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Acta Cryst. (1997). **C53**, 1414–1416

trans-Dichlorobis(ferrocenyldiphenylphosphine-*P*)platinum(II)–Benzene (1/2)

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Abstract

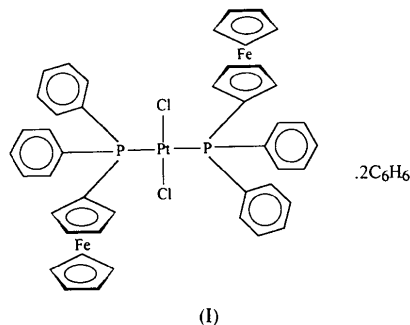
The structure determination of the title compound, [PtCl₂(C₂₂H₁₉FeP)₂].2C₆H₆, shows the Pt^{II} moiety to have a square-planar geometry with the bulky phosphine ligands in a *trans* orientation; each molecule crystallizes with two benzene solvent molecules. The compound crystallizes in the triclinic space group *P* $\bar{1}$ with one mole per unit cell. Bond distances and angles of the

coordination polyhedron are Pt–P = 2.318 (2), Pt–Cl = 2.301 (2) Å and P–Pt–Cl = 87.56 (7)°. The structure is compared to analogous platinum(II)–dichloro complexes containing two *trans* tertiary phosphine ligands.

Comment

Some of the work performed by our research group involves the tuning of chemical behaviour of complexes by introduction of certain functionalized ligand systems. The evaluation of the complex by means of as many techniques as possible, *e.g.*, X-ray structural, multinuclear NMR, IR spectroscopy and reaction kinetics is of prime importance to quantify the effect of the specific ligand on the complex under investigation. Complexes containing P atoms and ferrocene moieties can be ideally investigated by ³¹P NMR and cyclic voltametry.

One such system includes the systematic study of complexes of the general type [Pt(*R*)(Cl)(*L*)₂], where *L* can be tertiary phosphine, arsine or stibene ligands (Otto, Roodt & Leipoldt, 1995; Roodt, Otto & Leipoldt, 1995; Otto & Roodt, 1996). Ferrocenyldiphenylphosphine was one of the ligands used, where *R* = Me and Ph, and since there is so little known about this specific phosphine, we determined the X-ray structure of the title complex, (I), to obtain some additional information on the coordination mode of this unsymmetrical phosphine ligand.



The molecular geometry is shown in Fig. 1 and the title compound is compared with structural data for analogous compounds in the literature (Table 2). It is clear from Table 2 that a relatively short Pt–P bond length is obtained for the title compound, indicative of strong Lewis basicity. One would expect a rather large steric demand for this phosphine ligand which will tend to lengthen the bond. The Pt–Cl bond distances and P–Pt–Cl angles are within normal limits. The P–C bond distances to the phenyl rings are within normal limits for this type of bond, while the P–C bond with the ferrocenyl moiety is appreciably shorter, *i.e.* 0.032 (8) Å. The same tendency was also observed previously in a structural study of the uncoordinated PPh₂Fc ligand (Adeleke & Lui, 1993) (where Fc = ferrocenyl). All C–C bonds and angles in the benzene

solvent molecule are within normal ranges with averages of 1.35 (2) Å and 120 (1)°, respectively.

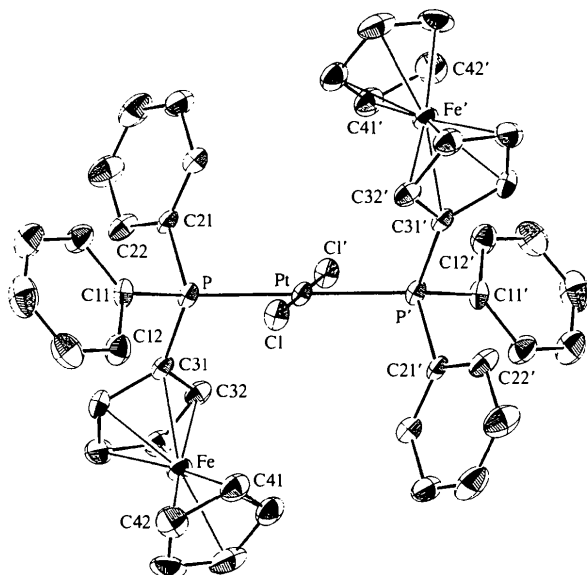


Fig. 1. An ORTEP (Johnson, 1976) drawing of the coordination compound showing the numbering scheme. Displacement ellipsoids correspond to 30% probability level. The benzene solvent molecules have been omitted for clarity.

