

[PdCl₂(dppfO₂-O,O')]: a simple palladium(II) complex with a rare tetrahedral structure

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Single-crystal X-ray diffraction analysis of PdCl₂(dppfO₂) [dppfO₂ = 1,1'-bis(oxodiphenylphosphoranyl)ferrocene] shows a rare tetrahedral geometry at a d⁸ metal centre; physical and spectroscopic characterisations indicate a paramagnetic species.

The coordination and catalytic chemistry of 1,1'-bis(diphenylphosphino)ferrocene (dppf) has been reviewed.¹ There are ample examples in the recent literature that demonstrate the significance of this diphosphine ligand.² Like other phosphines, it can be readily oxidised to its mono- and di-oxide forms.³ The structure of the latter, 1,1'-bis(oxodiphenylphosphoranyl)ferrocene (dppfO₂) is of interest to a number of groups, notably those of Hor,^{3b} Pilloni,^{3c} Postel^{3d} and Hashmi.^{3e} Phosphine oxides in general have attracted attention in view of their weak coordinating ability⁴ and their function as co-catalysts,⁵ crystallisation aids,⁶ etc. The chemistry of Ph₃PO, the most familiar phosphine oxide, is well established.⁴ The coordination ability of some diphosphine oxides⁷ is also known, although less so for dppfO₂.³ Our interest in Pd^{II}-dppf chemistry stems from the rich catalytic activities shown by many dppf complexes of Pd(II).^{2b-h} Some of these complexes are susceptible to oxidation in solution and the decomposition product is generally assumed to be chiefly free dppfO₂.^{3a} There is hitherto no report on the coordination chemistry of dppfO₂ with Pd(II) although such complexes with other diphosphine oxides are known.⁷ Herein, we report the isolation of a simple Pd(II)-dppfO₂ complex with a rare mononuclear tetrahedral Pd(II) centre which, to our knowledge, has not been reported in the literature. It is well known that d⁸ platinum metals overwhelmingly favour square planar structures and only Ni(II) forms a significant number of tetrahedral complexes.

Addition of dppfO₂ to [PdCl₂(MeCN)₂] in CH₂Cl₂ gives [PdCl₂(dppfO₂-O,O')] **1** in 81% yield.† This complex was originally obtained as a by-product in the reaction of [Pd₂(dppf)₂(μ-S)₂] with COS. Its isolation contrasts with an earlier unsuccessful attempt to crystallise a palladium-containing triphenylphosphine oxide complex.⁸ The IR spectrum of **1** (CH₂Cl₂) exhibits two strong ν(P–O) peaks at 1260 and 1269 cm⁻¹. The ³¹P NMR spectrum in CD₂Cl₂⁹ shows a broad peak at δ 34.0 and a minor resonance at δ 47.2, tentatively assigned to [PdCl₂(μ-dppfO₂)₂]. Upon standing for a week, this solution decomposes readily to give predominantly free dppfO₂ (δ 28.2). The electronic spectrum shows two bands at 20 264 [³T₁(F) → ³A₂(F)] and 26 900 cm⁻¹ [³T₁(F) → ³T₁(P)], similar to that of a typical tetrahedral nickel(II) complex.¹⁰ The magnetic moment¹¹ (2.48 μ_B) is lower than that of a typical Ni(II) tetrahedral complex (ca. 3.2 μ_B) but still consistent with paramagnetic Pd(II) with two unpaired electrons. The cyclic voltammogram shows a reversible one-electron couple with E_{1/2} = 0.410 V (vs. [FeCp₂]⁺/[FeCp₂]). Similar behaviour has been reported for PdCl₂(dppf) (0.430 V)^{2a} and dppfO₂ (0.573 V).^{3a} The remote possibility of an internal electron transfer that generates Pd(I) and Fe(III) is thereby eliminated. Similar observations were reported for some Cu(II)-dppfO₂ complexes^{3f} and point to an oxygen-donating dppfO₂ ligand coordinated to a paramagnetic Pd(II) centre. The rarity of the postulated structure merited a crystallographic analysis.‡ This confirmed a mononuclear

