Synthesis and Structure of the Distorted Octahedral Palladium(II) Complex $[Pd(tmpp)_2][BF_4]_2$ [tmpp = tris(2,4,6-trimethoxyphenyl)phosphine]

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The brick-red Pd^{II} complex $[Pd(tmpp)_2][BF_4]_2$ is isolated from the reaction of $[Pd(NCCH_3)_4][BF_4]_2$ and tmpp (tris(2,4,6-trimethoxyphenyl)phosphine) (2 equiv.) in acetone at −44 °C; the new phosphine compound constitutes a rare example of a distorted octahedral Pd^{II} compound and exhibits the shortest Pd–L_{ax} distances reported to date for six-coordinate Pd^{II} complexes.

Pd^{II} complexes typically exhibit square-planar geometries, although five coordinate species are occasionally encountered.[1] The first documentation of axial interactions in a Pd^{II} complex was reported in 1968 for *trans*-$PdI_2(PMe_2Ph)_2$, whose solid-state structure was found to involve long intramolecular interactions between Pd and β-H atoms of the phenyl rings (2.84–3.28 Å).[2a,b] The use of polydentate ligands with special geometric requirements to favour octahedral coordination of Pd^{II} has met with success in recent years, *e.g.* pseudo-octahedral Pd^{II} complexes with crown thioether ligands are known to adopt conformations with four short Pd–S bonds and two long Pd–S contacts (2.95–3.27 Å).[3–8] Herein we report the synthesis, X-ray structure and spectroscopic data for a Pd^{II} complex supported by two flexible ether-phosphine ligands that are free to adopt an η^2 or η^1 mode of binding in a square-planar molecule,[9,10b] but which bind η^3 in the present case to give a distorted six-coordinate compound.

An acetone solution containing tmpp (0.476 g, 0.900 mmol) was added dropwise to an acetone solution of $[Pd(NCCH_3)_4][BF_4]_2$[11] (0.200 g, 0.450 mmol) at −44 °C whereupon an immediate change from pale yellow to red ensued. The resulting solution was stirred for 40 min at −44 °C, evaporated to dryness *in vacuo* and recrystallized from an acetone–diethyl ether solution to give a brick-red solid in 82% yield.†

X-Ray quality single crystals of $[Pd^{II}(TMPP)_2][BF_4]_2$ **1** were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution of the compound.‡ An ORTEP drawing of the molecular cation as well as selected bond distances and angles for **1** is provided in Fig. 1. The Pd atom resides in the centre of a pseudo-octahedron defined by two phosphorus atoms [P(1), P(2)] and two ether-oxygen atoms [O(1), O(10)] in an equatorial arrangement, and two ether oxygen atoms [O(4) and O(13)] in axial sites. The distortion of the square-planar geometry around the Pd atom is easily understood in terms of the requirements of the five-membered metallacycles Pd(1)–P(1)–C(1)–C(2)–O(1) and Pd(1)–P(2)–C(19)–C(20)–O(10) that involve acute angles [P(1)–Pd(1)–O(1) = 78.3 (2)°], and P(2)–Pd(1)–O(10) = 78.1 (2)°]. The average Pd–O_{ax} distance of 2.651 Å is the shortest axial contact reported to date for a Pd^{II} compound.[2–8] In comparison, the corresponding distances in $Pd^{II}L_6$ complexes supported by trigonal (S,S,S) or (S,S,N) ligands fall in the range 2.95–3.27 Å.[3–8]

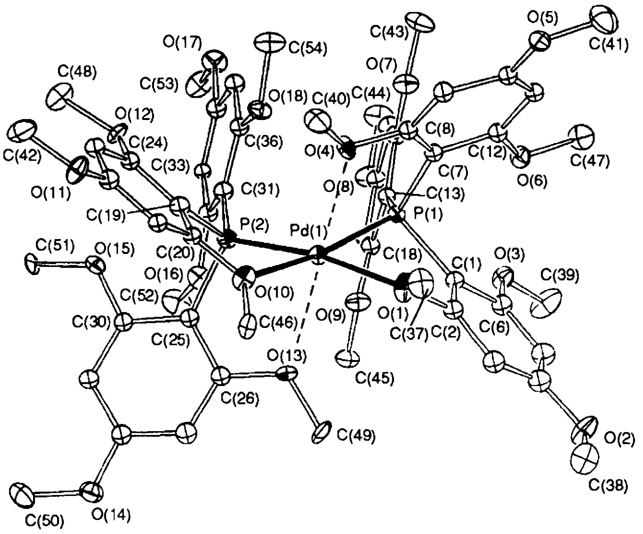

Fig. 1 ORTEP drawing of $[Pd(TMPP)_2]^{2+}$ **1** with 25% probability ellipsoids. Selected bond distances (Å) and angles (°): Pd(1)–P(1), 2.216 (4); Pd(1)–P(2), 2.215 (4); Pd(1)–O(1), 2.195 (7); Pd(1)–O(4), 2.671 (7); Pd(1)–O(10), 2.177 (8); Pd(1)–O(13), 2.632 (7); P(1)–Pd(1)–P(2), 105.92 (8); P(1)–Pd(1)–O(1), 78.3 (2); P(1)–Pd(1)–O(4), 77.3 (2); P(1)–Pd(1)–O(10), 168.2 (2); P(1)–Pd(1)–O(13), 113.1 (2); P(2)–Pd(1)–O(1), 170.1 (2); P(2)–Pd(1)–O(4), 108.0 (2); P(2)–Pd(1)–O(10), 78.1 (2); P(2)–Pd(1)–O(13), 77.9 (2); O(1)–Pd(1)–O(10), 99.6 (2).