The Fe—C bond lengths are all typical of those normally found in ferrocene compounds, averaging 2.036 (9) Å for the substituted ring and 2.039 (9) Å for the unsubstituted ring (Miller, Kazi & Wrighton, 1989). The P atom is tetrahedrally surrounded by the two phenyl rings, the ferrocenyl ligand and the metal atom. The C—P—Pt angles are all larger than the ideal of 109.5°, and range from 111.0 (3) to 118.2 (2)°, while all the C—P—C bond angles are smaller than expected for a normal tetrahedra, *i.e.* 103.3 (4)–104.0 (4)°. This deviation from normal tetrahedral angles was previously observed in free and coordinated phosphine ligands of this type (Houlton, Roberts, Silver & Drew, 1990) and was explained on the basis of the valence-shell electron-pair repulsion theory. The phosphorous lone pair will repel the bonding-pair electrons to a greater extent than each other, giving rise to C—P—C angles smaller than 109.5°. Upon coordination, the lone pair becomes a bonding pair, resulting in weakened repulsion and the angles becomes closer to the expected value. This observation also holds true in the current study where coordination gives rise to an average increase of 2.6 (4)°.

Experimental

Ferrocenyldiphenylphosphine (PPh₂Fc) was synthesized according to literature procedures (Sollott, Mertwoy, Portnoy

& Snead, 1963) and was purified by column chromatography (hexane/benzene 9:1). ¹H NMR (CDCl₃ = 7.24 p.p.m.): 4.06 (5H, *s*), 4.09 (2H, *q*), 4.36 (2H, *t*), 8.3–8.4 (10H, *m*); ³¹P NMR (CDCl₃, 161.903 MHz, H₃PO₄ = 0 p.p.m.): –16.18 (*s*). The title compound was prepared by reacting PPh₂Fc with [Pt(Cl)₂(SMe₂)₂]. Recrystallization from benzene yielded crystals suitable for X-ray analysis. IR (KBr): ν(Pt—Cl) = 349 cm⁻¹; ³¹P NMR (CDCl₃, 161.903 MHz, H₃PO₄ = 0 p.p.m.): 13.34 (triplet due to 34% ¹⁹⁵Pt), ¹J_{Pt—P} = 3773 Hz.

Crystal data

[PtCl₂(C₂₂H₁₉FeP)₂].2C₆H₆

*M*_r = 1162.59

Triclinic

P $\bar{1}$

a = 9.511 (1) Å

b = 12.754 (2) Å

c = 10.363 (1) Å

α = 97.42 (1)°

β = 87.45 (1)°

γ = 106.81 (1)°

V = 1193.2 (3) Å³

Z = 1

*D*_x = 1.618 Mg m⁻³

*D*_m = 1.623 Mg m⁻³

*D*_m measured by flotation in NaI/H₂O

Cu Kα radiation

λ = 1.54178 Å

Cell parameters from 15 reflections

θ = 30–50°

μ = 12.127 mm⁻¹

T = 293 (2) K

Cube

0.12 × 0.10 × 0.10 mm

Dark orange

Data collection

Syntex *P*-1 diffractometer

θ/2θ scans

Absorption correction: none

2925 measured reflections

2925 independent reflections

2901 reflections with

I > 2σ(*I*)

θ_{max} = 57.32°

h = 0 → 10

k = –13 → 13

l = –11 → 11

3 standard reflections

every 100 reflections

frequency: 60 min

intensity decay: 24%

Refinement

Refinement on *F*²

R [*F*² > 2σ(*F*²)] = 0.043

wR (*F*²) = 0.112

S = 1.050

2924 reflections

287 parameters

H atoms calculated riding on adjacent C atom

w = 1/[σ²(*F*_o²) + (0.0709*P*)² + 4.94*P*]

where *P* = (*F*_o² + 2*F*_c²)/3

(Δ/σ)_{max} = –0.001

Δρ_{max} = 2.015 e Å⁻³

Δρ_{min} = –1.707 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Pt—Cl	2.301 (2)	P—C11	1.828 (8)
Pt—P	2.318 (2)	P—C21	1.835 (8)
P—C31	1.798 (8)		
Cl—Pt—P	87.56 (7)	C11—P—C21	103.7 (4)
Cl—Pt—P	92.44 (7)	C31—P—Pt	115.2 (2)
C31—P—C11	103.3 (4)	C11—P—Pt	118.2 (2)
C31—P—C21	104.0 (4)	C21—P—Pt	111.0 (3)

Symmetry code: (i) 1 – *x*, 1 – *y*, 1 – *z*.

