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Preliminary Communication

Synthesis and X-ray crystal structure of a new palladium catalyst precursor containing an η^2-phosphinate *

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Abstract

The Pd^I dimer $[\{Pd(\mu\text{-}P^tBu_2)(P^tBu_2H)\}_2]$ reacts with dioxygen in toluene giving the hydrogenation catalyst $[Pd(O_2P^tBu_2)(OP^tBu_2)(HOP^tBu_2)]$, **2**. The X-ray crystal structure of **2** has shown an unprecedented coordination mode of the phosphinato-ligand, both its oxygen atoms being coordinated to the same Pd atom.

We have recently reported a simple and high yield synthesis of the Pd^I dimer $[\{Pd(\mu\text{-}P^tBu_2)(P^tBu_2H)\}_2]$, **1** [1]. Complex **1** deserves attention both as a potential precursor of new organometallics and for applications in catalysis for the following reasons. The Pd_2 unit in **1** is susceptible to both one- and two-electron redox processes, the two bridging phosphido-ligands should help to preserve the dinuclear structure, and the bulkiness of the ^tBu substituents on both bridging phosphides and on terminal secondary phosphines should favour substitution reactions by appropriate reagent molecules. The catalytic activity of complex **1** was assessed by Alper's group [2] in the hydrogenation of α,β-unsaturated ketones or aldehydes. Surprisingly, **1**, completely ineffective as such, is transformed by oxidation with O_2 into a catalyst efficient under mild conditions. We therefore tried to obtain a deeper insight into the reaction of complex **1** with dioxygen.

A suspension of **1** in toluene was stirred at 50°C under dioxygen; the red solid slowly disappeared yielding a clear orange solution which was evaporated to dryness. The yellow-orange residue was washed with small portions of cold pentane giving complex **2** in *ca.* 45% yield and good purity. The structure of complex **2** was solved by X-ray and spectroscopic analyses.

^1H, ^{13}C and ^{31}P NMR spectroscopies showed the presence of two different P^tBu_2 fragments in 2/1 ratio [3**]. Additionally, the ^1H NMR spectrum showed the presence of a very broad absorption at 15.4 ppm and the IR spectrum did not show any absorption attributable to $\nu(OH)$; both these features have previously been reported for systems containing the symmetrical hydrogen-bonded $M[(PR_2O)_2H]$ unit [4]. The complex **2** is thus $[Pd(O_2P^tBu_2)(P^tBu_2OHOP^tBu_2)]$ and the binuclear structure of **1** has not been retained. Preliminary results indicate that **2** has the same catalytic activity as a solution obtained by bubbling dioxygen into a suspension of **1**, and we have used it with dihydrogen to reduce cinnamaldehyde to cinnamyl alcohol and 3-phenylpropionaldehyde, and *p*-benzoquinone to hydroquinone. Figure 1 shows the packing of molecules in the crystal structure of **2** [5**]. The molecule is placed with the Pd, P2 and H(O1) [6**] atoms in special positions on a crystallographic twofold axis. The exact symmetry of the molecule is 2 (C_2, in the Schoenflies notation) but its approximate symmetry is *2mm* (C_{2v}) [7**].

The coordination around the palladium atom is planar, the maximum deviation from the plane being less than its standard deviation, but it is not exactly square, the O2–Pd–O2′ angle being 66.7°, imposed by the phosphinate size, and because of the difference between Pd–P1 and Pd–O2 bond distances. The Pd–P distance of 2.261 Å is almost the same as already observed in planar complexes of Pd^{II} with two phosphorus and two oxygen atoms as donors [8]. The Pd–O2 distance of 2.214 Å is markedly longer than the Pd^{II}–O distances normally found, which range between 2.05 and 2.08 Å.

No comparison is possible with other phosphinato-complexes of Pd^{II} since **2** is the only structurally characterized Pd^{II} compound containing that ligand. Moreover, it is interesting to note that phosphinato-complexes have been structurally characterized for many transition metals, such as Cu, Fe, Mn, Mo, Ni and Zn; however, only bonding patterns **1a** and **1b** have been

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* Dedicated to Professor Paolo Chiusoli, who made a significant contribution to the growth of metal assisted organic chemistry, on the occasion of his 70th birthday.

** Reference number with asterisk indicates a note in the list of references.

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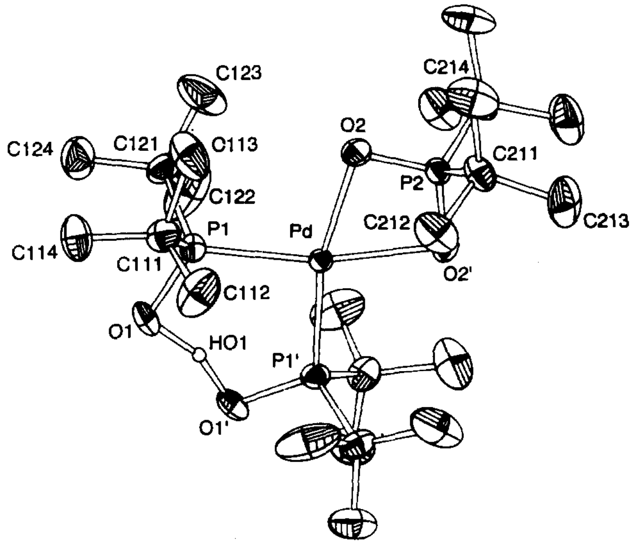
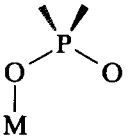
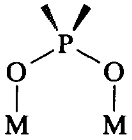


