A novel polynuclear palladium(II) complex with asymmetric coordination of palladium atoms

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The oxidation of $[Pd_2(dppm)_2Cl_2]$ with selenium in the presence of $NaSCH_2Ph$ in DMF gives rise to a novel polynuclear complex $[Pd_4(\mu_3\text{-}Se)_2(\mu\text{-}SCH_2Ph)_2(\mu\text{-}dppm)_2Cl_2]$; a single crystal X-ray diffraction analysis shows that all the palladium atoms in the compound are tetracoordinated with distorted square-planar geometry, of which two are asymmetrically coordinated with selenium, sulfur, chlorine, and phosphorus atoms.

Bis(diphenylphosphine)methane (dppm), as a constraining ligand, prefers to lock together two metal atoms in close proximity and favors unusual oxidation states; thus, most palladium complexes containing dppm are binuclear complexes doubly bridged by dppm and related ligands, such as $[Pd_2(\mu\text{-}dppm)_2X_2]$ (X = halogen, **1**),[1–4] and the oxidation state of palladium is mainly +1. Many studies have been carried out on the insertion of small molecules, such as CO, SO_2, RCN *etc.*, into the Pd–Pd bond in **1** to yield the so-called A-frame complexes with the maintenance of the oxidation state of palladium.[5] Studies on the insertion of an S or Se bridge into **1** to give rise to complexes $[Pd_2(\mu\text{-}E)(\mu\text{-}dppm)_2X_2]$ (E = S, Se; X = halogen) with a change of the oxidation state of palladium from +1 to +2 have also been reported,[6] whilst reports on the palladium complexes with mixed thiolate and diphosphine ligands, especially those having a palladium formal oxidation state of +2 and containing both dppm and thiolate ligands, are very scare. Very recently, Usón and co-workers have characterised octanuclear $\{[Pd(\mu\text{-}SC_6F_5)(\mu\text{-}dppm)Pd](\mu\text{-}SC_6F_5)\}_4$, in which the oxidation state of palladium remains +1.[7] We have been interested in the chemistry of metal–thiolate–diphosphine complexes and a series of complexes, such as $[Co\{Ph_2P(CH_2)_3PPh_2\}(SPh)_2]$,[8a] $[Co_2(SPh)_4(dppx)]$,[8b,c] and $[Pd(SR)_2(dppx)]$ [dppx = $Ph_2PCH_2PPh_2$, $Ph_2P(CH_2)_2PPh_2$][9] have been isolated. Herein we report the synthesis, crystal structure, and properties of a novel tetranuclear palladium(II) complex with asymmetric coordination of palladium atoms, $[Pd_4(\mu_3\text{-}Se)_2(\mu\text{-}SCH_2Ph)_2(\mu\text{-}dppm)_2Cl_2]\cdot 2DMF$ **2**.

In DMF solution, $[Pd_2(dppm)_2Cl_2]$ was reacted with Se and $NaSCH_2Ph$ giving rise to **2**.† In this reaction, Pd(I) was oxidised to Pd(II) and an Se atom was inserted into the binuclear complex to form the A-frame complex $[Pd_2(dppm)_2Cl_2(\mu\text{-}Se)]$; one of the dppm ligands in the A-frame complex was oxidised to dppmSe by excess Se and was cleaved in the presence of $NaSCH_2Ph$, one of the Cl^- ligands was removed and the A-frame complex was then condensed into the tetranuclear complex **2** through forming μ_3-Se and μ-SCH_2Ph.

$$[Pd_2(dppm)_2Cl_2] \xrightarrow{Se} [Pd_2Se(dppm)_2Cl_2] \xrightarrow[NaSCH_2Ph]{Se}$$

$$[Pd_4Se_2(SCH_2Ph)_2(dppm)_2Cl_2] + dppmSe + NaCl$$

A crystallographic analysis‡ reveals that the complex is a tetranuclear neutral complex. As shown in Fig. 1, two kinds of palladium environments are present: two of the four palladium atoms are each surrounded by two selenium, one sulfur, and one phosphorus atom forming a distorted square-planar arrangement; the other two are each asymmetrically surrounded by one selenium, one phosphorus, one sulfur, and one chlorine atoms in a highly distorted square-planar arrangement. The sulfur atom of each thiolate ligand is shared by two Pd atoms forming a μ-bridge, while each selenium acts as μ_3-bridge linking three palladium centres. The four palladiums form a zigzag chain with a Pd–Pd distance of 3.191(3) Å, much longer than that in $Pd_2(SCH_2CH_2S)_2(PPh_3)_2$ [3.038(2) Å],[10a] but shorter than that

