

Preliminary communication

Oxidative addition of O–H bond to a metal centre: synthesis and crystal structure of *trans*-(PhO)(H)Pd(PCy₃)₂ · PhOH

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Abstract

(Cy₃P)₂Pd (Cy = C₆H₁₁) reacts with PhOH in toluene to give the phenoxypalladium(II) hydride derivative *trans*-(PhO)(H)Pd(PCy₃)₂ · PhOH; the crystal structural study has established that the oxygen of the phenoxy group forms a hydrogen bridge with an uncoordinated phenol molecule, and has allowed direct location of the hydride atom (Pd–H, 1.57(2) Å).

The H–M–OR unit has several points of interest mainly arising from the simultaneous presence of the very reactive M–OR and M–H bonds. Examples are: (a) the involvement of alkoxypalladium derivatives in the conversion of alkenes, carbon monoxide, and methanol into esters [1–4]; (b) the migratory insertion of CO into the Th–H bond of the alkoxo-hydride derivative (η^5 -C₅Me₅)Th(H)(OCH-t-Bu₂) to give an η^2 -metal formyl [5]; and (c) the intermediacy of alkoxo-hydride species in catalytic hydrogen transfer reactions [6].

Formally L_nM(H)(OR) complexes can be directly derived by oxidative addition of alcohols to electron-rich transition metals, but there are very few examples of preparation of alkoxo-hydrido derivatives either by this route or by other synthetic methods [5,8]. Possible reasons are that activation of the O–H bond alcohols is difficult and that the electronic requirements of alkoxo and hydrido ligands are rarely compatible.

Here we report the synthesis and the crystal structure determination of *trans*-(PhO)(H)Pd(PCy₃)₂ · PhOH (I); this is the first determination for a complex containing both Pd–H and Pd–OPh units.

Complex I was obtained as a yellow crystalline solid by addition at room temperature of PhOH to a toluene solution of Pd(PCy₃)₂ [9] (2/1 ratio) followed by precipitation with n-hexane at –30°C (60% yield), satisfactory analytical results

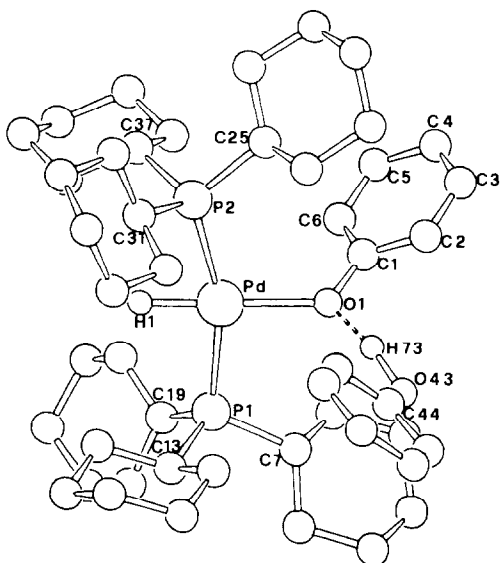


Fig. 1. The molecular structure of (I) showing the atom labelling. Only the H(hydride) and the H(bridge) are reported. Relevant bond distances (Å) and angles ($^{\circ}$) are: Pd–H(1) 1.57(2) (by direct location, without full refinement), Pd–P(1) 2.318(1), Pd–P(2) 2.330(1), Pd–O(1) 2.135(2), O(1)–C(1) 1.326(3), O(43)–C(44) 1.369(5), P(1)–Pd–H(1) 86(1), P(2)–Pd–H(1) 76(1), P(1)–Pd–P(2) 161.9(1), H(1)–Pd–O(1) 176(1), Pd–O(1)–C(1) 120.5(2).

were obtained for I. The main features of complex I were clarified by IR spectroscopy (Nujol mull): $\nu(\text{Pd-H})$ 2060w, 2040w; $\nu(\text{C=C})$ 1605m, 1585s cm^{-1} and ^1H NMR spectroscopy ($[\text{C}_6\text{H}_6]$ -toluene, 10 $^{\circ}\text{C}$, 300 MHz): δ 7.1 (11 H,m, $\text{C}_6\text{H}_5\text{O}$), 1.8 (66 H,m, C_3P), -17.5 (1 H,m, Pd-H); the shift of a signal from δ 8.4 (-40°C) to δ 5.6 (30°C) was clearly attributable to hydrogen bonding; this signal cannot be detected at 10°C , probably because it falls under the multiplet of the aromatic protons, this accounting for the incorrect ratio between the proton sets. The exact nature of I was revealed by the X-ray structural determination. Crystal data: $\text{C}_{42}\text{H}_{72}\text{OP}_2\text{Pd} \cdot \text{C}_6\text{H}_5\text{OH}$, $M = 855.5$, triclinic, space group $P\bar{1}$, a 13.535(6), b 16.131(4), c 11.759(5) Å, α 109.24(3), β 106.34(3), γ 84.21(3) $^{\circ}$, U 2325.98 Å 3 , $Z = 2$, D_c 1.22 g cm^{-3} , $F(000) = 916$, $\mu(\text{Mo } K_{\alpha})$ 4.94 cm^{-1} , θ range 2.5–25 $^{\circ}$, final R value 0.033, $R_w = 0.037$ for 6568 out of 8568 absorption-corrected independent reflections [$F_0 > 5\sigma(F_0)$] (transmission range 78–100%). Intensity data were collected at room temperature on an Euraf–Nonius CAD4 diffractometer by the ω – 2θ scan method. All non-H atoms were allowed to vibrate anisotropically. The H-atom bound to palladium(II) was found in a final Fourier difference map and in the refinement was fixed at the observed distance of 1.57(2) Å from Pd, a similar procedure was used for the H atom of the phenoxide group, this atom being kept at a distance of 1.18(1) Å from O(43). The remaining H atoms were added in calculated positions and refined riding on their respective C atoms. The structure was solved by Patterson methods; for all calculations the SHELX76 [10] package of crystallographic programs was used. The molecular structure of I is shown in Fig. 1. The palladium(II) atom possesses a severely distorted square planar coordination geometry. The two *trans*- PCy_3 groups bend towards the H(hydride) atom

