

Table 3. Selected bond lengths (Å) and angles (°) for some distorted trigonal-bipyramidal complexes of the type [MCl(dppe)₂]ⁿ⁺ (n = 0, 1), with Y-shaped equatorial planes

Complex	M—P _{ax}	M—P _{eq}	M—Cl	P _{eq} —M—P _{eq}
[RuCl(dppe) ₂] ⁺ ^a	2.371 (2) 2.372 (2)	2.243 (2) 2.238 (2)	2.395 (2)	95.0 (1)
[OsCl(dppe) ₂] ⁺ ^b	2.3634 (12) 2.3640 (12)	2.2416 (12) 2.2587 (13)	2.3760 (11)	94.24 (5)
TcCl(dppe) ₂ ^c	2.376 (2) 2.359 (2)	2.240 (2) 2.255 (2)	2.432 (2)	93.9 (1)
ReCl(dppe) ₂ ^d	2.366 (1) 2.380 (1)	2.269 (1) 2.256 (1)	2.403 (1)	93.7

References: (a) Chin, Lough, Morris, Schweitzer & D'Agostino (1994); (b) this work; (c) Burrell, Bryan & Kubas (1994); (d) Hughes, Pombeiro, Pickett & Richards (1983).

The hexafluorophosphate anion is rotationally disordered over two sites about the axial F—P—F axis, with occupancies of 0.68 (2)/0.32(2). In total, there are 1.5 CH₂Cl₂ molecules for every cation in three independent sites, with occupancies of 0.5, 0.75 and 0.25 for the C2S, C1S and C1S* molecules, respectively.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: SHELXTL/PC (Sheldrick, 1994). Program(s) used to solve structure: SHELXTL/PC. Program(s) used to refine structure: SHELXTL/PC. Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXTL/PC.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1187). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-(R)-{2-[1-(R)-(N,N-Dimethylamino)ethyl]-1,1'-(S,S)-biferrocen-2'-yl}ethyl-N,N-dimethylammonium Trichloro(dimethyl sulfoxide-S)platinate(II)

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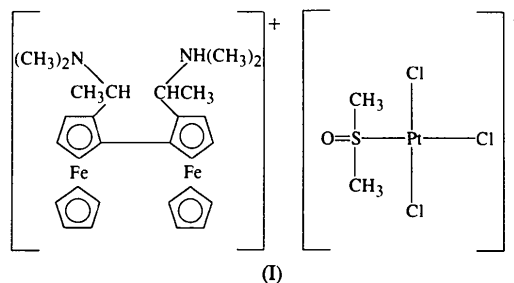
(Received 3 August 1995; accepted 25 March 1996)

Abstract

The structure of the title compound, [Fe₂(C₅H₅)₂-(C₁₈H₂₇N₂)] [PtCl₃(C₂H₆OS)], reveals an unusual twisting of the ferrocenyl moieties in the monoprotonated bis(amine) with respect to the interferrocenyl C—C bond. This deformation can be ascribed to hydrogen bonding between the ammonium proton and the unprotonated amine residue. The absolute configuration at each of the chiral C atoms is shown to be *R*, while the metallocene chiralities are *S*.

Comment

As part of our continuing investigations into the role of ferrocenyl (Ranatunge-Bandarage, Robinson & Simpson, 1994) and biferrocenylamines (Spescha, Duffy, Robinson & Simpson, 1994) as ligands for platinum with potential for enhanced antitumour activity, we attempted to substitute the complex [PtCl₂(dmsO)₂] (dmsO is dimethyl sulfoxide) with 2,2'-bis[1-(*N,N*-dimethylamino)ethyl]-1,1'-biferrocene. The reaction resulted in protonation of one of the amino groups. The resulting cation was isolated as the trichloro(dimethyl sulfoxide)platinate(II) salt, (I), and is the subject of this report.



The most unusual feature of the biferrocenyl moiety [Fig. 1(a) and Table 2] is the considerable twist of the cyclopentadiene rings of the fulvalene bridge unit. The angle between the C1—C5 and C11—C15 ring planes is 103.2 (8)°, and the separation of the N atoms of the di-

methylamino groups is only 2.91 (2) Å. The additional H atom that results from protonation of the N2 amine moiety is involved in hydrogen bonding to the adjacent N1 atom which stabilizes the molecule in this configuration. The structures of both the *meso* and racemic forms of the neutral 2,2'-bis[1-(*N,N*-dimethylamino)ethyl]-1,1'-biferrocene have been determined (Krajnik, Kratky, Schögl & Widhalm, 1990). While the *meso* form adopts the classical *trans* configuration with a strictly planar fulvalene ring, the corresponding twist angle in the racemic diastereoisomer is approximately 20°. The twist angle in the corresponding 2,2'-bis[1-(*N,N*-diethylamino)ethyl]ferrocene (Spescha, Duffy, Robinson & Simpson, 1994) is somewhat larger at 56.8(1)°, which was ascribed to the greater steric requirements of the diethylaminoethyl substituents.

