

Formation of a Novel Pd₄ Cluster from the Acetolysis of Bis[(*R*)-*N*- α -methylbenzyl-salicylideneaminato-*N,O*]palladium(II)

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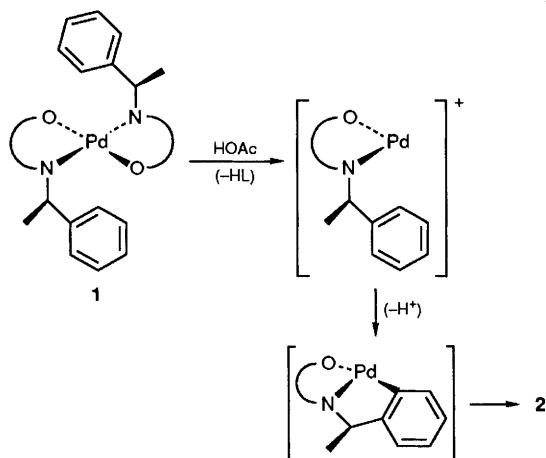
The title compound **1** is transformed into tetrakis[(*R*)-*N*- α -methylbenzylsalicylideneaminato-*C*^o,*N,O*]tetrapalladium(II) **2** upon long term standing in acetic acid; the novel structure of **2** is established spectroscopically and by X-ray diffraction.

As part of a project to develop chiral Pd^{II} complexes as asymmetric oxidation catalysts, we have been examining allylic oxidation reactions^{1,2} promoted by bis[(*R*)-*N*- α -methylbenzylsalicylideneaminato-*N,O*]palladium(II) **1** in acetic acid media. To explore the mechanisms of these reactions and the possible modes of catalyst activation–deactivation we have studied the stability of **1** in acetic acid. Reported herein is our discovery that acetolysis of **1** produces an unusual [Pd₄L₄] cluster [H₂L = (*R*)-*N*- α -methylbenzylsalicylideneamine] featuring a rare *C,N,O*-tridentate ligand derived from orthometallation of the pendant side chain.

Stirring an acetic acid solution of **1** at 20 °C for 3 days

followed by addition of water and extraction with CHCl₃ afforded crude **2**, which was obtained in pure form (96% yield) as a pale yellow, somewhat unstable crystalline solid after chromatography (benzene–silica gel). IR and ¹H NMR spectroscopic analysis[†] of **2** revealed the presence of salicyl-

[†] **2**: m.p. (decomp.) 253–255 °C; IR (KBr) ν /cm⁻¹ 1624, 1600, 1543, 1469, 1439, 1292; ¹H NMR (δ , CDCl₃) 0.73 (d, *J* 6.8 Hz, 3H), 1.40 (d, *J* 6.8 Hz, 3H), 4.22 (q, *J* 6.7 Hz, 1H), 4.85 (q, *J* 6.7 Hz, 1H), 6.3–7.4 (m, 14H), 7.78 (s, 1H), 7.93 (s, 1H), 8.11 (d, *J* 8.8 Hz, 1H), 8.30 (d, *J* 8.5 Hz, 1H); MS (FAB, *m/z*) 1317 [15, (sal-H)₄Pd₄H⁺], 660 [80, (sal)₂Pd₂⁺], 330 [20, (sal)Pd⁺].



ideneamino ligand(s). The existence of two different ligand environments was indicated by well-separated pairs of α -CH and $-\text{CH}(\text{CH}_3)$ resonances. The fast atom bombardment (FAB) MS of **2** shows a prominent set of peaks with a maximum m/z of 1317 corresponding to the formulation $\text{L}_4\text{Pd}_4\text{H}^+$.

To elucidate the detailed structure of **2** single crystals were obtained from CH_2Cl_2 -Et₂O and subjected to X-ray diffraction analysis.† The resulting ORTEP representations of the two crystallographically independent molecules of **2** (**a** and **b**) are provided in Fig. 1. The core of each molecule of **2** consists of an eight-membered ring of alternating Pd and O atoms derived from the salicylideneamino ligands. The remaining two sites of each square planar Pd coordination sphere are occupied by the salicylideneamino nitrogen and the *ortho* carbon of the *N*-benzyl unit. The resulting cluster has approximate C_2 symmetry [e.g. in **2b** the C_2 axis is perpendicular to and bisecting Pd(7)–Pd(8) and Pd(5)–Pd(6) axes] rendering the Pd(7)–Pd(8) pair (and associated ligands) different from the Pd(5)–Pd(6) pair, suggesting similar solution and solid state structures. The corresponding bond

