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

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Abstract

The molecular structure of the title compound, [Fe(C₅H₅)(C₂₁H₂₃NP)], C₂₆H₂₈FeNP, 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 α C 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⁻ = ClO₄⁻, BF₄⁻ or PF₆⁻] 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.

Experimental

A yellow single crystal $0.3 \times 0.3 \times 0.3$ mm was used in the crystallographic studies. Weissenberg and precession photographs taken with Cu $K\alpha$ radiation showed the crystal to be monoclinic and gave approximate unit-cell parameters. 12 reflexions with $2\theta > 23^\circ$ were accurately centred on a Picker FACS-I four-circle diffractometer employing monochromatic Mo $K\alpha_1$ radiation ($\lambda = 0.70926$ Å) and accurate unit-cell dimensions were obtained by least squares from their angular parameters. The intensities of 1583 unique

reflexions with $2\theta \leq 45^\circ$ were measured and, of these, 1472 with $I > 2.3\sigma_I$ $\{I = C - B(t_s/t_b); \sigma_I = [(t_s/t_b)^2 B + C + (0.03I)^2]^{1/2}$ where $C =$ integrated peak count, $B =$ total background count, $t_s =$ peak scan time, $t_b =$ total background count time} were regarded as observed and used in structure solution and refinement. A θ - 2θ scan running at 2° min^{-1} was used for the data collection. Data were collected in two shells: background counts of 4 s on each side of the peak and a base width of 1.4° which was increased for dispersion were used for reflexions with $2\theta \leq 30^\circ$, while background measurements of 10 s on each side and a base width of 1.0° were used for reflexions with $30^\circ < 2\theta \leq 45^\circ$. Two standard reflexions were measured at regular intervals to scale the data. A temperature of 295 K was maintained throughout. Crystal data are given in Table 1. Photographs taken of a crystal of (-)-PPFA showed a diffraction pattern identical to that of (+)-PPFA.

The structure was solved by conventional heavy-atom procedures. Full-matrix least-squares refinement of the non-hydrogen atoms with isotropic temperature factors yielded a value of 0.081 for R . The non-methyl H atoms were placed at their geometrically determined

Table 1. Crystal data

$\text{C}_{26}\text{H}_{28}\text{FeNP}$	V	1140.2 Å ³
$M_r = 441.3$	D_m	1.27 Mg m ⁻³
Monoclinic, $P2_1$	D_c ($Z = 2$)	1.285 Mg m ⁻³
$a = 11.026$ (7) Å	μ (Mo $K\alpha$)	0.761 mm ⁻¹
$b = 11.193$ (6)	Final R^*	0.047
$c = 9.653$ (5)	Final R_w^\dagger	0.056
$\beta = 106.85$ (4)°		

$$* R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$\dagger R_w = (\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2)^{1/2}$$

Table 2. Final atomic parameters

The values of the atomic fractional coordinates and their estimated standard deviations (in parentheses) are multiplied by 10^4 for the non-hydrogen atoms and by 10^3 for the H atoms. Thermal parameters (Å²) are multiplied by 10^3 .