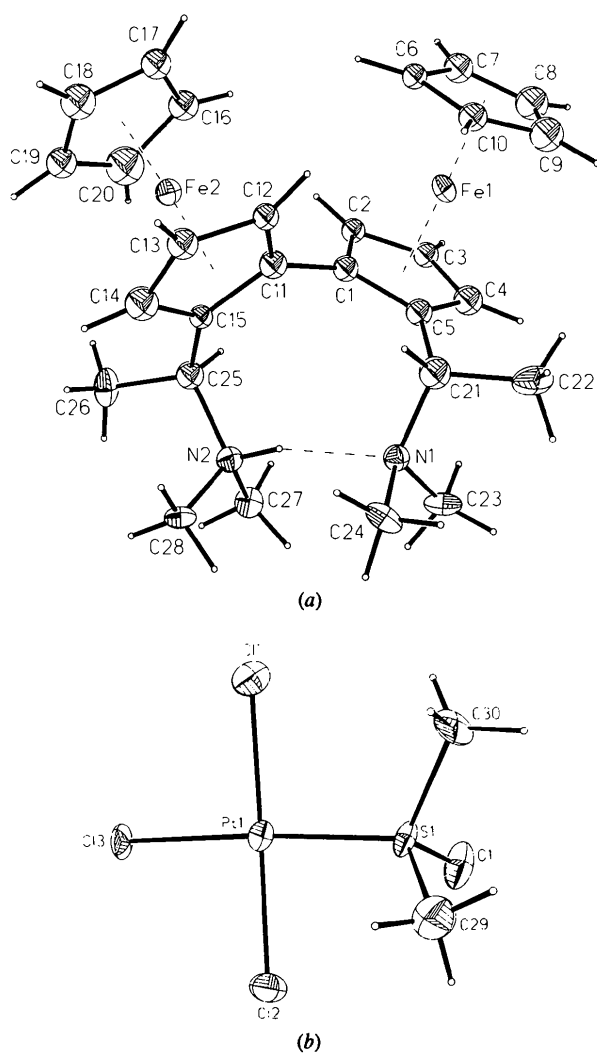


Fig. 1. ORTEP (Johnson, 1965) drawing of (a) the cation and (b) the anion, showing the atom-numbering schemes, with displacement ellipsoids drawn at the 50% probability level.

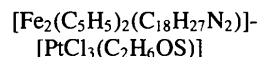
The absolute configuration of the chiral cation was confirmed from the value of the Flack (1983) parameter [$\chi = -0.01(2)$], with the stereochemistry at C21 and C25 being *R* and the planar chirality of the substituted cyclopentadiene rings both *S*.

The square-planar [PtCl₃(dmsoligand)]⁻ anion [Fig. 1(b) and Table 2] has the sulfoxide ligand coordinated *via* the S atom. The Pt—Cl and Pt—S bond distances and the angles subtended at the Pt atom are in reasonable agreement with those observed in previous structure determinations of this anion (for examples see Cantoni, Tiripicchio, Camellini & Annibale, 1991; Melanson, Hubert & Rochon, 1976; Veldman, Spek, Bloemink, Dorenbos, Heeterbrij & Reedijk, 1994).

Experimental

The title compound was obtained from the reaction between [PtCl₂(dmsoligand)₂] and 2,2'-bis[1-(*N,N*-dimethylamino)ethyl]-1,1'-biferrocene followed by slow evaporation from chloroform.

Crystal data



M_r = 892.86

Monoclinic

*P*2₁

a = 13.314 (8) Å

b = 9.983 (5) Å

c = 13.450 (7) Å

β = 117.63 (2)°

V = 1583.7 (15) Å³

Z = 2

D_x = 1.872 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 19 reflections

θ = 9.48–27.88°

μ = 5.656 mm⁻¹

T = 158 (2) K

Irregular prism

0.40 × 0.25 × 0.10 mm

Orange

Data collection

Siemens *P4* diffractometer

ω scans

Absorption correction:

empirical ψ scans

(Sheldrick, 1991)

T_{min} = 0.301, *T_{max}* =

0.537

2348 measured reflections

2191 independent reflections

1776 observed reflections

[*I* > 2σ(*I*)]

R_{int} = 0.0464

θ_{\max} = 22.49°

h = -12 → 14

k = 0 → 10

l = -14 → 12

3 standard reflections

monitored every 97

reflections

intensity decay: 4.21%

Refinement

Refinement on *F*²

R(*F*) = 0.0489

wR(*F*²) = 0.1097

S = 0.941

2191 reflections

259 parameters

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2]$ Absolute configuration:
 where $P = (F_o^2 + 2F_c^2)/3$ Flack (1983)
 $(\Delta/\sigma)_{\max} = -0.003$ Flack parameter = -0.01 (2)
 $\Delta\rho_{\max} = 1.58 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.48 \text{ e } \text{\AA}^{-3}$

