

The Synthesis and Crystal Structure of a Remarkable Binuclear, Double Pd–Cl–H–O–Pd Bridged Palladium Alcohol Complex. Catalytic Oxidations with Molecular Oxygen mediated by $\{[Me_2C(OH)CH_2CONMe_2]Pd(Cl)NO_2\}_2\}$

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The $Pd(Cl)NO_2$ complex of *N,N*-3-trimethyl-3-hydroxybutyramide is dimeric in the solid state with two $Pd-Cl-H-O-Pd$ hydrogen-bond bridges; however, in solution the complex is monomeric and catalytically active in the oxidation of alkenes.

The development of selective transition metal catalysed oxidations of alkenes with molecular oxygen continues to provide a formidable challenge.¹ It has been demonstrated that catalysts based on palladium(II)nitro complexes² offer in several cases excellent alternatives to the well-known Wacker process. We recently found that $(MeCN)_2Pd(Cl)NO_2$ **1** in the presence of Bu^tOH or Pr^tOH as ligand or solvent is capable of converting α -alkenes into aldehydes (60–70% selectivity) or methylketones (>90% selectivity) using molecular oxygen.³ These results point to catalytically active palladium alcohol complexes. Although complexes of alcohols with palladium have been postulated as intermediates in various reactions,⁴ well-defined palladium or platinum complexes⁵ containing coordinated alcohol moieties are hardly known. Palladium phenolate complexes, hydrogen bonded with a phenol, have recently been reported.⁶ We now report the preparation, molecular structure and catalytic activity of a unique binuclear, double hydrogen-bridged, palladium alcohol complex. Based on the knowledge that both tertiary alcohols³ and amides⁷ show beneficial effects on the oxidation of alkenes with palladium nitro complexes the bidentate β -hydroxyamide ligand, $Me_2C(OH)CH_2CONMe_2$ **2**,⁸ was examined.

Treatment of $(MeCN)_2Pd(Cl)NO_2$ with 2 equiv. of **2** in THF for 30 min and cooling for 24 h at 0 °C resulted in the formation of $\{[Me_2C(OH)CH_2CONMe_2]Pd(Cl)NO_2\}_2$ **3**. Crystallization resulted in the isolation of pure **3** as a red, crystalline compound† (50% yield) (Scheme 1).

X-Ray analysis of this complex (Fig. 1) revealed some remarkable features.‡

A binuclear structure is present with two Pd^{II} atoms occupying 1,5-positions in an eight-membered ring. Instead of

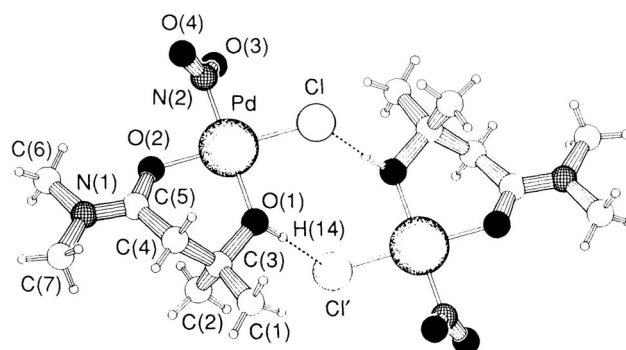
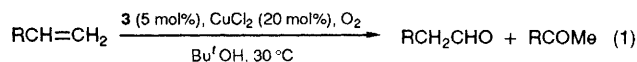


Fig. 1 PLUTO diagram **3** with adopted atom numbering scheme. Selected bond lengths (Å) and angles (°), with esds in parentheses: Pd–Cl 2.2997(17), Pd–O(1) 2.059(4), Pd–O(2) 2.038(4), Pd–N(2) 1.980(6), O(3)–N(2) 1.248(9), O(4)–N(2) 1.074(10), O(2)–C(5) 1.266(6), O(1)–C(3) 1.461(6), N(1)–C(5) 1.311(7), N(1)–C(6) 1.466(7), N(1)–C(7) 1.452(9), O(1)–Cl' 3.171(6), O(1)–H(14) 0.96(7), H(14)–Cl' 2.23(7); Cl–Pd–O(2) 179.32(13), O(1)–Pd–N(2) 179.48(18), Pd–O(2)–C(5) 124.4(3), Pd–O(1)–C(3) 122.8(3), O(1)–C(3)–C(4) 106.2(4), O(2)–C(5)–C(4) 120.5(4), O(1)–H(14)–Cl' 166(6).

