

Chemistry of Heterobimetallic Metal Complexes.

Part I. Synthesis, X-ray Structure and Solution Chemistry of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{PtCl}_2]$

D. A. CLEMENTE*, G. PILLONI

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Via Marzolo 1, 35100 Padua, Italy

B. CORAIN*, B. LONGATO

Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, C.N.R., Via Marzolo 1, 35100 Padua, Italy

and M. TIRIPICCHIO-CAMELLINI

Istituto di Chimica Generale, Università di Parma, Centro di Studio per la Strutturistica Diffattometrica del C.N.R., Via M. D'Azeglio 85, 43100 Parma, Italy

Received October 31, 1985

The aim of synthesizing homo- and hetero-polymetallic complexes has become rather popular in recent years. The basic background for this idea is the consideration that the coexistence of two or more metal atoms inside a coordination compound would be able, in principle, to create conditions for delicate and 'tunable' mutual cooperative effects of the metal centers in their chemical interaction with external substrates. The most impressive efforts in this field are certainly dedicated, to date, to the chemistry of metal clusters [1]. However, there is still room for the development of polymetallic complexes, in which metal-metal bonding is not operative, with 'tailored' ligand(s) designed to give peculiar chemical properties [2].

1,1'-Bis(diphenylphosphino)ferrocene $[\text{Fe}(\text{CpPPh}_2)_2]$ (1) was synthesized in 1971 [3] and was employed for preparing bimetallic complexes, some of which were found to be good catalysts for cross-coupling organic syntheses [4]. However, the syntheses and chemistry of simple complexes of the type $[\text{Fe}(\text{CpPPH}_2)_2\text{MX}_2]$ appear to have been rather ignored and we decided to undertake a systematic investigation of the solution and solid state chemistry of such species, with particular emphasis on their interaction with ligands of biological interest.

We report here the preparation, single crystal X-ray characterization and solution chemistry of $[\text{Fe}(\text{CpPPH}_2)_2\text{PtCl}_2]$ (2). 2 was prepared in 1972 [5], but we have developed a simpler synthetic approach, which gave us excellent yields of pure

product*. Recrystallization of crude 2 from acetone gave air-stable crystals with composition $[\text{Fe}(\text{CpPPh}_2)_2\text{PtCl}_2] \cdot ((\text{CH}_3)_2\text{CO})_{0.5}$ which were suitable for X-ray analysis**. 2 crystallizes in the monoclinic system, space group $C2/c$ with $a = 33.973(5)$, $b = 10.453(2)$, $c = 18.517(4)$, $\beta = 104.14(1)^\circ$; $Z = 8$; $D_c = 1.79 \text{ g cm}^{-3}$. The fractional coordinates for 2 are reported in Table I, and selected bond distances and angles are collected in Table II. The molecular structure of 2 is depicted in Fig. 1. 2 contains the ligand 1 coordinated to PtCl_2 via the two P atoms, as was found for the analogous complexes containing PdCl_2 and NiBr_2 [4, 6]. The ligand geometry around Pt^{II} is distorted square planar as shown by the larger P–Pt–P angle ($99.3(1)^\circ$) imposed by the ligand size. The Cl and P atoms are above and below the Cl_2P_2 plane ($\pm 0.011 \text{ \AA}$), while the Pt atom is displaced over the plane by $0.029 \text{ \AA}$. Similar distortions are found for the Pd analog [6]. The two cyclopentadienyl rings do not deviate significantly from planarity, but they are not parallel to each other in that they form an angle of 5.9° (to be compared to a value of 6.2° for the analogous Pd complex) [6]. The rings are in a staggered [6] configuration and their spacing decreases towards the P atoms. The acetone molecules trapped inside the lattice of 2 slightly interact with the C(7) atom ($\text{O} \cdots \text{C}(7)$ ($x, 1+y, z$) = $3.40 \text{ \AA}$) and the C=O bond is coincident with the binary axis.

In terms of molecular parameters, the most important feature is the very long $\text{Pt}^{\text{II}}\text{--Cl}$ bond found in 2, i.e., $2.404 \text{ \AA}$ (average) as compared with the values $2.27\text{--}2.33 \text{ \AA}$ observed in various *cis* Pt^{II} complexes [7a] and in the related complex *cis*- $[\text{PtCl}_2(\text{PMePh}_2)_2]$, i.e., $2.351 \text{ \AA}$ (average) [7b].

* PtCl_2 (266 mg, 1 mmol) was suspended in 30 ml benzene solution of 1 (554 mg, 1 mmol), which was refluxed for 20 h. After filtration, 2 was obtained as yellow crystals upon addition of ethanol (yield 93%).