This work is supported by a grant from the Division of Sciences, University of Otago, New Zealand.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1112). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	x	y	z	U_{eq}
Pt1	0.13252 (7)	0.82336 (10)	0.18220 (6)	0.0183 (2)
Cl1	0.2772 (5)	0.7982 (6)	0.1348 (5)	0.028 (2)
Cl2	-0.0101 (5)	0.8501 (8)	0.2322 (5)	0.029 (2)
Cl3	0.2481 (5)	0.9526 (6)	0.3362 (4)	0.0272 (15)
S1	0.0105 (5)	0.7124 (6)	0.0335 (4)	0.0203 (14)
O1	-0.0850 (13)	0.7944 (16)	-0.0497 (12)	0.038 (5)
C29	-0.046 (2)	0.572 (3)	0.073 (2)	0.041 (8)
C30	0.074 (2)	0.621 (3)	-0.040 (2)	0.033 (7)
C1	0.3010 (18)	0.777 (2)	0.7166 (18)	0.018 (5)
C2	0.2787 (17)	0.737 (2)	0.8061 (17)	0.017 (5)
C3	0.2375 (17)	0.601 (2)	0.7850 (17)	0.019 (5)
C4	0.2254 (18)	0.565 (2)	0.6796 (17)	0.024 (5)
C5	0.2670 (19)	0.672 (2)	0.6385 (19)	0.018 (6)
C21	0.2860 (18)	0.674 (2)	0.5346 (18)	0.025 (6)
C22	0.1979 (19)	0.587 (3)	0.4411 (17)	0.030 (6)
N1	0.4042 (14)	0.6264 (17)	0.5704 (14)	0.017 (4)
C23	0.423 (2)	0.482 (2)	0.593 (2)	0.034 (6)
C24	0.4404 (18)	0.664 (3)	0.4865 (19)	0.027 (6)
Fe1	0.1325 (3)	0.7315 (3)	0.6625 (2)	0.0185 (8)
C6	0.0463 (18)	0.906 (2)	0.6373 (16)	0.016 (5)
C7	0.0072 (16)	0.806 (3)	0.6903 (17)	0.025 (6)
C8	-0.0313 (19)	0.697 (3)	0.6252 (19)	0.031 (6)
C9	-0.0246 (19)	0.722 (3)	0.526 (2)	0.030 (6)
C10	0.0215 (16)	0.853 (3)	0.5321 (15)	0.020 (5)
C11	0.3488 (18)	0.906 (2)	0.7037 (17)	0.020 (5)
C12	0.2898 (19)	1.011 (2)	0.6272 (18)	0.016 (6)
C13	0.3735 (17)	1.104 (2)	0.6320 (17)	0.022 (5)
C14	0.482 (2)	1.062 (3)	0.7142 (18)	0.027 (6)
C15	0.4665 (16)	0.937 (2)	0.7539 (16)	0.014 (5)
C25	0.5592 (15)	0.846 (3)	0.8349 (14)	0.021 (5)
C26	0.6631 (18)	0.914 (2)	0.9215 (16)	0.027 (6)
N2	0.5902 (14)	0.7483 (18)	0.7647 (14)	0.018 (3)
C27	0.6446 (18)	0.626 (2)	0.8284 (17)	0.022 (4)
C28	0.6624 (16)	0.805 (3)	0.7206 (15)	0.020 (4)
Fe2	0.3810 (2)	1.0795 (3)	0.7879 (2)	0.0174 (7)
C16	0.3121 (18)	1.078 (2)	0.8968 (17)	0.026 (5)
C17	0.2774 (19)	1.194 (2)	0.8278 (18)	0.024 (6)
C18	0.3779 (19)	1.261 (3)	0.8495 (19)	0.032 (6)
C19	0.470 (2)	1.194 (2)	0.9216 (18)	0.025 (6)
C20	0.435 (2)	1.080 (3)	0.954 (2)	0.043 (7)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Pt1—S1	2.202 (6)	S1—O1	1.49 (2)
Pt1—Cl1	2.305 (6)	S1—C29	1.78 (3)
Pt1—Cl3	2.316 (6)	S1—C30	1.82 (2)
S1—Pt1—Cl1	93.0 (2)	S1—Pt1—Cl3	175.0 (2)
S1—Pt1—Cl2	87.9 (2)	Cl1—Pt1—Cl3	90.8 (2)
Cl1—Pt1—Cl2	179.1 (2)	Cl2—Pt1—Cl3	88.3 (2)

H atoms were included in calculated positions using standard *SHELXL93 HFIX* (Sheldrick, 1993) procedures and their parameters were not refined.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *ORTEP* (Johnson, 1965).

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Monosodium 4-Amino-1-hydroxy-1,1-butanedioldiphosphonate Trihydrate (Alendronate)

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Abstract

The cation in the title compound, $\text{Na}^+\cdot\text{C}_4\text{H}_{12}\text{NO}_7\text{P}_2^- \cdot 3\text{H}_2\text{O}$, has the expected zwitterionic character, with a terminal protonated amine group on one side of the