	x	y	z	U		x	y	z	U
Fe	988 (1)	2500 (-)	4612 (1)	*	C(34)	-33 (11)	670 (10)	9820 (12)	82 (3)
P	2284 (2)	3435 (2)	8088 (2)	*	C(35)	1262 (10)	510 (10)	10145 (12)	90 (3)
C(11)	-507 (7)	3493 (9)	4769 (9)	*	C(36)	1979 (9)	1328 (9)	9649 (10)	77 (3)
C(12)	-153 (8)	3843 (8)	3562 (10)	*	C(41)	3888 (7)	3343 (8)	9346 (8)	52 (2)
C(13)	-258 (8)	2854 (9)	2646 (9)	*	C(42)	4164 (8)	4135 (9)	10482 (10)	72 (3)
C(14)	-681 (8)	1877 (9)	3300 (10)	*	C(43)	5379 (9)	4182 (10)	11460 (11)	84 (3)
C(15)	-839 (7)	2270 (9)	4605 (10)	*	C(44)	6287 (9)	3457 (10)	11270 (10)	83 (3)
C(21)	2415 (6)	2646 (8)	6509 (7)	47 (2)	C(45)	6040 (9)	2687 (12)	10172 (10)	89 (3)
C(22)	2767 (7)	3200 (7)	5336 (8)	53 (2)	C(46)	4812 (8)	2611 (11)	9171 (9)	79 (2)
C(23)	2724 (7)	2297 (8)	4274 (8)	61 (2)	C(51)	3170 (9)	4917 (10)	3847 (11)	87 (3)
C(24)	2333 (8)	1231 (8)	4754 (9)	64 (2)	C(52)	3144 (7)	4468 (8)	5321 (8)	60 (2)
C(25)	2154 (7)	1400 (8)	6121 (8)	58 (2)	N(53)	4331 (7)	4627 (7)	6485 (8)	*
C(31)	1429 (7)	2312 (8)	8835 (8)	53 (2)	C(54)	5403 (12)	4055 (13)	6239 (14)	111 (4)
C(32)	130 (7)	2442 (10)	8547 (8)	65 (2)	C(55)	4597 (13)	5870 (14)	6892 (15)	125 (5)
C(33)	-583 (8)	1599 (10)	9031 (10)	74 (3)					
H(11)	-54	398	556	60	H(43)	557	473	1226	84
H(12)	12	463	339	58	H(44)	710	351	1193	83
H(13)	-8	285	174	67	H(45)	671	220	1006	89
H(14)	-82	109	292	60	H(46)	464	204	840	79
H(15)	-112	179	528	61	H(51)A	357	434	341	87
H(23)	292	241	338	61	H(51)B	361	565	394	87
H(24)	221	51	423	64	H(51)C	232	503	325	87
H(25)	191	80	668	58	H(52)	256	494	564	60
H(32)	-29	311	801	65	H(54)A	516	328	580	111
H(33)	-147	170	882	74	H(54)B	606	395	711	111
H(34)	-52	11	1017	82	H(54)C	571	452	557	111
H(35)	166	-17	1070	90	H(55)A	392	620	717	125
H(36)	287	120	986	77	H(55)B	469	630	606	125
H(42)	353	467	1060	72	H(55)C	536	592	765	125

* U_{ij} values have been deposited.

positions (angles 109.5, 120 or 126°, r_{C-H} 0.95 Å) and assigned the temperature factors of the C atoms to which they were attached. Their scattering-factor contributions were incorporated in further least-squares cycles but their parameters were not refined. A difference map at this stage revealed indications of thermal anisotropy near the Fe, P and N atoms and about the C atoms of the unsubstituted cyclopentadienyl ring; these atoms were given anisotropic temperature factors in further refinement which resulted in $R = 0.054$. A further difference map, using inner data only, exhibited peaks about the methyl C atoms. H atoms were positioned so as to approximate the observed electron density distribution and yet maintain tetrahedral geometries about the C atoms. A final difference map revealed some indications of anisotropy in the vicinity of the remaining cyclopentadienyl and phenyl rings, but as the peaks were reasonably small [all < 0.40 (6) e Å⁻³] and as the important features of the structure had already been determined, it was thought unnecessary to refine the model any further. All shift-to-error ratios were less than 0.1 in the final cycle.