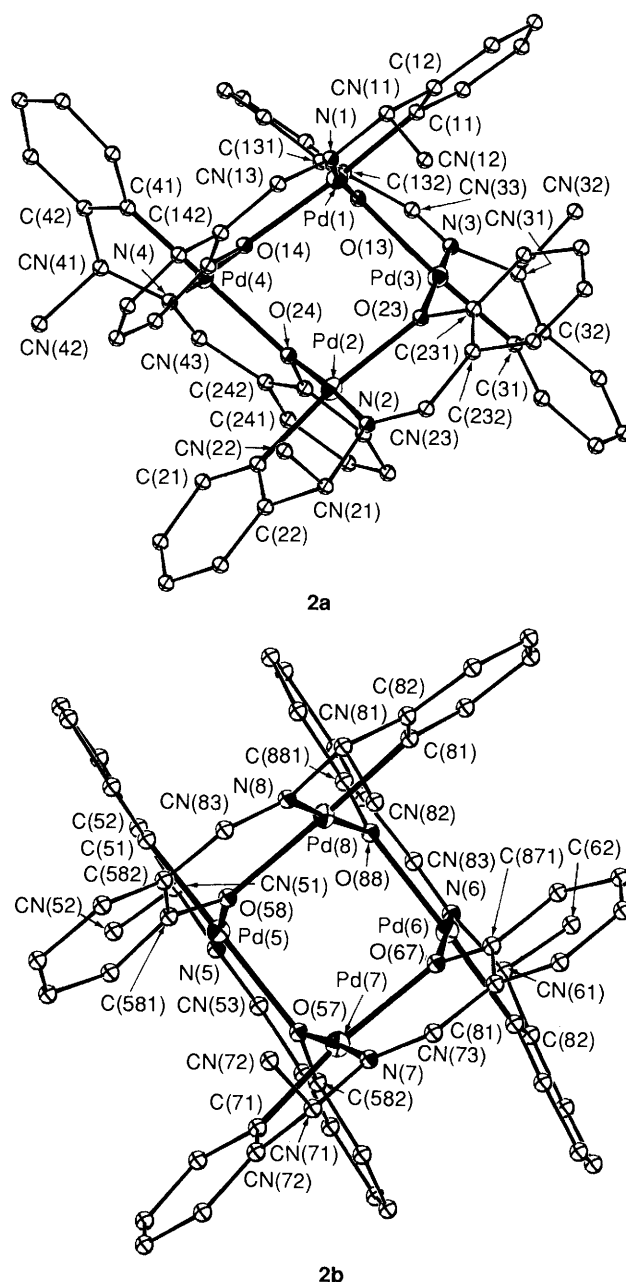


Fig. 1 X-Ray structure of the independent molecules of **2** (H atoms omitted for clarity). Selected average interatomic distances (Å) and angles (°) for **2a**: Pd–C 1.96(1), Pd–N 1.97(1), Pd–O 2.10(2); *trans*-N–Pd–O 174(2), *trans*-C–Pd–O 173(2), *cis*-O–Pd–O 92(2); *cis*-N–Pd–C 83(2), *cis*-N–Pd–O 91(1); Pd–Pd 3.74(35); for **2b**: Pd–C 1.97(1), Pd–N 1.97(1), Pd–O 2.11(2); *trans*-N–Pd–O 174(2), *trans*-C–Pd–O 173(2), *cis*-O–Pd–O 91(2), *cis*-N–Pd–C 83(2), *cis*-N–Pd–O 92(2); Pd–Pd, 3.62(14). Individual Pd–Pd distances are given in footnote §.

lengths in the independent molecules **2a, b** are virtually the same but their conformations differ significantly in the extent of splaying of the monomeric PdL units relative to each other.‡ The absence of significant Pd–Pd bonding interactions