Fig. 1. Perspective ORTEP view of the molecule of 2 with the atom numbering adopted in the structure determination. Only hydrogen atom H(O1) has been shown, for clarity. A twofold axis passing through P2, Pd and HO1 atoms correlates the two halves of the molecule; ′ means $1-x$, y, $1/2-z$. The thermal ellipsoids are represented at 30% probability. Most relevant bond distances (Å) and angles (°): Pd–P1 2.261(2), Pd···P2 2.710(3), Pd–O2 2.214(6), P2–O2 1.491(6), O1–H(O1) 1.19(2), P1–Pd–O2 99.9(2), P1–Pd–P1′ 93.5(1), O2–Pd–O2′ 66.7(2), Pd–O2–P2 91.9(3).

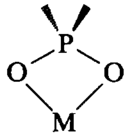
observed so far, whereas the present case corresponds to type **1c**.



1a



1b



1c

However, notwithstanding that the four-membered PS_2M cycle is well known for palladium and many other metals of Group 9, the cycle PO_2M is observed with metals of this Group only in the phosphate complex of Co^{III}, aquabis(ethylendiamine)(phosphato-*O*,*O*′)cobalt(III) [9]. Finally, PdO_2E cycles have not yet been structurally characterized either for E = C or for E = N.

A strict comparison can be made between the phosphinito ligand in **2** and in dimethylphosphinodithioato)(diphenylphosphinito)(diphenylphosphinous acid) palladium(II) [10]. In the latter, as in other cases [8], the short O···O separation between the phosphinite ligands (2.241 Å) has been assumed to indicate a symmetrical hydrogen bond. In our case the H(O1) atom has been fixed on the twofold axis, owing to the difficulty of refining close to the symmetry element. The Fourier map showed a broad maximum between atoms O1 and O1′. The very short O1···O1′ distance of 2.33 Å in **2** is in keeping with a strong symmetrical hydrogen bond, but it is also possible that the "special" position of the hydrogen atom on the twofold axis is the result of a statistical distribution of the H(O1) atom, connected with the O1 atom in some molecules and with the O1′ atom in some others. In both cases the hydrogen interaction between the oxygen atoms is strong, as confirmed also by the large O1–H(O1)–O1′ angle of 156.8°.

Apart from van der Waals interactions, the crystal packing does not show any other intermolecular bonding contact.

Full lists of atomic coordinates, thermal parameters and bond lengths and angles are available from the Cambridge Crystallographic Data Centre.

Acknowledgements

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References and notes

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3 ^{1}H NMR (C_6D_6): δ 15.4 (br s, 1H), 1.47 (d, ^3J(PH) = 14.7 Hz, 36H), 1.29 (d, ^3J(PH) = 13.2 Hz, 18H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 40.8 (d, ^1J(CP) = 32.2 Hz), 36.0 (d, ^1J(CP) = 75.9 Hz), 29.3 s, 27.1 s. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 122.5 (s, [(P^{t}Bu$_2$O)$_2$H]), 94.0 (s, [(P^{t}Bu$_2$O$_2$)]). Anal. Found: C, 47.9; H, 9.09; P, 15.4. $C_{24}H_{55}O_4P_3Pd$ calcd.: C, 47.5; H, 9.13; P, 15.3%.

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5 Crystal data. $C_{24}H_{55}O_4P_3Pd$, $M = 607.02$, monoclinic, space group $C2/c$, $a = 17.902(5)$, $b = 10.847(4)$, $c = 17.611(5)$ Å, $\beta = 114.17(6)°$, $U = 3120(2)$ Å^3, $d_c = 1.292$ Mg m^{-3}, $Z = 4$, Mo Kα radiation, $\lambda = 0.71069$, Ital Structure diffractometer, 2515 unique reflections with $I > 3\sigma(I)$, in the range $2.5 < \theta < 25°$. Structure solved by direct methods in the Cc space group refinement continued in the $C2/c$ space group because of an evident rotational symmetry of the molecule. Final R = 0.071, 148 refined parameters, max. residual peak 1.43 e Å^{-3} near to the H(O1) atom position.

6 The identification of the H(O1) atom as a hydrogen was inferred from spectroscopic and chemical evidence. The Fourier map showed an electronic density suggesting an atom with more electrons in this position. However, the use of the hydrogen scattering factor for this atom for the refinement reduced the thermal factor to nearly 1/100 of that of the other atoms.

7 As can be seen from Fig. 1 the methyl groups of the phosphines appear to have a very high thermal motion, but this is probably an artifact of the refinement program and some disorder. The same disorder produces a contact distance between the hydrogen atoms we have connected to C213 and C214′ atoms (both sp^3 geometry) which is too short.

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