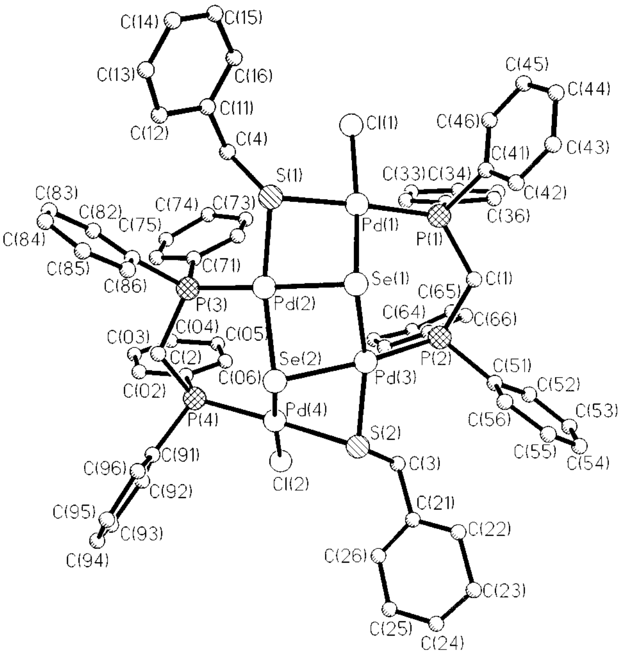

Fig. 1 Molecular structure of $[Pd_4(\mu_3\text{-}Se)_2(\mu\text{-}SCH_2Ph)_2(\mu\text{-}dppm)_2Cl_2]\cdot 2DMF$ with solvent molecules and H atoms omitted. Selected bond lengths (Å) and bond angles (°): Pd(1)–Pd(2), 3.181(3), Pd(2)–Pd(3) 3.228(3), Pd(3)–Pd(4) 3.166(3), Pd(1)–Se(1) 2.387(3), Pd(1)–Cl(1) 2.339(7), Pd(1)–P(1) 2.261(7), Pd(1)–S(1) 2.374(6), Pd(2)–Se(1) 2.432(4), Pd(2)–Se(2) 2.397(3) Pd(2)–P(3) 2.263(7), Pd(2)–S(1) 2.331(6), Pd(3)–Se(1) 2.383(4), Pd(3)–Se(2) 2.446(3), Pd(3)–P(2) 2.262(6), Pd(3)–S(2) 2.326(7) Pd(4)–Se(2) 2.393(4), Pd(4)–Cl(2) 2.345(8), Pd(4)–P(4) 2.264(7), Pd(4)–S(2) 2.381(8); Pd(1)–Pd(2)–Pd(3) 77.9(1), Pd(2)–Pd(3)–Pd(4) 77.0(1), Se(1)–Pd(1)–Cl(1) 173.1(2), Se(1)–Pd(1)–P(1) 94.7(2), Cl(1)–Pd(1)–P(1) 91.1(2), Se(1)–Pd(1)–S(1) 79.5(2), Cl(1)–Pd(1)–S(1) 94.5(2), P(1)–Pd(1)–S(1) 173.3(2), Se(1)–Pd(2)–Se(2) 83.7(1), Se(1)–Pd(2)–P(3) 171.7(2), Se(2)–Pd(2)–P(3) 97.8(2), Se(1)–Pd(2)–S(1) 79.4(2), Se(2)–Pd(2)–S(1) 157.4(2), P(3)–Pd(2)–S(1) 101.1(2), Se(1)–Pd(3)–Se(2) 83.7(1), Se(1)–Pd(3)–P(2) 96.8(2), Se(2)–Pd(3)–P(2) 169.6(2), Se(1)–Pd(3)–S(2) 159.1(2), Se(2)–Pd(3)–S(2) 79.8(2), P(2)–Pd(3)–S(2) 101.7(2), Se(2)–Pd(4)–Cl(2) 174.6(2), Se(2)–Pd(4)–P(4) 95.5(2), Cl(2)–Pd(4)–P(4) 89.4(3), Se(2)–Pd(4)–S(2) 79.8(2), Cl(2)–Pd(4)–S(2) 95.2(3), P(4)–Pd(4)–S(2) 173.8(2), Pd(1)–Se(1)–Pd(2) 82.6(1), Pd(1)–Se(1)–Pd(3) 115.2(1), Pd(2)–Se(1)–Pd(3) 84.2(1), Pd(2)–Se(2)–Pd(3) 83.6(1), Pd(2)–Se(2)–Pd(4) 112.5(1) Pd(3)–Se(2)–Pd(4) 81.7(1), Pd(1)–S(1)–Pd(2) 85.1(2), Pd(3)–S(2)–Pd(4) 84.5(2).

