the Br atoms are midway, within experimental error, between two Pt sites of a chain. Hence the 'long' unit cell originates mainly from the ClO_4^- distribution. The two independent Pt_2en sites are occupied by different enantiomeric forms of the complex molecule. This gives another weak contribution to the reflections with k odd. It could be argued whether this distribution of the two enantiomeric forms is the reason for or a consequence of the three-dimensional order. We argue that it is a consequence of the ordering imposed by the ClO_4^- distribution, for in nearly all Wolffram's salt analogues which contain two enantiomeric forms, these forms are distributed statistically over the complex sites. There is no obvious reason why the two forms should show the unusual ordering found in (1) if it is not a consequence of crystal forces originating from the distribution of the counter ions.

There are short contacts between the N atoms of the ligand and O atoms of the perchlorate ions as shown in Fig. 3. The shortest [2·92 (5) Å between N(2) and O(4)] suggest hydrogen bonds which may cause the three-dimensional order of the structure.

$[Pt(dapn)_2][Pt(dapn)_2I_2]I_4$ (2), on the other hand, exhibits neither the diffuse sheets nor the corresponding Bragg reflections. This could be explained by positioning the halogen atoms in the chain exactly midway between the Pt sites. However, this structure determination shows that this is not the case. Thus the other possible explanation should be correct: the Pt^{II}/Pt^{IV} distribution along the chain shows no long-range order. This suggests either the frequent occur-rence of intermediate states of the type I—Pt—I, or a rapid interchange of the I between the two possible sites. The latter interpretation describes an inter-conversion of Pt^{II} and Pt^{IV} through $Pt \leftarrow X \rightarrow Pt$ lattice vibrations. Neutron diffraction data would be necessary to prove this phonon-like behaviour.

Day (1977) has pointed out that changes in the oxidation states of the central metal, brought about by changes in the $Pt—X—Pt$ separations, should affect the in-plane metal to ligand bonds. This means a coupling of the phonons along the chains to the vibrations perpendicular to the chains, accompanied by a coupling of the electronic transitions. Raman investigations should provide more insight into these problems.

Fig. 4 shows the single-crystal optical-reflectance spectrum of (1) illustrating the anisotropic character of the optical properties. However, the band width and the intensity of the parallel reflectivity is considerably smaller than those reported for $[Pt(dapn)_2][Pt(dapn)_2-I_2](ClO_4)_2$ (Breer, Endres, Keller & Martin, 1978). This means that the electron mobility along the chains is larger in the latter compound, even if the difference between the $Pt^{II}—X$ and $Pt^{IV}—X$ bond lengths is more pronounced [0·19 Å compared to practically zero in (1)]. This unexpected fact could be accounted for in the following way: the differences in the $Pt^{IV}—I$ and the $Pt^{IV}—Br$ distances in the compound quoted above and in (1) (0·24 Å) correspond to the difference in the van der Waals radii (0·2 Å; Pauling, 1960). Hence the effective overlap $Pt^{IV}—X$ is practically the same in both compounds, and the unusually long $Pt^{II}—Br$ distance in (1) together with the lower polarizability of Br compared to I leads to less efficient electronic exchange between the Pt atoms. This would mean that placing the halogen midway between the Pt atoms is not sufficient to achieve pronounced one-dimensional electron mobility.
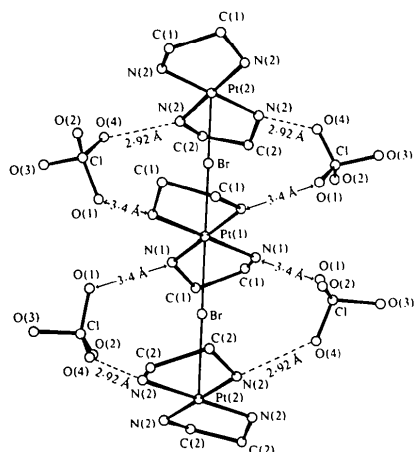

Fig. 3. Projection of the $Pt\cdots Br\cdots Pt$ chain into the bc plane. Hydrogen bonds between the ClO_4^- ions and N atoms of the ligand (N—O distances $<3\cdot0$ Å) are indicated by dotted lines. The circles indicate the centres of the atom positions.
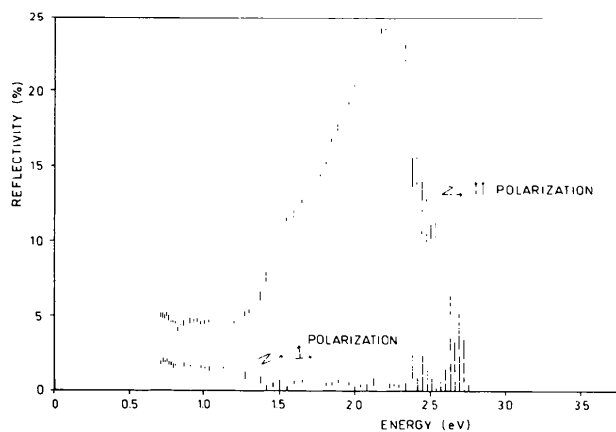

Fig. 4. Single-crystal reflectance spectra of $[Pten_2][Pten_2Br_2]-(ClO_4)_4$. The polarization of the incident light was parallel ($\uparrow\uparrow$ polarization) and perpendicular ($\perp$ polarization) to the $Pt\cdots Br\cdots Pt$ chain.

