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Oxidation of palladium(I) dimers: formation and X-ray crystal structure of $[(Me_3P)_2Pd(\mu\text{-}OH)_2Pd(PMe_3)_2](CF_3SO_3)_2$

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Abstract

Air oxidation of the phosphido-bridged Pd(I) dimer $[Pd_2(\mu\text{-}P^tBu_2)(PMe_3)_4](CF_3SO_3)$ gives the hydroxo-bridged Pd(II) dinuclear derivative $[(Me_3P)_2Pd(\mu\text{-}OH)_2Pd(PMe_3)_2](CF_3SO_3)_2$ (**1**) with a low yield. The same cation was obtained with a high yield by the reaction of $[PdCl_2(PMe_3)_2]$ with silver nitrate in wet acetone. The crystal structure of **1** was determined.

Keywords: Palladium; Dinuclear complexes; X-ray diffraction; Synthesis

1. Introduction

Although Pd–O bonds are commonly expected to be weak, a number of palladium alkoxo or hydroxo derivatives have been reported [1–3]. π donation from non-bonding electron pairs of the oxygen atom to empty metal orbitals contributes to strengthen the M–O bonds in early transition metal complexes [4]. Metal orbitals in late transition metal (LTM) complexes are often occupied by electron pairs and this would transform the above bonding interaction into a destabilizing four-electrone-two-orbital interaction [5]. Probably this is the reason why only a few palladium alkoxides or hydroxides have been reported [1,2].

As a consequence of the irrelevance of π bonding, the metal–oxygen bond of LTM alkoxides should be strongly polarized, with a high electron density at the oxygen atom [6]. This may be responsible for the strong hydrogen bonds observed between a LTM-bound oxygen atom and an O–H bond of an alcohol or phenol outside the coordination sphere of the metal [2,6]. As a further consequence of the high oxygen basicity, LTM alkoxides or hydroxides are frequently polynuclear, with the oxygen lone pairs engaged in the bridging rather than in the π-bonding interaction. Most of the known polynuclear palladium hydroxides have the structure $[(L)_2Pd(\mu\text{-}OH)_2Pd(L)_2]^{2+}$ where $(L)_2 = (PR_3)_2$ [3b], diphosphine [3a], phen [3e,f], bipy [3e,f] or $(C_6F_5^-)_2$ [3d].

In the course of our studies on the chemistry of palladium(I) phosphido-bridged dinuclear derivatives [7], we prepared the new PMe_3 complex $[Pd_2(\mu\text{-}P^tBu_2)(PMe_3)_4](CF_3SO_3)$ [8]. This compound is air stable in the solid state but easily oxidized in solution giving, inter alia, the new bridging palladium(II) hydroxo derivative $[(Me_3P)_2Pd(\mu\text{-}OH)_2Pd(PMe_3)_2](CF_3SO_3)_2$, (**1**). The X-ray crystal structure of complex **1** and an alternative high yield synthesis of the cation in the nitrate salt are now reported.

2. Results and discussion

When molecular oxygen was bubbled into a red solution of $[Pd_2(\mu\text{-}P^tBu_2)(PMe_3)_4](CF_3SO_3)$, it turned bright yellow in a few minutes and, after work-up, a pale-yellow solid was isolated and characterized as $[(Me_3P)_2Pd(\mu\text{-}OH)_2Pd(PMe_3)_2](CF_3SO_3)_2$ (**1**). Crystals suitable for the structural determination (see Section 3) were grown by slow evaporation of an acetone solution. Significant absorptions were found in the IR spectrum at 3400 cm^{-1} (strong, sharp, ν(OH)), and at 1247 vs, 1159 vs, 1032 vs and 637 vs cm^{-1} (uncoordi-

