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Racemic (α -Ferrocenylphenacyl)triphenylphosphonium Iodide

S. ZAKA AHMED,^a CHRISTOPHER GLIDEWELL^a AND GEORGE FERGUSON^b

^aSchool of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, and ^bDepartment of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1. E-mail: cg@st-andrews.ac.uk

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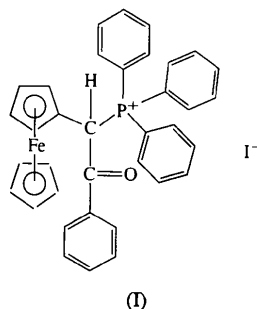
Abstract

In racemic (α -ferrocenylphenacyl)triphenylphosphonium iodide, $[Fe(C_5H_5)(C_3H_2_5OP)]I$, the cations are involved in C—H \cdots I⁻ interactions with short C \cdots I distances of 3.836 (7), 3.932 (7) and 3.995 (7) Å.

Comment

The structures of (ferrocenylmethyl)triphenylphosphonium iodide and 1,1'-ferrocenediylbis(methylphenylphosphonium iodide) (as the dichloromethane solvate), $[Fe\{(C_5H_4)CH_2P(C_6H_5)_3\}_2]^{2+} \cdot 2I^- \cdot CH_2Cl_2$, have recently been found to exhibit extensive three-dimensional networks of C—H \cdots I⁻ interactions (Glidewell, Zakaria, Ferguson & Gallagher, 1994). In a similar way, the structures of (ferrocenylmethyl)trimethylammonium iodide and hexa-*N*-methylferrocene-1,1'-diylbis(methylammonium iodide), $[Fe\{(C_5H_4)CH_2N(CH_3)_3\}_2]^{2+} \cdot 2I^-$, are also characterized by such interactions (Ferguson, Gallagher, Glidewell & Zakaria, 1994). In all of these structures there are C \cdots I⁻ distances in the range 3.8–3.9 Å. Such C—H \cdots I⁻ hydrogen bonds are uncommon; for example, in tetraphenylphosphonium iodide (Schweizer, Baldacchini & Rheingold, 1989) and dimethyldiphenylphosphonium iodide (Staples, Carlson, Wang & Fackler, 1995), compounds related to (ferrocenylmethyl)triphenylphosphonium iodide, there are no C \cdots I⁻ distances less than 4.0 Å; however, well documented examples occur in the structures

of benzyltriphenylphosphonium iodide (Archer, Modro & Nassimbeni, 1981), methylphenylphospholanium iodide, $[(CH_3)(C_6H_5)P(CH_2)_4]^+ \cdot I^-$ (Alver & Haltedahl, 1967), 3,3-dimethyl-1,1-diphenylphosphetanium iodide, $[(C_6H_5)_2PCH_2C(CH_3)_2CH_2]^+ \cdot I^-$ (Mazhar-ul-Haque, 1979), and bis[1,2-bis(diphenylphosphino)ethane]-platinum(II) diiodide deuteriochloroform solvate, $\{[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2Pt\}^{2+} \cdot 2I^- \cdot 2(CDCl_3)$ (Ferguson, Lough, McAlees & McCrindle, 1993). Particularly short C \cdots I⁻ distances (3.67 Å) occur in the fulleride salt $[(C_6H_5)_4P]_2(C_{60})I_{0.35}$ (Penicaud, Perez-Benitez, Gleason, Munoz & Escudro, 1993), but the apparent shortness may be influenced by the low occupancy (35%) of the iodide sites. Here we report the structure of (α -ferrocenylphenacyl)triphenylphosphonium iodide, $[(C_5H_5)Fe(C_5H_4)]CH(COC_6H_5)P(C_6H_5)_3]^+ \cdot I^-$, (I), a benzoylated derivative of (ferrocenylmethyl)triphenylphosphonium iodide, which also contains short C \cdots I⁻ distances.