Table 2. Comparison of *trans*-[Pt(Cl)₂(PR₃)₂] complexes (Å, °) *Acta Cryst.* (1997). C53, 1416–1420

PR ₃	Pt—P	Pt—Cl	P—Pt—Cl
Pcy ₃ ^a	2.337 (2)	2.317 (2)	88.8 (1)
PEt ₃ ^b	2.298 (18)	2.294 (9)	87.30 (14)
P ^t (Bu) ₂ (CHCH ₂ CH ₂) ^c	2.373 (1)	2.301 (1)	90.16 (4)
P{N(Me)CH ₂ CH ₂ } ₃ N ^d	2.349 (4)	Not reported	
P(NMe ₂) ₃ ^d	2.3312 (7)	Not reported	
PPh ₂ Fe ^e	2.318 (2)	2.301 (2)	87.56 (7)

Notes: (a) Del Pra & Zanotti (1980); (b) Messmer & Amma (1966); (c) Simms, Shang, Lu, Youngs & Ibers (1987); (d) Xi *et al.* (1990); (e) this study.

Due to decay as a result of loss of the benzene solvate, data collection was only performed to 2θ = 115°. Coating of the crystal to minimize decay made description of crystal faces impossible and hence no absorption corrections were performed. The collected data were corrected for intensity decay. Although μ has a high value, effective μ*t is small and constant due to the small equant crystal used for the data collection.

Data collection: Syntex P-1 software. Cell refinement: Syntex P-1 software. Data reduction: PROFIT (Streltsov & Zavodnik, 1989). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

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endo and *exo* Isomers of Isodicyclopentadienyltrichlorotitanium†

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Abstract

The diastereomeric *endo* and *exo* isomers of the title complex, [TiCl₃(C₁₀H₁₁)], have been synthesized by electrophilic attack of TiCl₄ on the *exo*- or *endo*-trimethylsilyl derivative of isodiCp (isodiCp = isodicyclopentadiene). This reaction proceeds with net inversion of configuration to give exclusively either the *endo*- or *exo*-(isodiCp)TiCl₃ compound. Although the two isomers have similar unit-cell constants, they crystallize in different space groups. The *endo* complex, (2), is in *Pbcm* with a crystallographic mirror plane, while the *exo* complex, (4), is in *Pca2*₁ with pseudo-mirror symmetry. Both molecules display a distorted tetrahedral geometry about the Ti atom. Each Ti atom is bonded in a η⁵ manner to the Cp ring of the isodiCp ligand, with Ti—ring centroid distances of 2.031 (2) and 2.013 (2) Å for (2) and (4), respectively. A slight bending of the isodiCp ligand about the bond shared by the Cp ring and the norbornane fragment is observed in both structures. The determination of the absolute structure of (4) defines the directionality of the packing along the polar *c* axis.

Comment

While the coordination of transition metals to C₂-symmetric annulated cyclopentadienyl anions necessarily gives rise to a single complex (Halterman, 1992), alternative recourse to C₁-symmetric 1,2-disubstituted cyclopentadienides allows for the possible production of pairs of π-facial isomers. This doubling of the number of possible products assumes practical utility when one face of the anion can be engaged in advance of the other by steric control (Paquette, Moriarty, McKinney & Rogers, 1989; Paquette, Moriarty & Rogers, 1989; Moriarty, Rogers & Paquette, 1989; Sivik, Rogers & Paquette, 1990; Rogers, Sivik & Paquette, 1993), by modulation of monomer–dimer equilibria in-

† Alternative name: trichloro[(1,2,3,3a,7a-η)-4,5,6,7-tetrahydro-4,7-methanoindenoid]titanium.