**A crystal of approximate dimensions $0.3 \times 0.3 \times 0.2 \text{ mm}$ was employed. Diffraction intensities were collected on a Philips PW-1100 diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). A total of 6114 reflections were processed ($3^\circ < 2\theta \leq 50^\circ$, $\theta\text{--}2\theta$ scan), of which 3232 have $I > 3\sigma(I)$ (observed reflections); merging of this data set gives 3141 independent reflections that were subsequently used for structure determination. The intensities were corrected for Lorentz, polarization and experimental absorption factors [10g]. The cell constants were determined by a least-squares refinement of the setting angles of 25 reflections. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares technique with $w = 1.2517/\sigma^2(F_o) + 4.68 \times 10^{-4} F^2$. The programs used were those of SHELX package [10b]. The final R factors are: $R = 0.052$, $R_w = 0.059$, Goodness of fit = 1.44.

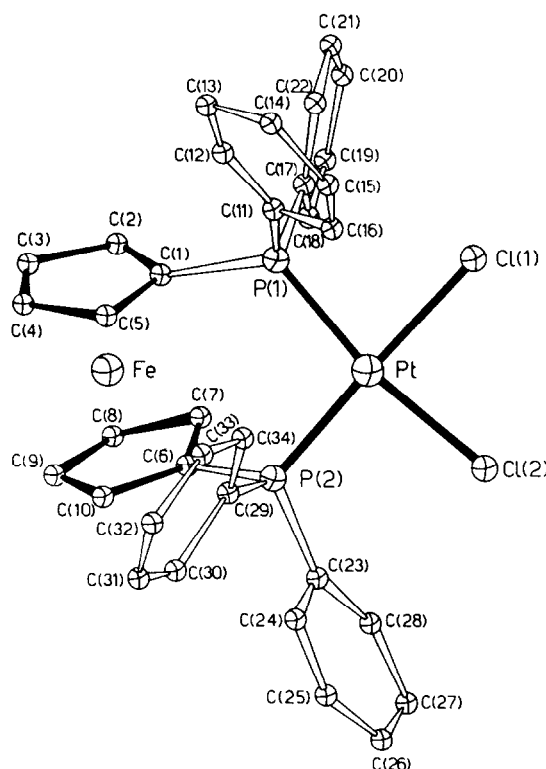
*Authors to whom correspondence should be addressed.

TABLE I. Fractional Coordinates for $[\text{Fe}(\text{CpPPH}_2)_2\text{PtCl}_2] \cdot (\text{CH}_3\text{CO-CH}_3)_{0.5}$

Atom	Atomic coordinates		
	x/a	y/b	z/c
Pt	0.1330(0)	0.2166(1)	0.3716(0)
Fe	0.0868(1)	-0.0248(2)	0.5184(1)
Cl(1)	0.1122(1)	0.4267(3)	0.3230(2)
Cl(2)	0.1636(1)	0.1945(3)	0.2686(2)
P(1)	0.1015(1)	0.2747(4)	0.4603(2)
P(2)	0.1557(1)	0.0216(4)	0.4156(2)
C(1)	0.0906(4)	0.1643(15)	0.5285(8)
C(2)	0.0496(4)	0.1234(16)	0.5325(9)
C(3)	0.0544(5)	0.0353(17)	0.5935(10)
C(4)	0.0970(5)	0.0283(17)	0.6287(10)
C(5)	0.1205(4)	0.1068(17)	0.5875(10)
C(6)	0.1182(4)	-0.0776(14)	0.4448(8)
C(7)	0.0759(4)	-0.0758(16)	0.4086(9)
C(8)	0.0569(5)	-0.1684(18)	0.4476(10)
C(9)	0.0869(5)	-0.2210(20)	0.5072(11)
C(10)	0.1256(4)	-0.1687(17)	0.5052(10)
C(11)	0.1294(4)	0.3979(15)	0.5216(8)
C(12)	0.1166(4)	0.4311(16)	0.5865(9)
C(13)	0.1386(4)	0.5217(16)	0.6349(9)
C(14)	0.1723(5)	0.5856(18)	0.6179(10)
C(15)	0.1846(4)	0.5474(17)	0.5542(10)
C(16)	0.1625(4)	0.4590(15)	0.5041(8)
C(17)	0.0501(4)	0.3321(16)	0.4168(9)
C(18)	0.0258(5)	0.2539(16)	0.3677(10)
C(19)	-0.0157(5)	0.2911(21)	0.3357(11)
C(20)	-0.0295(5)	0.4142(20)	0.3517(11)
C(21)	-0.0033(6)	0.4886(21)	0.4039(12)
C(22)	0.0374(5)	0.4533(18)	0.4349(10)
C(23)	0.1726(4)	-0.0834(15)	0.3520(9)
C(24)	0.1496(4)	-0.1931(16)	0.3216(9)
C(25)	0.1614(5)	-0.2712(19)	0.2704(11)
C(26)	0.1965(5)	-0.2444(17)	0.2491(10)
C(27)	0.2205(5)	-0.1389(20)	0.2770(11)
C(28)	0.2091(5)	-0.0594(17)	0.3308(10)
C(29)	0.1992(4)	0.0290(14)	0.4938(8)
C(30)	0.2198(4)	-0.0892(16)	0.5196(9)
C(31)	0.2544(5)	-0.0822(18)	0.5838(10)
C(32)	0.2667(5)	0.0313(17)	0.6160(10)
C(33)	0.2485(4)	0.1464(17)	0.5920(9)
C(34)	0.2130(4)	0.1467(16)	0.5286(9)
O	0.0000	0.9339(27)	0.2500
C(35)	0.0000	0.8144(33)	0.2500
C(36)	0.0371(7)	0.7408(25)	0.2422(15)