† X-Ray data for **2**: crystal from CH_2Cl_2 -diethyl ether, data collected at -110°C , $\text{C}_{60}\text{H}_{52}\text{N}_4\text{O}_4\text{Pd}_4 \cdot 1.5 (\text{C}_4\text{H}_{10}\text{O})$, $M = 1429.9$; space group $P2_12_12_1$, $a = 16.532(6)$, $b = 17.081(7)$, $c = 42.189(11)$ Å, $U = 11913.4$ Å³, $Z = 8$, $D_c = 1.594$ g cm⁻³, $F(000) = 5752$, $\lambda = (\text{Mo-K}\alpha = 0.71069$ Å), $\mu(\text{Mo-K}\alpha) = 11.5$ cm⁻¹. Cell dimensions and intensities of 11 382 reflections ($2\theta_{\text{max}} = 50^\circ$) were measured on an Enraf-Nonius CAD-4 diffractometer, using monochromated Mo-K α radiation. The data were corrected for Lorentz and polarization effects. No absorption correction was applied since it was judged to be insignificant. The atomic scattering factors were taken from the International Tables for X-ray crystallography. The structure was solved by direct methods and refined by the blocked-matrix least-squares method (SHELX-76). There are two independent molecules of **2** along with three solvent (diethyl ether) molecules in the asymmetric unit. Because of the large number of atoms (636 non-hydrogen atoms) in the unit cell, only the Pd atoms were refined anisotropically and all the other atoms isotropically. Hydrogen atoms could not be located and they were not included in the refinement. Despite the difficulties of handling the unusually large numbers of atoms including those of three solvent molecules, the structure was refined to a final R -value of 0.063 for 8567 observed reflections [$I > 2\sigma(I)$]. The final $R_w = 0.081$ and the $\rho_{\text{max}} = 1.2$ eÅ⁻³ in the final difference map. It is interesting to note that **2** also crystallizes in the monoclinic space group $P2_1$ (crystallization from toluene-hexane), with unit cell dimensions of: $a = 13.487(4)$, $b = 16.178(5)$, $c = 16.513(5)$ Å, $\beta = 91.34(4)^\circ$, $V = 3602.0$ Å³. Crystal quality of that batch was poor and the structure could only be refined to an R -value of 0.115. Nevertheless, the gross molecular features of **2** established in our previous determination are similar to those reported herein. 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.

‡ For example, within the 'coplanar' Pd–O–Pd–O units torsional angles range from 13 – 25° in **2a** vs. 0 – 8° in **2b**; similarly, corresponding Pd–Pd distances (Å) vary considerably in the two conformations, in **2a**: Pd(1)–Pd(2) 3.916(2), Pd(1)–Pd(1)–Pd(3) 3.487(2), Pd(1)–Pd(4) 3.583(2), Pd(2)–Pd(3) 3.567(2), Pd(2)–Pd(4) 3.525(2), Pd(3)–Pd(4) 4.383(2); in **2b**: Pd(5)–Pd(6) 3.784(2), Pd(5)–Pd(7) 3.580(2), Pd(5)–Pd(8) 3.481(2), Pd(6)–Pd(7) 3.474(2), Pd(6)–Pd(8) 3.607(2), Pd(7)–Pd(8) 3.782(2).

(Pd–Pd \geq 3.47 Å), the eight-membered, presumably flexible Pd₄O₄ ring, and the non-detection by NMR of isomers in solutions of **2** suggests that these differences may be derived from crystal packing forces.

Cluster **2** is thus a tetramer of the unsaturated fragment Pd[(*R*)-*N*- α -methylbenzylsalicylideneaminato-*C*^o,*N*,*O*]], which may be formed by protolytic cleavage of **1** followed by orthopalladation (Scheme 1). In contrast, protonolysis of Pd–salicylideneaminato complexes by mineral acids (HX) has been reported to produce *trans*-Pd(*N*-salicylideneaminato)₂-X₂.⁴ Retention of the chiral ligand in **2** to the exclusion of substitution by achiral acetate bodes well for the prospects of effecting catalytic asymmetric reactions using related complexes. The [(*R*)-*N*- α -methylbenzylsalicylideneaminato-*C*^o,*N*,*O*] ligand has not been previously observed and is a rare example of a heteroatomic *C*,*N*,*O*-bonded tridentate ligand. Finally, we have found that cluster **2** does catalyse allylic oxidation of cyclohexene (HOAc–MnO₂, 20 °C), albeit at a slower rate than **1**, suggesting that the reaction in Scheme 1 may be reversible.

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References

- 1 W. Kitching, Z. Rappoport, S. Winstein and W. G. Young, *J. Am. Chem. Soc.*, 1966, **88**, 2054; S. Uemura, S. Fukuzawa, A. Toshimitsu and A. Okanao, *Tetrahedron Lett.*, 1982, **23**, 87; J. E. McMurray and P. Kocovsky, *Tetrahedron Lett.*, 1984, **38**, 4187; A. Heumann and B. Akermark, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 453; S. Hansson, A. Heumann, T. Rein and B. Akermark, *J. Org. Chem.*, 1990, **55**, 975.
- 2 H. Yang and K. M. Nicholas, unpublished results, 1990.
- 3 S. Yamada and K. Yamanouchi, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 2543.
- 4 E. A. Andronov, Y. N. