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LETTER

Synthesis and crystal structure of the acetone solvate bis-[(μ-iodo)(bis-(diphenylphosphino)methane)platinum(II)] bis(tetrafluoroborate)

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dppm (dppm = bis(diphenylphosphino)methane) is a bidentate ligand whose versatility has been proven by the chemistry displayed by the large number of transition metal complexes which form [1–3].

In the case of halo–platinum compounds, it can give both mononuclear, [PtX_2(dppm)] (X = Cl, Br, I) and binuclear, [Pt_2X_2(μ-dppm$)_2$], compounds. The molecular structures of these species are examples of two different dppm coordination modes, namely chelated in [PtX_2(dppm)] [4, 5] and bridged in [Pt_2X_2(μ-dppm$)_2$] [6, 7]. Moreover, as a consequence of the geometry imposed by the dppm bridge, such binuclear complexes are characterized by a metal–metal bond.

In this report we describe the synthesis, characterization and crystal structure determination of [$Pt_2(\mu\text{-}I)_2$(dppm$)_2$][BF_4]$_2$, a new dppm–platinum compound containing a dihalo-bridged group.

Experimental

Preparation of compounds

The starting material [Pt(I)$_2$(dppm)] was prepared following the procedures reported in the literature [5].

[$Pt_2(\mu\text{-}I)_2$(dppm)$_2$][BF_4]$_2$ (1)

The reaction was performed in an oxygen-free nitrogen atmosphere. In a typical preparation, to a suspension of [Pt(I)$_2$(dppm)] (300 mg, 0.36 mmol) in dichloromethane (15 ml), $AgBF_4$ (82 mg, 0.42 mmol) was added. The resulting yellow mixture was stirred at room temperature for 15 days. The white precipitate which formed after that time was filtered and compound **1** was obtained as a microcrystalline white solid by recrystallization from acetone–petroleum ether. Yield 57%. *Anal.* Found: C, 37.80; H, 2.82. Calc. for $C_{50}H_{44}B_2F_8I_2P_4Pt_2$: C, 37.85; H, 2.79%. Λ_M (10^{-3} mol cm^{-3} in nitromethane) = 129.22 Ω^{-1} mol^{-1} cm^2. IR (KBr disc): ν = 1050 cm^{-1} (B–F). ^{1}H NMR (300 MHz, CD_2Cl_2, TMS internal standard): δ = 5.13 (t, ^2J(PH) = 11.9 Hz, ^3J(PtH) = 90 Hz, P–CH_2–P). ^{31}P NMR (121.5 MHz, CH_2Cl_2, 85% H_3PO_4 external standard): δ = −59.1 (s, J(PtP) = 2994 Hz).

Physical measurements

Infrared spectra were recorded on a Perkin-Elmer 1330 spectrometer. ^{1}H and ^{31}P NMR spectra were obtained on a Bruker WH 300 spectrometer. Conductivity measurements were performed using an LKB 5300 B Conductolyser conductivity bridge. Elemental analyses were carried out by the Microanalysis Laboratory of this Department.

X-ray data collection and refinement

A white crystal suitable for the structure analysis was obtained from acetone–petroleum ether and the intensities of X-ray reflections were measured on a Siemens R3m/V single crystal diffractometer.

Crystal data for $C_{50}H_{44}B_2F_8I_2P_4Pt_2 \cdot 2C_3H_6O$: M = 1702.4, a = 12.696(3), b = 12.272(2), c = 19.757(4) Å, β = 97.81(2)°, V = 3050(1) Å^3, Z = 2, D_{calc} = 1.854 g cm^{-3}, F(000) = 1624, Mo Kα radiation (λ = 0.71073), μ(Mo Kα) = 57.97 cm^{-1}, monoclinic, space group $P2_1/n$. A crystal of 0.36 × 0.22 × 0.16 mm was used to collect 6779 reflections in the range $3.0° < 2\theta < 50°$. Only 5396 independent reflections were observed (R_{int} = 0.0199). A correction for absorption (Ψ scan method [8]) was applied. The structure was solved by standard Patterson and Fourier methods and was refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were placed at calculated positions. The final cycles of refinement were carried out on the basis of 325 parameters for 3663 observed ($I > 3\sigma I$). The last cycle gave R = 0.0370, R_w = 0.0374 (weighting scheme $w^{-1} = \sigma^2(F) + 0.0002F^2$), S = 1.93. All calculations were performed with SHELXTL [9] and the PARST [10] set of programs. See also 'Supplementary material'.