(P(1)–Pd–P(2) 161.9(1)°) and appear to be “pushed away” from the phenoxyphenol coordination site. The very small deviations from the least-squares plane (max elevation 0.04 Å for Pd) confirm that the main cause of deformation is the steric pressure exerted by the phenoxyphenol system. The main features of the structure of I are the unprecedented direct location of the hydride ligand and the phenoxy phenol coordination system. Although direct comparison with other Pd–H bond lengths is not possible, the observed distance of 1.57(2) Å is in agreement with the values reported for some Rh–H distances [11] and with the sum of the Pd and H atomic radii. However, an unambiguous determination of the H atom position would require a neutron diffraction study.

The Pd–O distance of 2.135(2) Å falls within the range observed for other Pd–O bonds in square planar complexes [12].

The coordinated phenoxy group is found to form a hydrogen bond with a phenol molecule. Interestingly, also the H-atom in the bridge could be directly located from the X-ray diffraction experiment, the O...H–O angle is 168.3(2)° and the H-bond is asymmetric with distance from the O(phenoxy) (1.46(1) Å) longer than that from the O(phenol) atom (1.18(1) Å). It is noteworthy that C(1) appears to be displaced out of the plane orthogonal to the palladium(II) coordination square (as indicated by the torsion angles P(1)–Pd–O(1)–C(1) 124.6 and P(2)–Pd–O(1)–C(1) –58.9°) because of the presence of the H-bridged phenol molecule.

Future work will be aimed at examining the reactivity of Pd–H and Pd–OPh bonds and the activation of the O–H bond of aliphatic alcohols.

References

- 1 R.F. Heck, *J. Am. Chem. Soc.*, 94 (1972) 2712.
- 2 D.M. Fenton and P.J. Steinward, *J. Org. Chem.*, 37 (1972) 2034.
- 3 T. Fuchikama, K. Ohishi, and I. Ojima, *J. Org. Chem.*, 48 (1983) 3803.
- 4 H. Alper, B. Despeyroux, and J. Woell, *Tetrahedron Lett.*, 24 (1983) 5691.
- 5 K.G. Moloy, and T.J. Marks, *J. Am. Chem. Soc.*, 106 (1984) 7051, and ref. therein.
- 6 R.A.W. Johnstone, A.H. Wilbi, and I.D. Entwistle, *Chem. Rev.*, 85 (1985) 129.
- 7 K.A. Azam, A.J. Deeming, R.E. Kimber, and P.R. Shukla, *J. Chem. Soc., Dalton Trans.*, (1976) 1853; M. Akiyama, M.H. Chisholm, F.A. Cotton, M.W. Extine, D.A. Haitko, J. Leonelli, and D. Little, *J. Am. Chem. Soc.*, 103 (1981) 779; K.W. Chiu, R.A. Jones, G. Wilkinson, A.M.R. Galas, M.B. Hursthouse, and K.M. Aboul Malik, *J. Chem. Soc., Dalton Trans.*, (1981) 1204; L. Farrugia and M.L.H. Green, *J. Chem. Soc., Chem. Commun.*, (1975) 416.
- 8 L.J. Newman and R.G. Bergman, *J. Am. Chem. Soc.*, 107 (1985) 5314; M.D. Fryzuk, M. Ling lang, T. Jones, and F.W.B. Einstein, *Can. J. Chem.*, 64 (1986) 174; J.M. Manriquez, D.R. McAlister, R.D. Sanner, and J.E. Bercaw, *J. Am. Chem. Soc.*, 98 (1976) 6733.
- 9 *Inorg. Synth.*, 19 (1979) 103.
- 10 SHEL76 by G.M. Sheldrick, University of Cambridge, 1976.
- 11 R.G. Teller and R. Bau in: *Structure and Bonding*, Springer-Verlag Berlin Heidelberg, 44 (1981) 1.
- 12 P. Braunstein, D. Matt, Y. Dusansoy, J. Fischer, A. Mitschler, and L. Ricard, *J. Am. Chem. Soc.*, 103 (1981) 5115; T. Hosokawa, C. Calvo, H.B. Lee, and P.M. Maitlis, *J. Am. Chem. Soc.*, 95 (1973) 4914.