The structure consists of ion pairs (Fig. 1) within which there is a single short C—H \cdots I⁻ interaction involving C62, characterized by C \cdots I 3.836 (7) Å and C—H \cdots I 151°. There are also two further fairly short C—H \cdots I⁻ interactions involving C44 in the cation at $(-\frac{1}{2} + x, y, \frac{1}{2} - z)$ [C \cdots I 3.932 (7) Å, C—H \cdots I 134°] and C33 in the cation at $(\frac{3}{2} - x, \frac{1}{2} + y, z)$ [C \cdots I 3.995 (7) Å, C—H \cdots I 132°], which serve to generate a continuous network. The cations are chiral, but the space group accommodates equal numbers of *R* and *S* enantiomers. The almost perfectly staggered conformation about the C1—C2 bond is such that O2 and H1 are anti-periplanar, while O2 and P1 are synclinal; despite this, the O \cdots P distance of 3.184 (6) Å is significantly shorter than the sum of van der Waals radii (3.45 Å; Bondi, 1984). Since the O atom undoubtedly carries a partial negative charge, the occurrence of an attractive P \cdots O interaction is not surprising. Similar, although stronger, attractive interactions have been observed previously in acyl and sulfonyl ylides of arsenic and antimony (Ferguson, Glidewell, Lloyd, Metcalfe & Ruhl, 1987; Ferguson *et al.*, 1988). The conformation about the C1—P1 bonds departs from perfect staggering by *ca* 14 (2)°. The C1—P1 bond [1.845 (6) Å] is significantly longer than the corresponding bonds in both (ferrocenylmethyl)triphenylphosphonium iodide [1.813 (2) Å] and

1,1'-ferrocenediylbis(methylphenylphosphonium iodide) [1.815 (4) and 1.818 (4) Å] (Glidewell *et al.*, 1994), and the C1—C2 bond length is significantly above the upper quartile value (1.521 Å) for bonds of this type (Allen *et al.*, 1987); otherwise the metrical dimensions of the cation are unexceptional. As usual, the ferrocene fragment has an almost eclipsed conformation; the mean value of the torsion angles C1*i*—Cp1—Cp2—C2*i* (*i* = 1, 2; Cp1, Cp2 are the ring centroids) is 9.5 (4)° and the two C₅ rings are only 2.3 (4)° from being parallel.

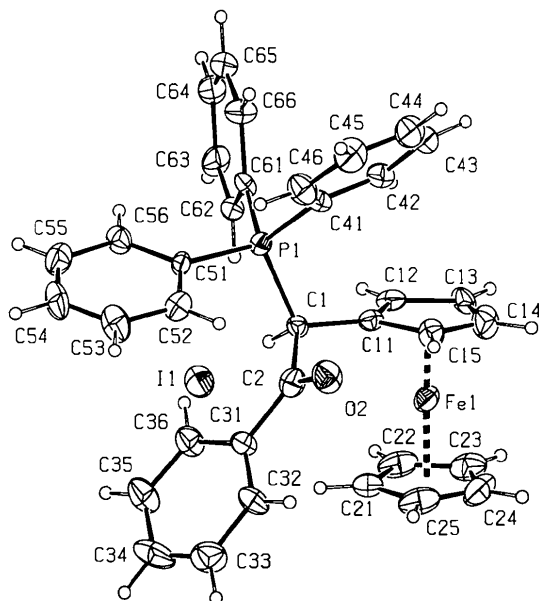


Fig. 1. A view of the asymmetric unit showing the *R* enantiomer of the cation, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

A sample of (α -ferrocenylphenacyl)triphenylphosphonium iodide was prepared by a modification of the published procedure (Pauson & Watts, 1963). A solution of (ferrocenylmethyl)triphenylphosphonium iodide in dry diethyl ether was treated with an equimolar quantity of phenyllithium, followed by an equimolar quantity of benzoyl chloride. Crystals suitable for single-crystal X-ray diffraction were grown from aqueous acetone. NMR (CDCl₃ solution): δ_{H} 3.78 (*m*, 1H), 4.10 (*m*, 1H), 4.22 (*m*, 1H) and 4.91 (*m*, 1H) (C₅H₄); 3.80 (*s*, 5H, C₅H₅); 7.40 [*d*, 1H, ²*J*(HP) = 8.5 Hz, CH]; 7.5–7.8 (*m*, 20H, 4 × C₆H₅); δ_{C} 46.2 [*d* × *d*, ¹*J*(PC) = 43.7 Hz, HCP]; 68.8 (*d*), 69.0 (*d*), 69.7 (*d*), 71.9 (*d*) and 73.8 (*s*) (C₅H₄); 69.6 (*d*, C₅H₅); 117.5 [*s* × *d*, ¹*J*(PC) = 83.8 Hz], 129.8 [*d* × *d*, *J*(PC) = 12.6 Hz], 134.6 [*d* × *d*, *J*(PC) = 9.6 Hz] and 134.8 (*d*) (C₆H₅P); 129.6 (*d*), 130.8 (*d*), 134.8 (*d*) and 135.9 (*s*) (C₆H₅CO); 192.5 (*s*, CO); δ_{P} 24.3 p.p.m.

Crystal data

[Fe(C₅H₅)(C₃₁H₂₅OP)]I
M_r = 692.32

Mo *K* α radiation
 λ = 0.7107 Å

Orthorhombic
Pbca
a = 16.949 (2) Å
b = 17.907 (2) Å
c = 19.662 (3) Å
V = 5967.7 (13) Å³
Z = 8
D_x = 1.541 Mg m⁻³
D_m not measured

Data collection

Enraf–Nonius CAD-4
diffractometer
 $\theta/2\theta$ scans
Absorption correction:
five ψ scans at 4°
steps (North, Phillips &
Mathews, 1968)
T_{min} = 0.837, *T_{max}* =
0.997
6473 measured reflections

Cell parameters from 25
reflections
 θ = 9.20–14.35°
 μ = 1.621 mm⁻¹
T = 294 (1) K
Triangular-shaped plate
0.39 × 0.39 × 0.29 mm
Red

6473 independent reflections
2270 observed reflections
[*I* > 2 σ (*I*)]
 θ_{max} = 26.9°
h = 0 → 21
k = 0 → 22
l = 0 → 25
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.0552
wR(*F*²) = 0.1132
S = 0.802
6473 reflections
361 parameters
H atoms riding [SHELXL93
(Sheldrick, 1993) defaults,
C—H 0.93 to 0.98 Å]

$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\text{max}} = 0.509 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.406 \text{ e } \text{Å}^{-3}$
Extinction correction: none
Atomic scattering factors
from *International Tables*
for *Crystallography* (1992,
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
I1	0.60568 (3)	0.17123 (3)	0.01255 (2)	0.0576 (2)
Fe1	0.90153 (6)	0.12833 (6)	0.02802 (4)	0.0443 (3)
P1	0.75766 (10)	0.06276 (10)	0.22992 (8)	0.0333 (4)
O2	0.8637 (3)	−0.0511 (3)	0.1456 (3)	0.0621 (15)
C1	0.7875 (3)	0.0611 (3)	0.1397 (3)	0.031 (2)
C2	0.8066 (4)	−0.0205 (4)	0.1205 (3)	0.047 (2)
C11	0.8558 (4)	0.1113 (4)	0.1226 (3)	0.037 (2)
C12	0.8505 (4)	0.1880 (3)	0.1042 (3)	0.043 (2)
C13	0.9289 (5)	0.2153 (4)	0.0922 (3)	0.056 (2)
C14	0.9791 (5)	0.1553 (5)	0.1020 (4)	0.062 (2)
C15	0.9372 (4)	0.0914 (4)	0.1216 (3)	0.047 (2)
Cp1†	0.9103 (5)	0.1523 (4)	0.1085 (3)	
C21	0.8349 (5)	0.0759 (5)	−0.0436 (3)	0.060 (2)
C22	0.8430 (6)	0.1505 (5)	−0.0595 (4)	0.067 (3)
C23	0.9235 (6)	0.1663 (5)	−0.0676 (3)	0.071 (3)
C24	0.9631 (5)	0.0995 (6)	−0.0565 (4)	0.073 (3)
C25	0.9099 (6)	0.0436 (5)	−0.0414 (4)	0.070 (3)
Cp2†	0.8949 (6)	0.1072 (5)	−0.0537 (4)	
C31	0.7534 (5)	−0.0620 (4)	0.0728 (3)	0.045 (2)
C32	0.7827 (5)	−0.1256 (4)	0.0435 (3)	0.051 (2)
C33	0.7343 (6)	−0.1655 (5)	0.0005 (4)	0.074 (3)
C34	0.6585 (7)	−0.1444 (5)	−0.0105 (4)	0.080 (3)
C35	0.6287 (5)	−0.0818 (5)	0.0204 (4)	0.070 (2)
C36	0.6767 (4)	−0.0393 (4)	0.0604 (4)	0.055 (2)
C41	0.8410 (4)	0.0554 (4)	0.2852 (3)	0.038 (2)
C42	0.8961 (4)	0.1120 (4)	0.2853 (3)	0.046 (2)
C43	0.9606 (4)	0.1093 (5)	0.3285 (4)	0.055 (2)
C44	0.9696 (5)	0.0488 (5)	0.3699 (4)	0.063 (2)