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nated triflate anion) [9]. A single singlet at 9.12 ppm was observed in the $^{31}P\{^1H\}$ NMR spectrum, consistent with the symmetrical structure of the cation. The ^1H NMR spectrum consisted of a doublet at 1.55 ppm ($^2J(PH) = 11$ Hz; PMe_3) and a broad singlet at −0.28 ppm in 18:1 integral ratio. The high field absorption was in the range observed for other bridging hydroxy derivatives of palladium or platinum $[(dppp)Pd(\mu\text{-}OH)_2Pd(dppp)]^{2+}$ (dppp = 1,3-bis(diphenylphosphino)-propane), $\delta(OH) = -2.30$ ppm [3a]; $[(C_6F_5)_2M(\mu\text{-}OH)_2M(C_6F_5)_2]^{2-}$ (M = Pd), $\delta(OH) = -2.84$ ppm [3d]; (M = Pt) $\delta(OH) = -1.21$ ppm [3d]; $[(L)_2Pt(\mu\text{-}OH)_2Pt(L)_2]^{2+}$ ($(L)_2 = Fe(\eta^5\text{-}C_5H_4PPh_2)_2$), $\delta(OH) = -0.14$ ppm [10]; $[(Ph_3P)_2Pd(\mu\text{-}OH)_2Pd(Ph_3P)_2)^{2+}$, $\delta(OH) = 2.00$ ppm [3b]). At least one other unidentified phosphorus-containing product was observed in the ^{31}P NMR spectrum of the reaction mixture (singlet at 43 ppm), and the yields of **1** were always under 40%. Although the mechanism of formation of the cation contained in complex **1** was not investigated, we were able to prepare the nitrate salt with a nearly quantitative yield, by the alternative classical route previously reported for $[(L)_2M(\mu\text{-}OH)_2M(L)_2]^{2+}$ (M = Pt, L = PR_3 [10]; M = Pd, L = bipy or phen [3e]; M = Pd or Pt, L = PR_3) [3b]). Reaction of $[PdCl_2(PMe_3)_2]$ with silver nitrate in wet acetone gave $[(Me_3P)_2Pd(\mu\text{-}OH)_2Pd(PMe_3)_2](NO_3)_2$ (**2**) as a pale-yellow solid with more than 90% yield and its ^1H and $^{31}P\{^1H\}$ NMR spectra were identical with those of **1**.

3. Crystal and molecular structure of 1

Crystals of **1**, obtained as described above, were utilized for the X-ray analysis. Selected bond distances and angles are listed in Table 1 and Fig. 1 shows an ORTEP projection with the atom-numbering scheme. A centre of inversion in the middle of the Pd–Pd vector generates a planar symmetrical $Pd_2(\mu\text{-}O)_2$ core (Pd–O(1), 2.075(3) Å; Pd–O(1′), 2.081(3) Å; Pd–O–Pd′, 99.8(1)°). Each palladium atom also bears two terminally bonded phosphine molecules and exhibits an only slightly distorted square-planar geometry (O–Pd–O, 80.2(1)°; P(1)–Pd–P(2), 94.75(4)°; P(1)–Pd–O(1′), 91.90(8)°; P(2)–Pd–O(1), 93.17(8)°). The maximum deviation for the atoms Pd, O(1), O(1′), P(1) and P(2) from a least-squares plane is 0.02 Å. The structure of the $Pd_2(\mu\text{-}O)_2(P)_4$ core is very reminiscent of the known analogous compounds, but in this case the two square-planar moieties lie in the same plane, whereas in other cases they are folded along the O–O hinge with the following dihedro angles: $[(dppp)Pd(\mu\text{-}OH)_2Pd(dppp)]^{2+}$, 34.0° [3a]; $[(hfacac)Pd(\mu\text{-}OMe)_2\text{-}Pd(hfacac)]$ (Hhfacac = hexafluoropentane-2,4-dione), 26.0° [3c]; $[(Et_3P)_2Pt(\mu\text{-}OH)_2Pt(PEt_3)_2]^{2+}$, 36.4° [11]. The Pd–O bond distances are 2.075(3) Å for Pd-O(1) and 2.081(3) Å for Pd–O(1′), almost the same as observed for $[(dppp)Pd(\mu\text{-}OH)_2Pd(dppp)]^{2+}$(2.081(4) Å) [3a]. The two palladium atoms are 3.179(1) Å apart, in keeping with the absence of a metal–metal bond [3a].