TABLE II. Selected Bond Lengths (Å) and Angles (deg) for $[\text{Fe}(\text{CpPPH}_2)_2\text{PtCl}_2] \cdot (\text{CH}_3\text{CO-CH}_3)_{0.5}$ ^a

Pt-P(1)	2.252(4)	Cl(1)-Pt-Cl(2)	86.3(1)
Pt-P(2)	2.260(4)	Cl(1)-Pt-P(1)	83.0(1)
Pt-Cl(1)	2.413(3)	P(1)-Pt-P(2)	99.3(1)
Pt-Cl(2)	2.396(4)	Cl(2)-Pt-P(2)	91.4(1)
Pt-Fe	4.278(2)		
Fe-C ₅ H ₄ P			
{ 1.99(2) 2.06(2) 2.07(2) 2.06(2) 2.03(2)			
{ 2.00(2) 2.05(2) 2.09(2) 2.06(2) 2.05(2)			
Mean C(1)-C(2)	1.445(2)		
Mean C(2)-C(3)	1.450(2)		
Mean C(3)-C(4)	1.430(2)		

^aEstimated standard deviations in parentheses.Fig. 1. Drawing of the molecular structure of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-PPh}_2)_2\text{PtCl}_2]$ projected on the coordination square plane. The numbering system used is also shown.

2 is moderately soluble in polar organic solvents, and its ^1H NMR spectrum in CDCl_3 shows the Cp protons as two multiplets in the range δ 4.33–4.16. The ^{31}P NMR spectrum in CDCl_3 displays a singlet at δ 13.06 (vs. H_3PO_4) flanked by two satellites due to coupling with ^{195}Pt ($|J| = 3769$ Hz). The J value is indicative of the existence in solution of the *cis* geometry around the Pt atom [8]. Moreover, the resonance of coordinated P atoms in 2

appears at lower field with respect to free 1 (δ -17.16).

In view of the recognized activity of $[\text{Fe}(\text{Cp})_2]^+$ as antineoplastic species [9], we investigated the redox behaviour of 2 and its cyclovoltammetric pattern in $\text{C}_2\text{H}_4\text{Cl}_2$ is depicted in Fig. 2. It is seen that 2 undergoes a highly reversible redox process in which the oxidation of Fe^{II} occurs at much higher anodic potentials ($\Delta E^\circ \approx 600$ mV) than in

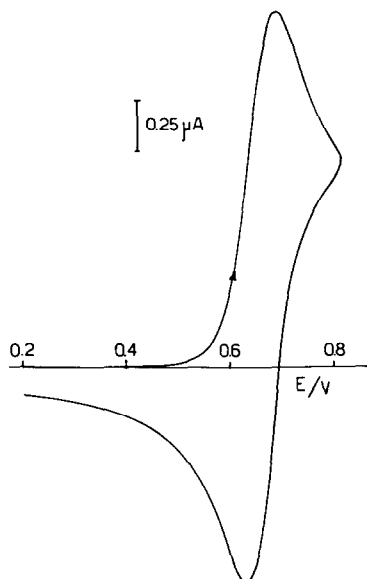


Fig. 2. Cyclic voltammogram for oxydation of 3.1×10^{-3} M $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{PtCl}_2]$ in 1,2-dichloroethane containing $(n\text{-Bu}_4\text{N})\text{ClO}_4$ at 25°C (Pt microelectrode, $\text{Ag}/0.1\text{ M AgClO}_4$ in CH_3CN as reference electrode). Scan rate 150 mV s^{-1} .

ferrocene. $[\text{Fe}(\text{CpPPH}_2)_2\text{PtCl}_2]\text{BF}_4$ could be isolated, albeit not in a very pure form, from $\text{C}_2\text{H}_4\text{Cl}_2$ solutions of **2** upon oxidation with NOBF_4 .*

***2** (474 mg, 0.58 mmol) was dissolved in anhydrous $\text{C}_2\text{H}_4\text{Cl}_2$ under argon, and solid NOBF_4 (71 mg, 0.61 mmol) was added under vigorous stirring. The suspension was stirred for three h under dynamic subatmospheric pressure to remove NO. A green precipitate was obtained upon filtration (yield 65%). *Anal.* Calc. for $\text{C}_{38}\text{H}_{28}\text{F}_4\text{Cl}_2\text{BFePt}$: C, 45.03; H, 3.11. Found: C, 43.81; H, 2.98%. Magnetic measurements gave μ (corrected) = 2.59 BM.

Acknowledgement

We thank Mr. F. De Zuane for the magnetic moment measurements.

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