Results and discussion

The reaction between [Pt(I)$_2$(dppm)] and $AgBF_4$ gives a white solid whose microanalytical data and

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TABLE 1. Selected bond distances (Å) and angles (°) in complex **1**

Pt(1)–I(1)	2.662(1)	Pt(1)–P(2)	2.243(2)
Pt(1)–I(1a)	2.669(1)	P(1)–C(25)	1.840(1)
Pt(1)–P(1)	2.240(2)	P(2)–C(25)	1.817(1)
I(1)–Pt(1)–I(1a)	86.6(1)	P(1)–Pt(1)–P(2)	71.9(1)
I(1)–Pt(1)–P(1)	173.0(1)	Pt(1)–I–Pt(1a)	93.4(1)
I(1)–Pt(1)–P(2)	101.7(1)	Pt(1)–P(1)–C(25)	93.8(3)
I(1a)–Pt(1)–P(1)	100.0(1)	Pt(1)–P(2)–C(25)	94.3(3)
I(1a)–Pt–P(2)	171.5(1)	P(1)–C(25)–P(2)	92.0(4)

conductivity measurements account for the $[Pt_2(I)_2(dppm)_2][BF_4]_2$ (**1**) stoichiometry. NMR spectroscopy shows the presence of two equivalent platinum-bonded dppm ligands, while the binuclear nature has been confirmed by X-ray structural analysis.

The crystal structure of complex **1** consists of diplatinum cations (Fig. 1), BF_4^- anions and acetone molecules of solvation. Selected bond distances and angles are given in Table 1.

In the unit cell only one [PtI(dppm)] moiety is present, repeated four times for the space group symmetry ($P2_1/n$, $Z=4$). The dimeric molecule is obtained from a [PtI(dppm)] moiety when a crystallographic center is applied.

The complex cation contains two platinum atoms, each of them bonded to a chelated dppm ligand and to two iodine atoms, in square planar environments. The metal coordination planes are coplanar and form a Pt_2I_2 rhombus with I–Pt–I and Pt–I–Pt angles of 86.6(1) and 93.4(1)°, respectively. The trend previously described for similar Pd_2X_2 fragments is then confirmed [11]. Moreover, as found for $[Pd(I)_2(dppm)]$ [12], the Pt–I distances (2.699(1) and 2.662(1) Å) as well as the Pt–P bond lengths (2.239(2) and 2.242(2) Å) account for iodine and phosphorous coordinated in a mutually *trans* geometry. The Pt---Pt separation is 3.881(8) Å. The P–Pt–P–C skeleton is essentially planar with P–Pt–P and P–C–P angles of 71.9(1) and 92.1(4)°, respectively, which give rise, as usual, to a quite strained four membered P–M–P–C ring (M = Pd [13]; M = Rh [14]).

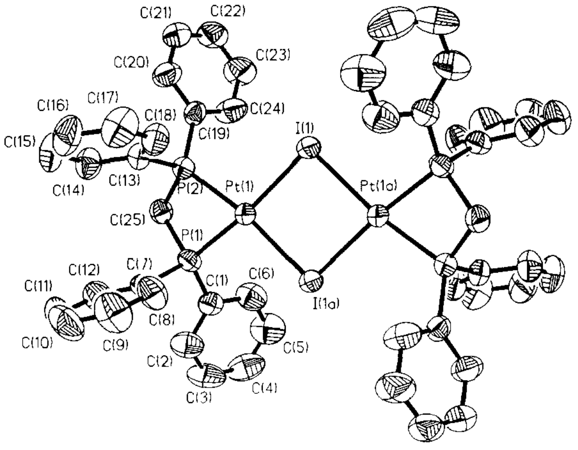

Fig. 1. View of the cation $[Pt_2(\mu\text{-}I)(dppm)_2]^{2+}$ of compound **1** with the atomic numbering scheme.

The BF_4^- anions are regular (B–F bonds and F–B–F angles in the ranges 1.29(3)–1.34(2) Å and 101.9(2)–114.0(2)°, respectively) and are involved in contacts with the cation through hydrogen bonds (i.e. $F(2^i)$---H(25b) = 2.48(1) Å, $F(4^i)$---H(6) = 2.47(1) Å: $i = x-1, y-1, z$).

The oxygen atoms of the two acetone molecules interact with phenyl hydrogens (O^i---H(9) = 2.56(1) Å: $i = 1-x, -y, -z$; O^i---H(21) = 2.42(1) Å: $i = x-\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$).

Supplementary material

Tables with the final atomic coordinates for the non-hydrogen atoms and for hydrogen atoms, the total bond distances (Å) and angles (°), the thermal parameters and a list of observed and calculated structure factors are available from the authors on request.

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