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Key indicators

Single-crystal X-ray study

$T = 100\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.032

wR factor = 0.087

Data-to-parameter ratio = 16.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

trans-Bis(azaferrocene)dichloropalladium(II)

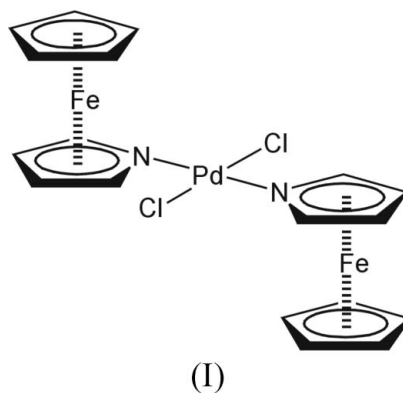
In the title compound, $[\text{PdCl}_2(\eta^5\text{-C}_4\text{H}_4\text{N})(\eta^5\text{-C}_5\text{H}_5)\text{Fe}]_2$, the Pd^{II} atom lies on an inversion center in a slightly distorted square-planar arrangement of *cis* Cl and N ligands. The azaferrocene ligands display a typical sandwich structure with practically parallel Cp and pyrrolyl rings. Weak hydrogen-bond interactions ($\text{C}-\text{H}\cdots\text{Cl}$) are found in the structure.

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Comment

The nearest heteroatom analog of ferrocene, azaferrocene, $(\eta^5\text{-C}_4\text{H}_4\text{N})(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$, displays rich and varied coordination chemistry. Complexes of this compound, which acts as a 2e donor ligand toward metal macrocyclic complexes such as cobaloximes and metalloporphyrins, have been obtained and structurally characterized (Zakrzewski & Giannotti, 1994, 1995). Some of them exhibit unusual photochemical properties due to the redox activity of the azaferrocene ligand. Combined structural and spectroscopic study on the $M(\text{CO})_5$ complexes of azaferrocene ($M = \text{Cr}, \text{Mo}$ or W) suggested moderate σ -donating and relatively weak π -accepting properties of this ligand (Silver *et al.*, 1997). Complexes of azaferrocene with electron-rich M^{II} centres ($M = \text{Pd}$ and Pt) were synthesized by Pyshnograeva *et al.* (1984) but were not structurally characterized. In this report, we present the crystal structure of (I), the complex of *trans*-dichlorobis(azaferrocene)palladium(II) prepared in the reaction of $\text{Pd}(\text{benzotrifluoride})_2\text{Cl}_2$ with azaferrocene. Crystals suitable for X-ray diffraction study were grown from layered dichloromethane–pentane.



The coordination geometry around Pd is exactly planar, with bond lengths and angles as shown in Table 1. The length of the Pd–Cl bonds is similar to those observed in *trans*- PdCl_2L_2 complexes, where $L = \text{pyridine}$ (Viossat *et al.* 1993), 4-ferrocenylpyridine (Rajput *et al.*, 2004) and (pyridinylmeth-

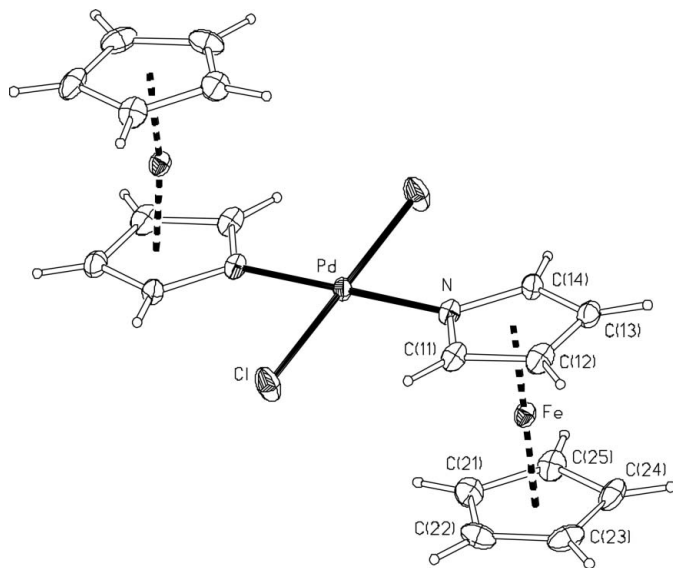


Figure 1
The structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. [Symmetry code for unlabeled atoms: $-x, -y, -z$.]