in $Pt_2\{SCH_2CH_2C(CH_3){=}CH_2\}_2(PPh_3)_2I_2$ [3.539(1) Å].[11] The average Pd–S–Pd angle [98.6(2)°] is much more obtuse than that in $Pd_2(SCH_2CH_2S)_2(PPh_3)_2$ [80.63(6)°][10a] and the average Ni–S–Ni angles in $Ni_2(SCH_2CH_2S)_2(PPh_3)_2$ (82.41°)[10b] and $Ni_2\{SCH(CH_3)CH_2S\}_2(PPh_3)_2$ (81.11°).[10c] The average Pd–P bond length of 2.291(6) Å is similar to those reported in the Pd–S–P complexes.

^{31}P NMR spectra of the complex show two peaks at 18.595 and 14.493 ppm. It is clear that the P nucleus is deshielded to downfield, indicating that the electrons are transferred from phosphorus atoms to the metal atoms to cause the P nucleus to be deshielded to downfield and the chemical shifts increased.

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Notes and References

† *Synthesis* of $[Pd_4(\mu_3\text{-}Se)_2(\mu\text{-}SCH_2Ph)_2(\mu\text{-dppm})_2Cl_2]\cdot 2DMF$: $NaSCH_2Ph$ (0.42 g, 3 mmol) and selenium powder were dissolved in 15 cm^3 of DMF and the solution was stirred for 12 h. A suspension of $[Pd_2(dppm)_2Cl_2]$ (1.52 g, 6 mmol) in 15 ml of DMF was then added to the solution which turned gradually red-brown with a small amount of black precipitate. The final reaction solution was filtered and the dark-red filtrate was kept at 4 °C. After two weeks, red plate crystals of **2** were collected and washed with distilled water and acetone(yield 22%). Found: C, 45.90; H, 4.12; N, 1.58. Calc. for $C_{70}H_{72}N_2O_2P_4S_2Cl_2Se_2Pd_4$: C, 46.30; H, 4.00; N, 1.54%. IR(KBr): 445(m), 426(m), 375(w), 340(w), 318(w), 300(w), 270(w) cm^{-1}.

‡ *Crystallographic data:* crystal dimensions: 0.25 × 0.30 × 0.30 mm, $C_{70}H_{72}N_2O_2P_4S_2Cl_2Se_2Pd_4$, M = 1815.7, space group $P1$ (no. 2), a = 11.203(2), b = 14.928(2), c = 22.354(3) Å, α = 82.27(2), β = 86.86(2), γ = 74.62(2)°, V = 3890(1) Å^3 , μ = 2.091 mm^{-1}, Z = 2, $R(R_w)$ = 0.086(0.097). Cell dimension measurements and data collections were performed on a Siemens Smart CCD diffractometer with graphite-monochromated Mo-Kα radiation at 23 ± 1 °C. Intensity data were obtained in the range $3.0 \leqslant 2\theta \leqslant 50.0°$ by using the ω scan technique. The data reductions were performed on a Silicon Graphics computer station with Smart CCD software. For the structural analyses, all calculations were performed on an HP/586 computer using SHELXL-PC. The positions of all the palladium, selenium, sulfur, and phosphorus atoms were determined by direct methods, and successive difference electron density maps located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C–H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent C atoms before the final cycle of least-squares refinement. One phenyl ring exhibiting disorder was fixed as an idealized rigid group. The final anisotropic refinement of all non-hydrogen atoms on F_o for 5438 observations [$F \geqslant 4.0\sigma(F)$] and 593 variables led to convergence. CCDC 182/985.