neutral complex with a chelating dppfO₂ and two terminal chlorides (Fig. 1). The near-ideal tetrahedral geometry at the Pd(II) centre is exemplified by the large intra- and inter-ligand angles [O1–Pd1–O2, C11–Pd1–Cl2 and O–Pd–Cl angles of 104.3(3), 120.4(2) and 107.8° (av.), respectively]. The dihedral angle between the {PdO₂} and {PdCl₂} planes (84.2°) also reflects a tetrahedral rather than a 'distorted square-planar' description. O-donation leads to lengthening of the P–O bonds (av. 1.512 Å) compared to those in dppfO₂ (1.495 Å³). This is also consistent with a stronger P–C (C₅ plane) bond (av. P–C 1.772 Å) compared to those in [PdCl₂(dppf)] (av. P–C 1.804 Å^{2d}). There is little geometric distortion of the ferrocenyl C₅ moieties, the C₅ rings being planar with tilts of 3.6(7)° and torsional twist of <2° (close to mirror symmetry). C1–P1 and C6–P2 deviate slightly from the mean plane by +0.12 and +0.008°, respectively.

The analogous NiCl₂(dppfO₂) complex can be obtained only in poor yields from NiCl₂·6H₂O and dppfO₂ in propan-2-ol at room temperature or under reflux. Attempts to synthesise the platinum analogue have been unsuccessful. This is not surprising in view of the even stronger preference of Pt(II) for square planar coordination. The tetrahedral geometry of **1** is probably imposed by the large bite angle as a consequence of the sterically demanding chelating ring in dppfO₂. Its isolation demonstrates, for the first time, that tetrahedral Pd(II) is sustainable even in a mononuclear structure in which the metal centre is not constrained by neighbouring metal moieties.

[PdCl₂(dppf)] is probably the most well known dppf complex and finds extensive uses in catalysis (e.g. Grignard synthesis,^{2b-d} hydrodehalogenation,^{2f} etc.). Although this catalyst has demonstrated superior activity in many situations,^{2d,e} in certain cases, its effectiveness is poor^{2b,c} and reasons for this are

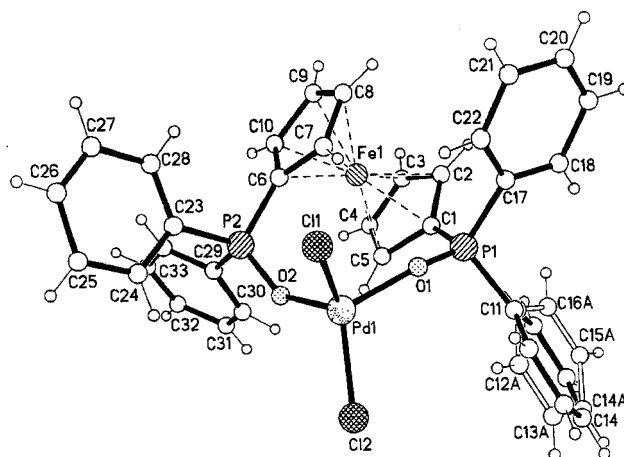


Fig. 1 Molecular structure of [PdCl₂(dppfO₂-O,O')]. Selected bond lengths (Å) and angles (°): Pd(1)–O(1) 1.974(8), Pd(1)–O(2) 1.968(7), Pd(1)–Cl(1) 2.222(4), Pd(1)–Cl(2) 2.204(3), P(1)–O(1) 1.495(9), P(2)–O(2) 1.529(6), P(1)–C(1) 1.780(9), P(1)–C(11) 1.781(10), P(1)–C(17) 1.781(9), P(2)–C(6) 1.764(11), P(2)–C(23) 1.785(13), P(2)–C(29) 1.791(10), O(1)–Pd(1)–O(2) 104.3(3), Cl(1)–Pd(1)–Cl(2) 120.4(2), O(1)–Pd(1)–Cl(1) 100.2(3), O(1)–Pd(1)–Cl(2) 112.7(3), O(2)–Pd(1)–Cl(1) 110.8(3), O(2)–Pd(1)–Cl(2) 107.3(2), P(1)–O(1)–Pd(1) 158.3(6), P(2)–O(2)–Pd(1) 139.9(5).