yl)phosphates (Kalinowska *et al.*, 2005). The Pd–N bonds are significantly longer than such bonds in the complex of unsubstituted pyridine [2.023 (2) Å; Viossat *et al.*, 1993]. Other complexes mentioned above show lengths of the Pd–N bond similar to that in the complex with unsubstituted pyridine. The above facts indicate that azaferrocene is a weaker ligand toward a d^8 Pd^{II} center than pyridine. It is worth noting that with the d^6 W(CO)₅ center azaferrocene forms a W–N bond of the same length as with pyridine. This suggests that weaker bonding of azaferrocene to an electron-rich Pd^{II} center may be due to weak electron-accepting properties of this ligand, which should, in this case, play a more important role than in the case of the electron-poorer W center. The pyrrolyl ligands are coplanar with the PdCl₂N₂ coordination. The azaferrocene ligands display a typical sandwich structure with practically parallel Cp and pyrrolyl rings [the dihedral angle between the mean planes of these ligands is 2 (3)°] and an eclipsed conformation (angle C14–center of the pyrrolyl ligand–center of the Cp ligand–C25 is -2.5 (3)°). In the crystal structure, some weak C–H···Cl interactions are been found (Table 2). The CH proton (H23) of the Cp ring is oriented towards the Cl atom, and is engaged in weak hydrogen-bonding interactions (H···Cl = 2.76 Å, mean C–H···Cl = 171°).

Experimental

A solution of (PhCN)₂PdCl₂ (69 mg, 0.18 mmol) and azaferrocene (68 mg, 0.36 mmol) in benzene (6 ml) was stirred for 1 h at room temperature. The product was precipitated with pentane, filtered off and dried. The yield was 81 mg (81%). Elemental analysis found: C 39.29, H 3.27, N 5.32, Cl 12.80%; C₁₈H₁₅Fe₂PdCl₂N₂ requires: C 39.21, H 3.29, N 5.08, Cl 12.86%. Crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a concentrated solution of the complex in dichloromethane.

Crystal data

[Fe₂Pd(C₅H₅)₂(C₄H₄N)₂]
 $M_r = 551.34$
 Orthorhombic, *Pbca*
 $a = 9.574$ (4) Å
 $b = 11.592$ (5) Å
 $c = 16.060$ (5) Å
 $V = 1782.4$ (12) Å³

$Z = 4$
 $D_x = 2.055$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 2.91$ mm⁻¹
 $T = 100$ (2) K
 Plate, black
 $0.21 \times 0.18 \times 0.04$ mm

Data collection

Kuma KM-4 CCD kappa-axis diffractometer
 ω scans
 Absorption correction: analytical (CrysAlis CCD; Oxford Diffraction, 2004)
 $T_{\min} = 0.674$, $T_{\max} = 0.896$

10701 measured reflections
 1940 independent reflections
 1788 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.075$
 $\theta_{\max} = 27.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.087$
 $S = 1.14$
 1940 reflections
 115 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 1.2026P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.33$ e Å⁻³
 $\Delta\rho_{\min} = -0.70$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Pd–N	2.045 (2)	Fe–C22	2.047 (3)
Pd–Cl	2.3057 (9)	Fe–C25	2.050 (3)
Fe–N	2.009 (2)	Fe–C24	2.051 (3)
Fe–C14	2.018 (3)	Fe–C21	2.058 (3)
Fe–C11	2.023 (3)	Fe–C12	2.076 (3)
Fe–C23	2.046 (3)	Fe–C13	2.077 (3)
N ⁱ –Pd–N	180.00 (13)	N ⁱ –Pd–Cl	90.42 (7)
N ⁱ –Pd–Cl ⁱ	89.58 (7)	N–Pd–Cl	89.58 (7)
N–Pd–Cl ⁱ	90.42 (7)		

Symmetry code: (i) $-x, -y, -z$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C23–H23···Cl ⁱⁱ	0.93	2.76	3.678 (3)	171

Symmetry code: (ii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$.

All H atoms were located in difference Fourier maps, and in the final refinement cycles they were treated as riding on their parent atoms, with C–H = 0.93 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$. The highest residual density peak is located 0.88 Å from the Pd atom.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2004); program(s) used to solve structure: *XS* in *SHELXTL* (Bruker, 1999); program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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