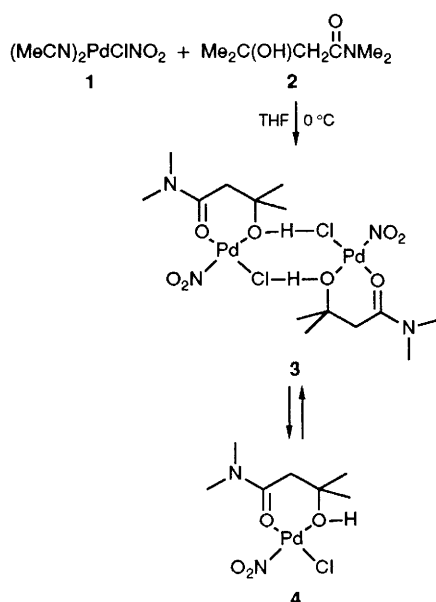


the commonly found $Pd-Cl-Pd$ bridges two previously unknown $Pd-Cl-H-O-Pd$ bridges are formed. The two bridging hydrogen bonds are almost linear $[O(1)-H(14)\cdots Cl' = 166(6)^\circ]$ whereas the central eight-membered ring has a chair-like folded conformation. The geometry around each Pd^{II} is planar with the β -hydroxyamide acting as a chelating ligand. The deviation of the palladium atom out of the mean plane is 0.001(10) Å. In accordance with the commonly observed *O*-coordination of transition metal complexes of group 8 with amide ligands⁹ Pd^{II} exhibits the *O*-coordination mode in **3**. It should be noted that the bond lengths of Pd to the amide oxygen $[Pd-O(2) 2.038(4) \text{ Å}]$ and to the *tert*-alcohol oxygen $[Pd-O(1) 2.059(4) \text{ Å}]$ are comparable. The difference in bond length of 0.17 Å between $N(2)-O(3)$ and $N(2)-O(4)$ is rather unusual and may be the consequence of minor disorder, as is indicated by the relatively high thermal motion parameters of this group. The nitro group is strongly twisted out of the mean plane through the $Pd-Cl-[Me_2C(OH)CH_2CONMe_2]$ unit. An interplanar angle of the planes through $Pd-N(2)-O(3)-O(4)$ and $Cl-N(2)-O(1)-O(2)$ of $64.9(3)^\circ$ is found.

An investigation towards the nature of the complex in solution strongly indicated the formation of mononuclear structure $Me_2C(OH)CH_2CONMe_2Pd(Cl)NO_2$ **4**. In THF (tetrahydrofuran) a monomeric complex, most probably **4**, is

† Satisfactory elemental analyses were obtained.

‡ *Crystal data* for **3**, $C_7H_{15}N_2O_4PdCl$, $M_r = 333.08$, red block-shaped crystal ($0.2 \times 0.3 \times 0.5 \text{ mm}$), triclinic, space group $P\bar{1}$ (No. 2), $a = 8.1444(10)$, $b = 9.0628(12)$, $c = 9.1228(10) \text{ Å}$, $\alpha = 82.291(11)$, $\beta = 64.848(10)$, $\gamma = 88.618(11)^\circ$, $V = 603.60(14) \text{ Å}^3$, $Z = 2$, $D_{\text{calc}} = 1.832 \text{ g cm}^{-3}$, $F(000) = 332$, $\mu(\text{Mo-K}\alpha) = 17.4 \text{ cm}^{-1}$, 2510 independent reflections ($2.3^\circ < \theta < 27.5^\circ$, $\omega/2\theta$ scan, $\Delta\omega = 0.89 + 0.35 \tan \theta^\circ$, $T = 298 \text{ K}$, Zr-filtered Mo-K α radiation) on an Enraf-Nonius CAD-4F diffractometer. Three reference reflections showed no significant decay during 7 h of X-ray exposure time. The structure was solved by automated Patterson methods (SHELXS86). Refinement on F was carried out by full-matrix least-squares techniques (SHELX76); final R value 0.037, $wR = 0.054$, $w^{-1} = 1/[\sigma^2(F) + 0.0014 F^2]$, $S = 0.84$ for 2130 reflections with $I > 2.5 \sigma(I)$. Hydrogen atoms were included in the refinement on calculated positions ($C-H = 0.98 \text{ Å}$) riding on their carrier atoms, except for the hydroxy hydrogen atom, which was located on a difference Fourier map. All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms were refined with an overall isotropic thermal parameter of 0.101(6) Å². Weights were introduced in the final refinement cycles. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1

present as was concluded from a molecular mass measurement using Clark's modification of the Signer method.¹⁰ At equilibrium a molecular mass of 329 was found (calc. 333). The ^1H NMR ($[\text{D}_8]\text{THF}$) spectra measured at temperatures varying from -40 to 50°C did not give any indication for the presence of more than one monomeric species. The IR spectrum (Nujol) showed that the ν_{CO} stretching vibration had shifted from 1670 in the free ligand to 1600 cm^{-1} in the coordinated ligand, indicating coordination of oxygen to the metal centre. ^1H NMR spectroscopy and molecular mass measurements lead to the conclusion that the two hydrogen-bond bridges observed in **3** in the solid state are not strong enough to prevent this complex from dissociating in solution to the mononuclear complex **4**.

Some preliminary experiments showed that complex **3** is remarkably stable—it does not decompose when exposed to air or moisture. The catalytic activity of **3** towards alkenes was investigated in Bu^tOH under the same conditions as reported previously.^{3,7} The rates of oxidation of alkenes with O_2 and **3** as a catalyst (5 mol%), for instance are comparable with the rates reported for the oxidation catalysed by $(\text{MeCN})_2\text{Pd}(\text{Cl})\text{NO}_2$, 9 equiv. (based on Pd) of oct-1-ene were oxidized after 18 h (eqn. 1). The oxidation products obtained were octanal (30%) and octan-2-one (70%) and only traces of isomeric alkenes were observed.

The addition of four equiv. of ligand **2** resulted in a complete inhibition of the oxidation reaction. Unfortunately, the use of an intramolecular tertiary hydroxy group did not result in a higher selectivity towards aldehyde formation.

The unexpected observation of the eight-membered double H-bonded binuclear Pd-complex and the structural characterization of a complex with a *tert*-alcohol as a coordinating ligand strongly support the role of alcohols as bridging or coordinating ligands in some Pd-catalysed reactions as proposed previously, and implications for the design of new Pd-catalysts can be foreseen.

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