Table 1
Selected bond distances (Å) and angles (°).

Bond distances	
Pd–P(1)	2.242(1)
Pd–P(2)	2.239(1)
Pd–O(1)	2.075(3)
Pd–O(1′)	2.081(3)
Pd...Pd′	3.179(1)
O(1)–H(1)	0.87
Bond angles	
O(1)–Pd–O(1′)	80.2(1)
P(1)–Pd–P(2)	94.75(4)
P(1)–Pd–O(1)	171.84(8)
P(1)–Pd–O(1′)	91.90(8)
P(2)–Pd–O(1)	93.17(8)
P(2)–Pd–O(1′)	173.35(8)
Pd–O(1)–Pd′	99.8(1)

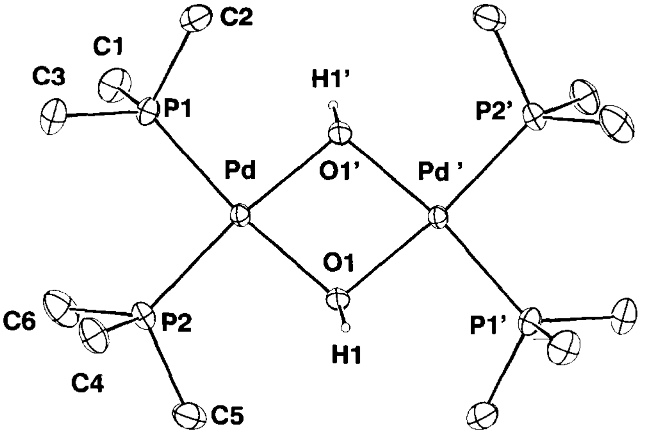

Fig. 1. An ORTEP projection of the cation $[(Me_3P)_2Pd(\mu\text{-}OH)_2Pd(PMe_3)_2]^{2+}$, and the atom-numbering scheme.

4. Experimental section

4.1. General data

$[PdCl_2(PMe_3)_2]$ was prepared according to published procedures [12]. Solvents were dried by conventional methods and distilled prior to use. IR spectra (Nujol mulls; KBr plates) were recorded on a Perkin–Elmer fourier transform IR 1725X spectrometer. NMR spectra were recorded on a Varian Gemini 200 BB. Frequencies are referred to Me_4Si (^1H) or 85% H_3PO_4(^{31}P).

4.2. Oxidation of $[Pd_2(\mu\text{-}P^tBu_2)(PMe_3)_4](CF_3SO_3)$

$[Pd_2(\mu\text{-}P^tBu_2)(PMe_3)_4](CF_3SO_3)$ (116 mg, 0.143 mmol) was dissolved in tetrahydrofuran (THF) (50 ml);

the flask was filled with O_2 and vigorously stirred; the red solution turned yellow in a few minutes and a yellow solid started to precipitate. The suspension was stirred for 24 h at room temperature and concentrated to a small volume. After addition of Et_2O (20 ml) the yellow solid was filtered off and vacuum dried and identified as **1** (42 mg; 35% yield). Elem. Anal. Found: C, 19.6; H 4.38. $C_{14}H_{38}F_6O_8P_4Pd_2S_2$ calc.: C, 19.8; H, 4.51%.