presently not well understood. It is commonly accepted that PdCl₂(dppf) loses its catalytic efficiency after losing its phosphine ligand (in the form of dppfO₂) via PdCl₂(dppfO₂). Isolation of **1** and its reasonable stability suggested that the current perception is not necessarily correct. The loss of activity rather may be linked to the geometric changes for Pd(II) upon oxidation of its dppf ligand. For example, we have recently demonstrated that C–C coupling and hydride transfer^{2g,h} occur very efficiently on a planar Pd(II) core. Oxidative addition of tetrahedral Pd(0) gives a Pd(II) intermediate which must be geometrically rigid¹² for effective reductive elimination to occur. Loss of such rigidity could adversely affect the catalytic efficiency. Oxidation of the phosphine ligand also leads to a change in bite angle which would have an effect on catalytic activities.¹³

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Notes and references

† *Synthesis* of [PdCl₂(dppfO₂-O,O')]: addition of dppfO₂ (0.074 g, 0.126 mmol) to a CH₂Cl₂ solution (40 cm³) of [PdCl₂(MeCN)₂] (0.032 g, 0.125 mmol) resulted in a brown suspension that was stirred for 12 h. Filtration and concentration gave an orange solution. Layering of hexane on this solution gave red crystals of **1**, which were collected and washed with hexane and Et₂O (yield 81%). Found: C, 53.42; H, 4.02; Cl, 10.17. Calc. for C₃₄H₂₈Cl₂O₂P₂FePd: C, 53.47; H, 3.70; Cl, 9.28%.

‡ *Crystallographic data*: C₃₄H₂₈Cl₂FeO₂P₂Pd **1**: *M* = 763.65, crystal dimensions: 0.33 × 0.18 × 0.13 mm, monoclinic, space group *Cc* (no. 9), *a* = 10.0444(2), *b* = 19.4070(3), *c* = 16.3157(1) Å, β = 91.340(2), *V* = 3179.58(8) Å³, *Z* = 4, μ(Mo-Kα) = 1.321 mm⁻¹. 7985 reflections measured, 4010 unique (*R*_{int} = 0.0297), final *R*1 and *wR*2 values 0.0679 and 0.2104 for 3799 independent reflections [*I* ≥ 2σ(*I*)] and 344 parameters. The data collection was performed at 295 K on a Bruker SMART CCD area-detector by the ω-scan method, within the limits 2.1 ≤ θ ≤ 25.0°. The data were corrected for absorption using an empirical method (SADABS^{14a}) and the structure was solved by direct methods and refined by full-matrix least squares (SHELXTL^{14b}). One of the phenyl rings (C11–C16) attached to P(1) was found to be disordered. Two disorder models (occupancies 0.7/0.3) were included in the least-squares refinements. Individual isotropic thermal parameters were refined for the major disorder component and common isotropic thermal parameter was refined for the other ring. Both the rings were treated as regular hexagons. Riding models were used to place all the hydrogen atoms in their idealized positions. CCDC 182/1307. See <http://www.rsc.org.suppdata/cc/1999/1477/> for crystallographic data in .cif format.

1 K.-S. Gan and T. S. A. Hor, in *Ferrocenes—Homogeneous Catalysis, Organic Synthesis, Materials Science*, ed. A. Togni and T. Hayashi,