Variable-temperature ^1H NMR studies of **1** in $[^2H_6]$acetone from +20 to −80 °C (Fig. 2) indicate that the tmpp ligand is involved in a fluxional process; such behaviour has been noted for other d^6 and d^8 complexes of this ligand.[10] The ^1H NMR spectrum at −80 °C reveals six distinct resonances between δ 5.60 and 6.80 assigned to inequivalent *meta* protons, six resonances between δ 3.30–4.25 due to inequivalent *ortho*-methoxy groups, and one broad resonance at δ 3.83 due to three *para*-methoxy substituents.‡ This spectrum is consistent with the free rotation of the uncoordinated aryl group. A ^{31}P

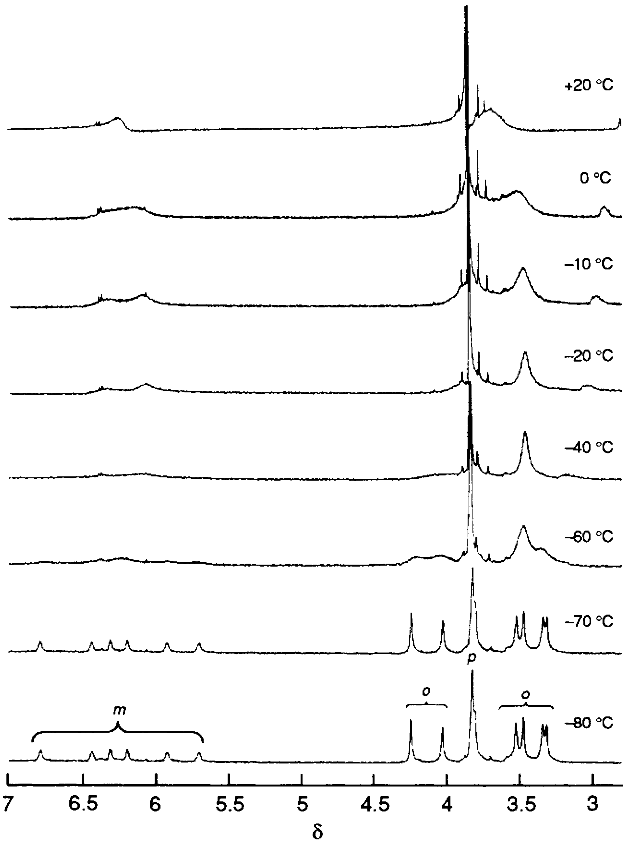

Fig. 2 Variable-temperature ^1H NMR spectra of **1** in $[^2H_6]$acetone from +20 °C to −80 °C (*o*, *ortho* methoxy groups; *p*, *para* methoxy groups; *m*, *meta* protons)

NMR spectrum of **1** in [$^2H_6$]acetone at room temp. exhibits a single resonance at δ +1.67. These NMR data are in accord with the presence of only one type of unsymmetrically coordinated phosphine ligand and support a close relationship between the solution and solid-state structures of the cation.

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Footnotes

† [Pd(TMPP)$_2$][BF$_4$]$_2$ **1**: ^{1}H NMR (δ in [$^2H_6$]acetone, −80 °C), –OMe: 3.32 (s, 6H), 3.34 (s, 6H), 3.47 (s, 6H), 3.52 (s, 6H), 3.83 (br, 18H), 4.03 (s, 6H), 4.25 (s, 6H); *meta*-H: 5.70 (br, 2H), 5.92 (br, 2H), 6.19 (br, 2H), 6.30 (br, 2H), 6.43 (br, 2H), 6.78 (br, 2H). ^{31}P NMR (δ in acetone-d$_6$), +1.67. UV-VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 485 (2.3×10^4), 373 (3.7×10^4), 260 (1.7×10^5). CV (CH_2Cl_2): $E_{p,c}(1) = -1.03$, $E_{p,a}(1) = -0.90$, $E_{p,c}(2) = -0.75$, $E_{p,a}(2) = -0.56$ V, $E_{p,a}(3) = +0.90$ V *vs.* Ag/AgCl.

‡ *Crystal data* for **1**: $PdP_2C_{54}O_{18}H_{66}B_2F_8$, $M_r = 1345.07$, orthorhombic space group $Pna2_1$, $a = 20.71$ (1), $b = 17.838$ (3), $c = 15.908$ (2), $V = 5876$ (5), Z = 4, $D_c = 1.520$ g cm^{-3}, $F(000) = 2768$, μ (Mo-Kα) = 4.56 cm^{-1}. Data were collected on a Rigaku AFC6S diffractometer at −110 °C by using ω–2θ scan method with 2θ in the range $4 \leqslant 2\theta \leqslant 47°$ and were corrected for Lorentz and polarization effects. Of the 4837 unique data collected, 4181 data with $I > 0.01\sigma(I)$ were used for F^2 refinement, while 3298 data with $I > 3.00\sigma(I)$ were used for F refinement. The phenyl rings of the tmpp ligands were refined isotropically for the F^2 refinement and were treated as rigid groups for the F refinement to reduce the number of parameters. F^2 refinement of 585 parameters resulted in residuals of $R = 0.075$ and $R_w = 0.101$, while refinement on F of 433 parameters resulted in residuals of $R = 0.057$ and $R_w = 0.074$. Attempts to solve the structure in the higher symmetry space group *Pnma* (No. 62) were unsuccessful. Both enantiomorphs of the noncentrosymmetric space group (No. 33) were refined, but no statistically significant difference in the residuals R and R_w (0.0751, 0.1009 and 0.0750, 0.1009, respectively) were observed.

Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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