4.3. Preparation of $[Pd_2(\mu\text{-}OH)_2(PMe_3)_4](NO_3)_2$(2)

$[PdCl_2(PMe_3)_2]$ (721 mg, 2.19 mmol) was dissolved in acetone methylene chloride (1 : 1; 30 ml). A solution of silver nitrate (750 mg, 4.41 mmol) in water (30 ml) was slowly added, and silver chloride began to separate out. The suspension was stirred overnight at room temperature, AgCl was filtered off, and the filtrate was concentrated to a small volume about (5 ml). Complex **2** was precipitated by addition of Et_2O (20 ml), filtered and vacuum dried, yielding 689 mg (93%). Elem. Anal. Found: C, 19.9; H 5.58. $C_{12}H_{38}N_2O_8P_4Pd_2C$, 21.3; H, 5.67%.

5. Molecular structure determination

Crystals suitable for X-ray diffraction were obtained as described above. The crystal data was as follows: $C_{14}H_{38}F_6O_8Pd_2S_2$; $M_w = 849.27$; crystal size 0.3 × 0.3 × 0.1 mm; monoclinic; space group, $P2_1/n$; $a = 6.740(1)$, $b = 20.564(5)$, $c = 11.645(3)$ Å, $\beta = 105.41(2)°$; $V = 1555.9(6)$ Å^3; $Z = 2$, $D_c = 1.813$ g cm^{-1}; $F(000) = 848.00$. Data were collected at −18°C on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation; 2193 reflections ($3.0° < \theta < 26.0°$) were measured; 1669 unique reflections with $I > 2.0\sigma(I)$ were used for further computations.

The structure was solved by conventional heavy-atom methods and subsequent Fourier difference syntheses. Full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. The H(1) (H(1′)) atom was located in a difference Fourier synthesis and included with fixed positional and refined isotropic thermal parameters in the calculations. All other hydrogen atoms were calculated in idealized positions with isotropic thermal parameters of $B(\mathrm{H}) = 1.3B(\mathrm{C})$ and allowed to ride on their C atoms.

Refinement converged with 164 parameters using a statistical weighting scheme $w = 1/\sigma^2(F_0)$ at values of $R = 0.029$ and $R_w = 0.038$ with a goodness of fit of 1.519.

Atomic coordinates are given in Table 2. Calculations were performed using the SDP system of programs [13].

Table 2
Positional parameters and their estimated standard deviations

Atom	x	y	z	B_{eq} (Å^2)
Pd	0.38808(5)	0.45209(2)	0.06984(3)	1.784(8)
S	0.4470(2)	0.33814(7)	0.6748(1)	3.28(3)
P(1)	0.1183(2)	0.38513(6)	0.0072(1)	2.32(3)
P(2)	0.4463(2)	0.42475(6)	0.2620(1)	2.31(3)
F(1)	0.1757(8)	0.2879(3)	0.4966(4)	10.6(2)
F(2)	0.0823(6)	0.2916(2)	0.6566(4)	9.3(1)
F(3)	0.0852(7)	0.3761(3)	0.5595(5)	10.5(2)
O(1)	0.6374(5)	0.5151(2)	0.1025(3)	2.31(7)
O(2)	0.4247(7)	0.3735(2)	0.7755(4)	5.4(1)
O(3)	0.5284(7)	0.3748(3)	0.5941(4)	6.2(1)
O(4)	0.5327(9)	0.2757(2)	0.7029(5)	8.3(2)
C(1)	0.1884(8)	0.3033(2)	−0.0209(5)	3.6(1)
C(2)	−0.0385(8)	0.4135(3)	−0.1338(5)	3.7(1)
C(3)	−0.0675(8)	0.3768(3)	0.0934(5)	3.6(1)
C(4)	0.2784(8)	0.4624(3)	0.3416(4)	3.6(1)
C(5)	0.6968(9)	0.4515(3)	0.3463(5)	4.3(2)
C(6)	0.452(1)	0.3390(3)	0.2965(5)	4.4(1)
C(7)	0.186(1)	0.3228(3)	0.5942(5)	5.3(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(\frac{4}{3}[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ac(\cos\beta)\beta(1,3)]$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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