First complex containing a $Pd_4(\mu_4\text{-}O)$ functional group

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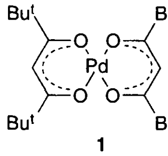
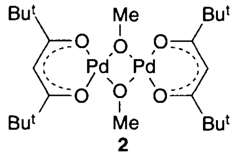
The first complex containing the $Pd_4(\mu_4\text{-}O)$ linkage, previously known only in the binary oxide PdO, is prepared and characterised.

The $M_4(\mu_4\text{-}O)$ group is present in many binary metal oxides and is also known in some coordination complexes, such as in the basic metal acetates $[M_4(\mu_4\text{-}O)(\mu\text{-}O_2CMe)_6]$, (M = Be, Zn, Co).[1] Compounds containing such bridging oxo groups are of interest in chemistry,[1] biochemistry,[2] magnetochemistry[3] and catalysis.[4] However, most known complexes are with the lighter transition-metal elements including cobalt and copper,[1–5] with few for heavier transition-metal elements[1,6] and none at all for nickel, palladium or platinum. The $M_4(\mu_4\text{-}O)$ group is present in the binary oxide PdO[7] and also as subsurface oxide during oxidation reactions catalysed by palladium metal and so it would be of considerable interest to form complexes containing the $Pd_4(\mu_4\text{-}O)$ group to model such functionality.[4] The recently reported complex $[Pd_6Cu_4Cl_{12}O_4(hmpa)_4]$, (hmpa = hexamethylphosphoramide), contains four $Pd_3Cu(\mu_4\text{-}O)$ groups and is a useful oxidation catalyst[8] while several compounds have been suggested on the basis of spectroscopic data to contain $Pd_2(\mu\text{-}O)$ groups.[9] This article reports the first complex to contain the elusive $Pd_4(\mu_4\text{-}O)$ and also what is, to the best of our knowledge, the first structure determination on a homonuclear oxopalladium complex of any kind. The $M_4(\mu_4\text{-}O)$ group appears to be unknown for platinum group elements though an interesting derivative with M = Au was reported recently.[10]

By following a method similar to that reported previously,[11] the reaction of $PdCl_2$ with Li(dpm) (dpm = dipivaloylmethanato, $Bu^tCOCHCOBu^{t-}$, in methanol gave a mixture of $[Pd(dpm)_2]$ **1** (30%) and $[Pd_2(dpm)_2(\mu\text{-}OMe)_2]$ **2** (70%). When this mixture was dissolved in CCl_4, the initially yellow solution changed to red at the solution–air interface, and the red colour slowly diffused through the solution. When monitored by NMR, the signals from compound **2** slowly decayed as those of a new complex **3** grew; the resonances of **1** remained unchanged. Recrystallization of the mixture from hexane then gave red crystals of the new complex **3** along with yellow crystals of **1**.



1



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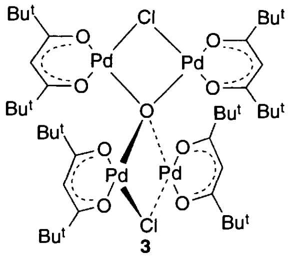

3

Complex **3** has been characterised by an X-ray structure determination† to be $[Pd_4(dpm)_4(\mu\text{-}Cl)_2(\mu_4\text{-}O)]$ and its structure is shown in Fig. 1. The central μ_4-oxygen atom, O(5), lies on a crystallographic C_2 axis and is surrounded by a distorted tetrahedron of Pd atoms, each of which is incorporated into a Pd(dpm) chelate ring. Two equivalent edges of the Pd_4 tetrahedron are μ-bridged by chloro ligands which complete the square-planar coordination of each palladium atom. The bond lengths and angles which define the $(\mu_4\text{-}O)Pd_4$ unit in **3** [Pd–O(5) 2.020(1), 2.028(2) Å, Pd–O(5)–Pd 98.6–118.0°] bear a striking resemblance to those found in the binary oxide PdO [Pd–O 2.01(1) Å, Pd–O–Pd 98(2), 116(4)°].[7] However, in PdO the widely different Pd–O–Pd angles seem to arise from the need to accommodate square planar palladium atoms in the crystal; in **3** the μ-Cl ligands complete four-membered $Pd_2Cl(\mu_4\text{-}O)$ rings which are folded across their Cl···O diagonal by 33.3°. The cross-ring Pd···Pd distance [3.069(1) Å] is thereby shortened relative to the other edges of the Pd_4 tetrahedron [3.365(1)–3.473(1) Å] and could be considered indicative of a very weak Pd···Pd bonding interaction.[9]

The mechanism of formation of **3** from **2** is not yet understood, but has been shown to require both oxygen and a chlorinated solvent. Once formed, complex **3** is an air-stable red