1 (*a*) M. J. H. Russel and C. F. J. Barnard, *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, p. 1103; (*b*) A. L. Balch, *Reactivity of Metal–Metal Bonds*, ed. M. H. Chisholm, *ACS Symp. Ser.*, 1981, **155**, 167.

2 (*a*) R. J. Puddephatt, *Chem. Soc. Rev.*, 1983, **12**, 99; (*b*) R. Poilblanc, *Coord. Chem. Rev.*, 1988, **86**, 191.

3 A. L. Balch, in *Homogeneous Catalysis with Metal Phosphine Complexes*, ed. L. H. Pignolet, Plenum, New York, 1983, p. 167.

4 P. M. Maitlis, P. Espinet and M. J. H. Russel, *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 6, p. 265.

5 (*a*) P. Braunstein, J.-M. Jud, Y. Dusausou and J. Fisher, *Organometallics*, 1983, **2**, 180; (*b*) P. Braunstein, J.-M. Jud, Y. Dusausou and J. Fisher, *J. Chem. Soc., Chem. Commun*., 1983, 5; (*c*) M. C. Grossel, R. P. Moulding and K. R. Seddon, *J. Organomet. Chem.*, 1983, **253**, C52; (*d*) P. Braunstein, C. de Meric de Bellefon and M. Ries, *ibid*., 1984, **262**, C14; (*e*) P. Braunstein, J. Kervennal and J.-L. Richert, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 768.

6 (*a*) A. L. Balch, L. S. Benner and M. M. Olmstead, *Inorg. Chem*., 1979, **18**, 2996; (*b*) G. Besenyei, C. L. Lee, J. Gulinski, S. J. Retting, B. R. James, D. A. Nelson and M. A. Lilga, *ibid*., 1987, **26**, 3622; (*d*) G. Besenyei, L. Pàrkànyi, L. I. Simàndi and B. R. James, *ibid*., 1995, **34**, 6118.

7 (*a*) R. Usón, J. Forniés, L. R. Falvello, I. Usón and S. Herrero, *Inorg. Chem.*, 1993, **32**, 1066; (*b*) R. Usón, J. Forniés, S. Fernandez, M. A. Usón, I. Usón and S. Herrero, *Inorg. Chem.*, 1997, **36**, 1912.

8 (*a*) G. W. Wei, M. C. Hong, Z. Y. Huang and H. Q. Liu, *J. Chem. Soc., Dalton Trans.*, 1991, 3145; (*b*) G. W. Wei, H. Q. Liu, Z. Y. Huang, M. C. Hong, L. R. Huang and B. S. Kang, *Polyhedron*, 1991, **10**, 553; (*c*) G. W. Wei, H. Q. Liu, Z. Y. Huang, L. R. Huang and B. S. Kang, *J. Chem. Soc., Chem. Commun.*, 1989, 1839.

9 (*a*) W. P. Su, M. C. Hong, Z. Y. Zhou, F. Xue, H. Q. Liu and T. C. W. Mak, *Acta Crystallogr., Sect. C*, 1996, **52**, 2691; (*b*) W. P. Su, M. C. Hong, R. Cao and H. Q. Liu, *Acta Crystallogr., Sect. C*, 1997, **53**, 66; (*c*) W. P. Su, R. Cao, M. C. Hong, Z. Y. Zhou, F. Xue, H. Q. Liu and T. C. W. Mak, *Polyhedron*, 1997, **16**, 2531.

10 (*a*) R. Cao, M. C. Hong, F. L. Jiang and H. Q. Liu, *Acta Crystallogr., Sect. C*, 1995, **51**, 1280; (*b*) R. Cao, Z. Y. Huang, X. J. Lei, M. C. Hong and H. Q. Liu, *Chin. J. Chem.*, 1992, **10**, 227; (*c*) R. Cao, Z. Y. Huang, X. J. Lei, M. C. Hong and H.Q. Liu, *Acta Crystallogr., Sect. C*, 1992, **48**, 1654.

11 E. W. Abel, D. E. Evans, J. R. Koe, M. B. Hursthouse, M. Mazid, M. F. Mahon and K. C. Molloy, *J. Chem. Soc., Dalton Trans.*, 1990, 1697.

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