Table 3. *Interatomic distances (Å) and angles (°)*

Fe—C(11)	2.030 (8)	Fe—C(21)	2.046 (7)
Fe—C(12)	2.032 (8)	Fe—C(22)	2.038 (8)
Fe—C(13)	2.033 (8)	Fe—C(23)	2.045 (8)
Fe—C(14)	2.031 (8)	Fe—C(24)	2.030 (9)
Fe—C(15)	2.029 (8)	Fe—C(25)	2.050 (8)
C(11)—C(12)	1.39 (1)	C(21)—C(22)	1.44 (1)
C(12)—C(13)	1.40 (1)	C(22)—C(23)	1.43 (1)
C(13)—C(14)	1.41 (1)	C(23)—C(24)	1.39 (1)
C(14)—C(15)	1.39 (1)	C(24)—C(25)	1.40 (1)
C(15)—C(11)	1.41 (1)	C(25)—C(21)	1.45 (1)
C(31)—C(32)	1.39 (1)	C(41)—C(42)	1.37 (1)
C(32)—C(33)	1.39 (1)	C(42)—C(43)	1.40 (1)
C(33)—C(34)	1.33 (1)	C(43)—C(44)	1.34 (1)
C(34)—C(35)	1.38 (1)	C(44)—C(45)	1.33 (1)
C(35)—C(36)	1.38 (1)	C(45)—C(46)	1.42 (1)
C(36)—C(31)	1.39 (1)	C(46)—C(41)	1.36 (1)
N(53)—C(54)	1.42 (1)	N(53)—C(55)	1.45 (2)
C(52)—C(22)	1.48 (1)	C(52)—C(51)	1.52 (1)
P—C(21)	1.802 (7)	C(52)—N(53)	1.47 (1)
P—C(31)	1.838 (8)	P—C(41)	1.836 (8)
Cp(1)—Fe—Cp(2)*	177.9	C(31)—P—C(41)	102.0 (3)
C(21)—P—C(31)	100.0 (4)	C(21)—P—C(41)	103.5 (3)
P—C(21)—C(22)	124.1 (6)	P—C(21)—C(25)	129.1 (6)
C(15)—C(11)—C(12)	107.8 (8)	C(25)—C(21)—C(22)	106.8 (6)
C(11)—C(12)—C(13)	108.4 (8)	C(21)—C(22)—C(23)	107.4 (7)
C(12)—C(13)—C(14)	108.0 (8)	C(22)—C(23)—C(24)	108.4 (7)
C(13)—C(14)—C(15)	107.7 (8)	C(23)—C(24)—C(25)	109.8 (8)
C(14)—C(15)—C(11)	108.1 (9)	C(24)—C(25)—C(21)	107.6 (7)
P—C(31)—C(32)	117.9 (7)	P—C(41)—C(42)	116.1 (6)
P—C(31)—C(36)	125.1 (6)	P—C(41)—C(46)	124.5 (7)
C(36)—C(31)—C(32)	117.0 (8)	C(46)—C(41)—C(42)	119.3 (8)
C(31)—C(32)—C(33)	120.9 (9)	C(41)—C(42)—C(43)	120.7 (9)
C(32)—C(33)—C(34)	121.0 (9)	C(42)—C(43)—C(44)	119.4 (10)
C(33)—C(34)—C(35)	120.2 (10)	C(43)—C(44)—C(45)	120.8 (10)
C(34)—C(35)—C(36)	119.5 (10)	C(44)—C(45)—C(46)	121.1 (10)
C(35)—C(36)—C(31)	121.4 (9)	C(45)—C(46)—C(41)	118.8 (10)
C(21)—C(22)—C(52)	124.1 (7)	C(23)—C(22)—C(52)	128.4 (7)
C(52)—N(53)—C(54)	114.7 (8)	C(52)—N(53)—C(55)	112.9 (9)
C(51)—C(52)—N(53)	115.0 (7)	C(22)—C(52)—N(53)	107.4 (7)
C(54)—N(53)—C(55)	111.4 (9)	C(22)—C(52)—C(51)	114.1 (8)

* Cp(*n*) is the centroid of cyclopentadienyl ring *n*.

Table 4. *Deviations of atoms (Å) from the least-squares planes*

The equations of the planes are referred to the orthogonal axes *a*, *b*' and *c**. Asterisks indicate atoms not included in the least-squares calculation. E.s.d. = 0.008–0.012 Å.

(I) Cyclopentadienyl ring (1)		(II) Cyclopentadienyl ring (2)	
C(11)	−0.001	C(21)	0.000
C(12)	0.000	C(22)	0.004
C(13)	0.001	C(23)	−0.008
C(14)	−0.002	C(24)	0.010
C(15)	0.002	C(25)	−0.005
Fe*	−1.645	Fe*	1.644
		P*	0.062
		C(52)*	−0.027
(III) Phenyl ring (3)		(IV) Phenyl ring (4)	
C(31)	0.003	C(41)	−0.001
C(32)	−0.009	C(42)	0.004
C(33)	0.009	C(43)	−0.005
C(34)	−0.004	C(44)	0.001
C(35)	−0.004	C(45)	0.002
C(36)	0.002	C(46)	−0.002
P*	0.048	P*	0.109
		N(53)*	3.075

$$(I) \quad -0.8485x + 0.2482y - 0.4673z = 0.5189$$

$$(II) \quad -0.8658x + 0.2298y - 0.4445z = -2.7212$$

$$(III) \quad 0.1170x - 0.5318y - 0.8388z = -8.3300$$

$$(IV) \quad 0.4422x + 0.6905y - 0.5724z = -1.6187$$

Computing was carried out using programs reported by Einstein & Jones (1972). The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma_F^2$. Neutral scattering factors (*International Tables for X-ray Crystallography*, 1974; Stewart, Davidson & Simpson, 1965) were employed and anomalous-dispersion corrections applied for Fe and P (Cromer & Liberman, 1970), but no correction was made for absorption. Final atomic parameters are given in Table 2, interatomic distances and angles in Table 3 and least-squares planes in Table 4.*