- 1995, ch. 1, p. 3; S.-W. A. Fong and T. S. A. Hor, *J. Cluster Sci.*, 1998, **9**, 351.
- 2 (a) B. Corain, B. Longato, G. Favero, D. Ajò, G. Pilloni, U. Russo and F. R. Kreissl, *Inorg. Chim. Acta*, 1989, **157**, 259; (b) T. Kobayashi, T. Sakakura and M. Tanaka, *Tetrahedron Lett.*, 1985, **26**, 3463; (c) J. F. Hartwig, *Angew. Chem., Int. Ed.*, 1998, **37**, 2090; (d) T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi and K. Hirotsu, *J. Am. Chem. Soc.*, 1984, **106**, 158; (e) L. Schmitz, M. Rehahn and M. Ballauff, *Polymer*, 1993, **34**, 646; (f) B. Wei, S. H. Li, H. K. Lee and T. S. A. Hor, *J. Mol. Catal. A: Chem.*, 1997, **126**, L83; (g) Y. Xie, B.-M. Wu, F. Xue, S.-C. Ng, T. C. W. Mak and T. S. A. Hor, *Organometallics*, 1998, **17**, 3988; (h) Y. Xie, G. K. Tan, Y. K. Yan, J. J. Vittal, S.-C. Ng and T. S. A. Hor, *J. Chem. Soc., Dalton Trans.*, 1999, 773.
- 3 (a) G. Pilloni, B. Longato and B. Corain, *J. Organomet. Chem.*, 1991, **420**, 57; (b) Z.-G. Fang, T. S. A. Hor, Y.-S. Wen, L.-K. Liu and T. C. W. Mak, *Polyhedron*, 1997, **16**, 377; (c) G. Pilloni, B. Corain, M. Degano, B. Longato and G. Zanotti, *J. Chem. Soc., Dalton Trans.*, 1993, 1777; (d) V. Munyjabo, M. Postel, J. L. Roustan and C. Bensimon, *Acta Crystallogr., Sect. C.*, 1994, **50**, 224; (e) M. Bolte, F. Naumann and A. S. K. Hashmi, *Acta Crystallogr., Sect. C.*, 1997, **53**, 178; (f) G. Pilloni, G. Valle, C. Corvaja, B. Longato and B. Corain, *Inorg. Chem.*, 1995, **34**, 5910.
- 4 (a) N. Burford, *Coord. Chem. Rev.*, 1992, **112**, 1 and references within; (b) C.-M. Che, T.-F. Lai, W.-C. Chung, W. P. Schaefer and H. B. Gray, *Inorg. Chem.*, 1987, **26**, 3907.
- 5 D. C. Billington, I. M. Helps, P. L. Pauson, W. Thomson and D. Willison, *J. Organomet. Chem.*, 1988, **354**, 233.
- 6 W. J. Evans, J. W. Grate and R. J. Doedens, *J. Am. Chem. Soc.*, 1985, **107**, 1671.
- 7 T. C. Blagborough, R. Davis and P. Ivison, *J. Organomet. Chem.*, 1994, **467**, 85; A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27; R. J. Coyle, Y. L. Slovokhotov, M. Y. Antipin and V. V. Grushin, *Polyhedron*, 1998, **18**, 3059.
- 8 A. L. Spek, *Acta Crystallogr., Sect. C.*, 1987, **43**, 1233.
- 9 Bruker AMX 500 spectrometer at 202.46 MHz; chemical shifts are externally referenced to 85% H₃PO₄.
- 10 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, New York, 1984, ch. 27, p. 1345.
- 11 Magnetic measurements were obtained on a Johnson Matthey MKII magnetic susceptibility balance. Observed magnetic susceptibility values were corrected for diamagnetism using Pascal's constants (B. N. Figgis and J. Lewis, *The Magnetochemistry of Complex Compounds*, in *Modern Coordination Chemistry*, ed. J. Lewis and R. G. Wilkins, Interscience, New York, 1960, ch. 6, p. 400) except for the diamagnetic contribution of dppfO₂ which is determined experimentally as -240 × 10⁻⁶ cm³ mol⁻¹.
- 12 Geometric rigidity enables the *cis* ligands to be in close proximity and their labilisation under the influence of the *trans* ligands.
- 13 B. C. Hamann and J. F. Hartwig, *J. Am. Chem. Soc.*, 1998, **120**, 3694.
- 14 (a) SMART & SAINT Software Reference Manuals, version 4.0, Siemens Energy & Automation, Inc., Analytical Instrumentation, Madison, WI, 1996; (b) G. M. Sheldrick, *SADABS*, a software for empirical absorption correction, University of Göttingen, 1993.

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