C45	0.9165 (5)	-0.0075 (5)	0.3718 (4)	0.065 (2)
C46	0.8498 (4)	-0.0046 (4)	0.3299 (4)	0.055 (2)
C51	0.6887 (4)	-0.0115 (4)	0.2447 (3)	0.035 (2)
C52	0.7106 (4)	-0.0865 (4)	0.2373 (3)	0.051 (2)
C53	0.6559 (5)	-0.1433 (4)	0.2460 (4)	0.065 (2)
C54	0.5798 (5)	-0.1253 (5)	0.2593 (4)	0.068 (3)
C55	0.5571 (4)	-0.0526 (5)	0.2663 (4)	0.061 (2)
C56	0.6103 (5)	0.0035 (4)	0.2601 (3)	0.046 (2)
C61	0.7112 (3)	0.1503 (3)	0.2479 (3)	0.033 (2)
C62	0.6722 (4)	0.1907 (4)	0.1981 (3)	0.046 (2)
C63	0.6320 (4)	0.2561 (4)	0.2149 (4)	0.055 (2)
C64	0.6305 (4)	0.2797 (4)	0.2812 (5)	0.062 (2)
C65	0.6680 (5)	0.2397 (5)	0.3313 (4)	0.063 (2)
C66	0.7087 (4)	0.1753 (4)	0.3154 (3)	0.053 (2)

† Cp1 and Cp2 are the centroids of rings C11–C15 and C21–C25, respectively.

Table 2. Selected geometric parameters (Å, °)

Fe1—Cp1	1.646 (7)	C11—C12	1.424 (8)
Fe1—Cp2	1.655 (7)	C11—C15	1.425 (8)
P1—C1	1.845 (6)	C12—C13	1.436 (9)
P1—C41	1.788 (6)	C13—C14	1.384 (9)
P1—C51	1.794 (7)	C14—C15	1.402 (9)
P1—C61	1.790 (6)	C21—C22	1.380 (10)
O2—C2	1.217 (7)	C21—C25	1.397 (10)
C1—C2	1.545 (8)	C22—C23	1.403 (10)
C1—C11	1.504 (8)	C23—C24	1.389 (10)
C2—C31	1.498 (9)	C24—C25	1.380 (10)
Cp1—Fe1—Cp2	177.7 (3)	P1—C1—C2	107.9 (4)
C41—P1—C51	111.2 (3)	P1—C1—C11	114.6 (4)
C41—P1—C61	107.0 (3)	C2—C1—C11	110.4 (5)
C61—P1—C51	109.3 (3)	O2—C2—C1	119.6 (6)
C1—P1—C61	108.9 (3)	O2—C2—C31	120.7 (7)
C1—P1—C51	108.8 (3)	C1—C2—C31	119.7 (6)
C1—P1—C41	111.5 (3)		
C41—P1—C1—C11	-46.5 (6)	P1—C1—C2—O2	-67.4 (7)
C51—P1—C1—C11	-169.6 (5)	C11—C1—C2—C31	-123.4 (6)
C61—P1—C1—C11	71.4 (5)	P1—C1—C2—C31	110.7 (6)
C11—C1—C2—O2	58.6 (8)		

Examination of the structure with *PLATON* (Spek, 1995a) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD-4-PC* (Enraf–Nonius, 1992). Cell refinement: *SET4* and *CELDIM* (Enraf–Nonius, 1992). Data reduction: *DATRD2* in *NRCVAX94* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX94*. Program(s) used to refine structure: *NRCVAX94* and *SHELXL93* (Sheldrick, 1993). Molecular graphics: *NRCVAX94*, *ORTEPII* (Johnson, 1976), *PLATON*, *PLUTON* (Spek 1995b). Software used to prepare material for publication: *NRCVAX94*, *SHELXL93* and *WordPerfect* macro *PREPCIF*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Chloromethylbis(tri-*p*-tolylarsine)-platinum(II)

STEFANUS OTTO AND ANDREAS ROODT*

Department of Chemistry, University of the Orange Free State, Bloemfontein 9300, South Africa. E-mail: char@uovsvm1.uovs.ac.za

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Abstract

The title compound, *trans*-[PtCl(CH₂){As(C₆H₄CH₃)₃]₂, is one of the few bis tertiary arsine complexes of platinum(II). The complex exhibits square-planar geometry with the two arsine ligands in a non-linear *trans* orientation with an As1—Pt—As2 bond angle of 175.66 (4)°. The large *trans* influence of the methyl substituent is manifested in the long Pt—Cl bond distance of 2.397 (3) Å.