Absolute configuration

The absolute configuration of (+)-PPFA was assigned as {(1*S*)-(2*R*)-diphenylphosphiniferrocenylethyl}dimethylamine by Hayashi, Yamamoto & Kumada (1974) on the basis of the absolute configuration of its precursor, (1-ferrocenylethyl)dimethylamine (Battelle, Bau, Gokel, Oyakawa & Ugi, 1972, 1973); the present study verifies this assignment. A Hamilton (1965) test

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34694 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Bijvoet ratios*

<i>hkl</i>	X_c	X_o
0 1 3	0.277	0.29 (4)
0 3 1	-0.142	-0.14 (3)
1 3 0	-0.144	-0.10 (5)
2 1 2	1.053	1.05 (15)
2 2 1	0.147	0.14 (3)
2 2 2	0.093	0.10 (3)
3 1 1	-0.132	-0.13 (4)
4 1 0	0.098	0.09 (4)
4 2 0	-0.164	-0.13 (3)

showed that the *R* factor for this configuration was significantly lower than that obtained for the other enantiomer at better than 99.5% probability. A comparison of the Bijvoet ratios [$X = 2(I_{hkl} - I_{\bar{h}\bar{k}l}) / (I_{hkl} + I_{\bar{h}\bar{k}l})$] of nine inner reflexions with $F_c(hkl)$ differing from $F_c(\bar{h}\bar{k}l)$ by more than 5% also supports this assignment (see Table 5). For each of these reflexions the intensities of hkl , $\bar{h}\bar{k}l$, $h\bar{k}l$ and $\bar{h}kl$ were measured and used to derive the errors in X_o .

Discussion

A view of the molecule is presented in Fig. 1. The substituents on the ferrocene assume conformations which minimize non-bonding interactions between each other and the H atoms of both cyclopentadienyl rings: the most bulky groups are axial and directed away from the unsubstituted cyclopentadiene, and the smallest groups [the phosphine electron lone pair and H(52)] face inwards. This contrasts with [(NBD)Rh(±)-PPFA]PF₆ where the amine group takes an equatorial

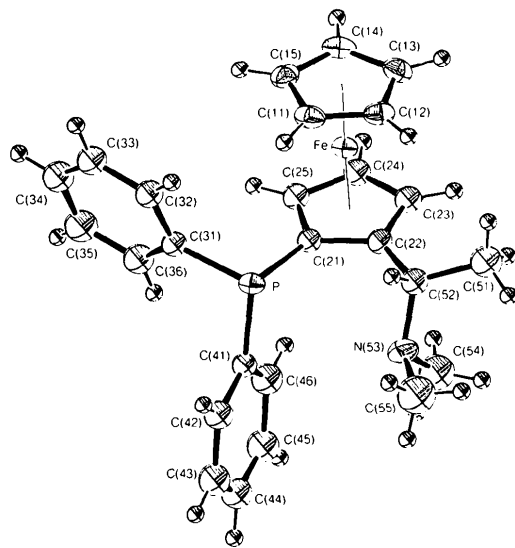


Fig. 1. Projected view of the molecule showing the atom-labelling scheme. Atoms other than H are represented by 25% probability ellipsoids.

site to allow the molecule to operate as a bidentate ligand bonding to the Rh atom through P and N, and C(51) is shifted to the axial position (Cullen, Yeh, Einstein, Huang & Willis, 1979).