References

BEKAROGLU, Ö., BREER, H., ENDRES, H., KELLER, H. J. & NAM GUNG, H. (1977). *Inorg. Chim. Acta*, **21**, 183–186.
BERDESINSKY, W. & NUBER, B. (1966). *Neues Jahrb. Mineral. Abh.* **104**, 113–146.
BREER, H., ENDRES, H., KELLER, H. J. & MARTIN, R. (1978). *Acta Cryst.* B**34**, 2295–2297.
BROWN, K. L. & HALL, D. (1976). *Acta Cryst.* B**32**, 279–281.
CLARK, R. J. H., FRANKS, M. L. & TRUMBLE, W. R. (1976). *Chem. Phys. Lett.* **41**, 287–292.
CRAVEN, B. M. & HALL, D. (1961). *Acta Cryst.* **14**, 475–480.
DAY, P. (1975). *Low-Dimensional Cooperative Phenomena*, edited by H. J. KELLER, NATO-ASI Series B8, pp. 191–214. New York: Plenum.
DAY, P. (1977). *Chemistry and Physics of One-Dimensional Metals*, edited by H. J. KELLER, NATO-ASI Series 25B, pp. 197–224. New York: Plenum.

EL SHARIF, M., ENDRES, H., KELLER, H. J., MARTIN, R. & TRAEGER, U. (1978). *Ann. NY Acad. Sci.* **313**, 663–671.
ENDRES, H., KELLER, H. J., MARTIN, R., NAM GUNG, H. & TRAEGER, U. (1979). *Acta Cryst.* B**35**, 1885–1887.
HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
HANSON, H., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
INTERRANTE, L. V., BROWALL, K. W. & BUNDY, F. P. (1974). *Inorg. Chem.* **13**, 1158.
INTERRANTE, L. V. & BUNDY, F. P. (1977). *J. Inorg. Nucl. Chem.* **39**, 1333–1337.
MATSUMOTO, N., YAMASHITA, M. & KIDA, S. (1978). *Mem. Fac. Sci. Kyushu Univ. Ser. C*, **11**, 209–216.
MATSUMOTO, N., YAMASHITA, M. & KIDA, S. (1979). *Acta Cryst.* B**35**, 1458–1460.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
ROBIN, M. B. & DAY, P. (1967). *Adv. Inorg. Chem. Radiochem.* **10**, 247–422.
RYAN, T. D. & RUNDLE, R. F. (1961). *J. Am. Chem. Soc.* **83**, 2814–2816.
STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). *The XRAY 70 system*. Computer Science Center, Univ. of Maryland, College Park, Maryland.
WALLÉN, J., BROSSET, C. & VANNERBERG, N. G. (1962). *Ark. Kemi*, **18**, 541–551.
YAMASHITA, M., MATSUMOTO, N. & KIDA, S. (1978). *Inorg. Chim. Acta*, **31**, L381–L382.

Molecular Structure and Absolute Configuration of (+)$_D$-[1-(2-Diphenylphosphino-ferrocenyl)ethyl]dimethylamine

BY FREDERICK W. B. EINSTEIN AND ANTHONY C. WILLIS

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Abstract

The molecular structure of the title compound, [Fe(C_5H_5)($C_{21}H_{23}$NP)], $C_{26}H_{28}$FeNP, has been determined from X-ray diffraction data and refined by least squares to $R = 0.047$ (1472 reflexions with $I > 2.3 \sigma_I$). Crystals are monoclinic, space group $P2_1$, $a = 11.026$ (7), $b = 11.193$ (6), $c = 9.653$ (5) Å, $\beta = 106.85$ (4)°, $Z = 2$. The absolute configuration of the disubstituted ferrocene is R and the ethyl αC atom is S.

The rhodium(I) complexes of several chiral phosphines have been found to be effective catalysts for asymmetric hydrogenation reactions (Sinou & Kagan, 1976; Fryzuk & Bosnich, 1977, and references therein;

Cullen & Yeh, 1977). One such phosphine ligand is [1-(2-diphenylphosphinoferrocenyl)ethyl]dimethylamine (PPFA) which possesses a chiral centre at the amine-substituted C atom and can be prepared as either optical isomer (Battelle, Bau, Gokel, Oyakawa & Ugi, 1972). [(diene)Rh(+)-PPFA]$^+X^-$ [diene = norbornadiene (NBD) or cyclooctadiene; $X^- = ClO_4^-$, BF_4^- or PF_6^-] and [(diene)Rh(−)-PPFA]$^+X^-$ have been used in the specific hydrogenation of α-acetamidocinnamic acid, giving high optical yields of R and S products respectively (Cullen & Yeh, 1977). As part of a study of the structures of these complexes, we report here the crystal structure of the parent (+)-PPFA ligand to confirm the absolute configuration and to allow us to compare the geometry of the free ligand with that of the coordinated species.