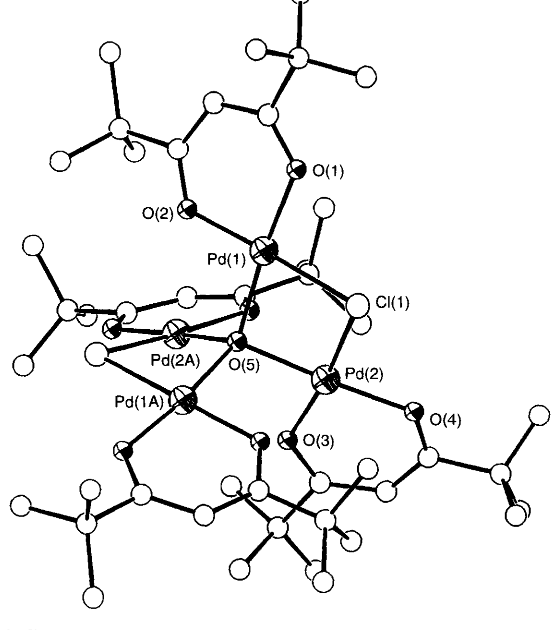

Fig. 1 The molecular structure of $[Pd_4(dpm)_4(\mu\text{-}Cl)_2(\mu_4\text{-}O)]$ **3**. Atoms are shown as spheres of arbitrary radius. Hydrogen atoms and the disorder of one *tert*-butyl group are not displayed. Selected distances (Å) and angles (°): Pd(1)–O(2) 1.977(2), Pd(1)–O(1) 1.979(2), Pd(1)–O(5) 2.028(2), Pd(1)–Cl(1) 2.324(1), Pd(1)–Pd(2) 3.069(1), Pd(2)–O(3) 1.969(2), Pd(2)–O(4) 1.973(2), Pd(2)–O(5) 2.020(1), Pd(2)–Cl(1) 2.341(1); O(1)–Pd(1)–O(5) 175.0(1), O(2)–Pd(1)–Cl(1) 172.2(1), O(4)–Pd(2)–O(5) 176.2(1), O(3)–Pd(2)–Cl(1) 172.3(1), Pd(1)–Cl(1)–Pd(2) 82.3(1), Pd(2)–O(5)–Pd(2A) 118.0(1), Pd(2)–O(5)–Pd(2A) 118.0(1), Pd(2)–O(5)–Pd(1A) 112.5(1), Pd(1A)–O(5)–Pd(1) 117.8(1). Symmetry code: (A) $-x, y, -z + 1/2$.

solid which decomposes before melting at around 145 °C; it is soluble in many organic solvents and is not decomposed even in the presence of dilute acid. The stability is remarkable and is probably at least partly due to steric protection of the $Pd_4(\mu_4\text{-}O)$ unit by the bulky *tert*-butyl groups. The ^1H and ^{13}C NMR spectra in $CDCl_3$ are fully consistent with the structure determined by X-ray diffraction. For example, there are two *tert*-butyl resonances in the ^1H NMR spectrum due to the non-equivalent *tert*-Bu groups of each dpm ligand.‡ The presence of chloride in the complex was confirmed by energy dispersive X-ray spectroscopy (EDX), which gave a Pd : Cl ratio of *ca.* 2.

In conclusion, this work has described the synthesis and characterization of the first complex reported to contain a $Pd_4(\mu_4\text{-}O)$ group and the first μ_4-oxo complex of any nickel group element. The easy formation of **3**, especially in a reaction involving air, suggests that the μ_4-oxo group might form more easily than previously thought for the platinum-group metals and that it could be involved in catalytic oxidation by palladium (and other platinum-group metal) complexes.[12] Complex **3** provides a particularly close model for the coordination geometry of the oxo ligand in palladium(II) oxide.

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Footnotes

† *Crystal data* for **3**. $C_{44}H_{76}Cl_2O_9Pd_4$, $M = 1245.55$, monoclinic, space group $C2/c$, $a = 20.693(2)$, $b = 23.525(2)$, $c = 14.379(2)$ Å, $\beta = 127.328(7)°$, $U = 5566.1(8)$ Å^3 (from setting angles of 25 reflections with $20.2 \leqslant \theta(\text{Mo-K}\alpha) \leqslant 21.3°$), $Z = 4$, $D_c = 1.486$ Mg m^{-3}, $\mu = 1.412$ mm^{-1}, $F(000) = 2520$.

Intensities of 13036 reflections with $2.6 \leqslant \theta(\text{Mo-K}\alpha) \leqslant 33°$ and $-31 \leqslant h \leqslant 26$, $-36 \leqslant k \leqslant 3$, $-2 \leqslant l \leqslant 22$ were measured at 20 °C from ω–2θ scans on an Enraf-Nonius CAD4 diffractometer with Mo-Kα X-rays ($\lambda = 0.71073$ Å), using a red block-shaped crystal of dimensions 0.22 × 0.13 × 0.12 mm. The mean intensity of three standard reflections showed no significant change during the experiment. Analytical absorption correction (transmission factors 0.782–0.875) and subsequent merging gave 10477 independent reflections ($R_{int} = 0.032$). Refinement on F^2 of 265 parameters using 10463 observations, with anisotropic displacement parameters for all non-hydrogen atoms, converged ($\Delta/\sigma < 0.01$) at $R_1 = 0.037$, $wR_2 = 0.084$ for 6969 reflections with $I > 2\sigma(I)$, and $R_1 = 0.077$, $wR_2 = 0.104$ for all 10477 data, $|\Delta\rho| < 0.68$ e Å^{-3}, $w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 4.19P]$ where $P = (F_o^2 + 2F_c^2)/3$.[13] All *tert*-butyl methyl C-atoms have large and anisotropic displacement parameters and for one such group each methyl C-atom is disordered over two sites with equal probability. Riding hydrogen-atoms, except for those of the disordered *tert*-butyl group, were included in the calculations. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/260.

‡ NMR in $CDCl_3$: δ_H 0.98 (s, 9 H, Bu^t), 1.48 (s, 9 H, Bu^t), 5.67 (s, 1 H, CH), δ_C 28.48 (CH_3), 29.11 (CH_3), 40.41 (CMe_3), 40.78 (CMe_3), 91.55 (CH), 195.20 (CO), 195.33 (CO).

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