Bond lengths and angles are generally as expected. The Fe—C distances of 2.029 (8)–2.033 (8) Å for ring (1) and 2.030 (8)–2.050 (8) Å for ring (2) are similar to those found for ferrocene (1.99–2.08 Å; Dunitz, Orgel & Rich, 1956) and its derivatives (e.g. Krukoniš, Silverman & Yannoni, 1972, and references therein). The cyclopentadienyl rings are nearly eclipsed [the dihedral angles C(1a)—Cp(1)—Cp(2)—C(2a), where Cp(*n*) is the centroid of cyclopentadienyl ring *n*, are in the range 8.3–9.7°] and exhibit no significant deviations from fivefold symmetry. The C—C bonds for ring (1) average 1.40 and ring (2) 1.42 Å, compared with the 'accepted' value of 1.43 Å (Churchill & Kalra, 1973). The shortening arises from thermal librations of the ring and so is greater in the unsubstituted cyclopentadienyl group as it is less constrained.

The three C—P—C angles [100.0, 102.0 and 103.5 (4)°] are appreciably less than the ideal tetrahedral angle of 109.5°, in agreement with simple valence-shell electron-pair-repulsion considerations when the electron lone pair on the P atom is taken into account. The resultant crowding of the phenyl and cyclopentadienyl rings causes the P—C—C angles to be asymmetric. Both these features were also observed in triphenylphosphine (Daly, 1964).

In contrast, the three C—N—C angles are all slightly larger than 109.5°. This may arise from a small degree of double-bond character between C(52) and N(53), possibly arising from a long-range interaction between H(52) and P [H(52)⋯P = 2.99 Å]. (–)-Methadone (Bürgi, Dunitz & Shefter, 1973; Bye, 1974) and (*S,R,S*)-Fe(C₅H₅){1-[CH(OH)(*p*-C₆H₄OCH₃)]-2-[CH(CH₃)N(CH₃)₂](C₅H₃)} (Battelle *et al.*, 1972, 1973) also possess dimethylamine groups with C—N—C angles greater than 109.5°, but, in these compounds, there are long-range interactions between the N lone pair and nearby electropositive atoms.

The C—C bonds within the phenyl rings range from 1.33 (1) to 1.42 (1) Å although there appears to be no chemical significance in the variations. The temperature factors of the individual C atoms are relatively large, showing that these groups have considerable thermal motion.

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Crystal Structure of (–)₅₈₉ Ammineglycinato(1,4,7-triazacyclononane)cobalt(III) Diiodide 0·84-Hydrate

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Abstract

Crystals of the title compound, $[\text{Co}(\text{C}_6\text{H}_{15}\text{N}_3)(\text{C}_2\text{H}_4\text{NO}_2)(\text{NH}_3)]\text{I}_2 \cdot 0\cdot84\text{H}_2\text{O}$, are orthorhombic, $P2_12_12_1$, with $a = 15\cdot075$ (3), $b = 17\cdot674$ (4), $c = 12\cdot625$ (3) Å and $Z = 8$. The structure was refined by a block-diagonal least-squares method to a final R value of 0·0253 for 4675 independent reflections with $|F_o| > 3\sigma(|F_o|)$ collected by X-ray diffractometry. The absolute configuration of the complex ion (–)₅₈₉[Co(gly)(NH₃)(tacn)]²⁺ (gly: glycinate; tacn: 1,4,7-triazacyclononane) can be designated as *a*-ammine-*bc*-glycinato-*def*-(1,4,7-triazacyclononane)cobalt(III). The water molecules exhibit positional disorder.

Introduction

The title compound was recently prepared and resolved into optical isomers (Shimba, Fujinami & Shibata, 0567-7408/80/010043-05\$01.00

1979). This complex has three different ligands, which are unidentate, bidentate and cyclic terdentate. The optical activity of this complex ion arises from the chiral disposition of the unidentate and the bidentate ligands with respect to the terdentate ligand as well as from the ring conformation of the terdentate ligand. The absolute configuration of this complex ion could not be assigned on the basis of its circular-dichroism spectrum, since no reference complex of known absolute configuration was available. The compound, therefore, was subjected to X-ray structure analysis in order to reveal the conformational details of the complex ion and to establish the empirical relation between the absolute configuration and the CD spectrum.

Experimental

The plate-like crystals are dark orange-red. The crystal data are: $[\text{Co}(\text{C}_6\text{H}_{15}\text{N}_3)(\text{C}_2\text{H}_4\text{NO}_2)(\text{NH}_3)]\text{I}_2 \cdot 0\cdot84\text{H}_2\text{O}$
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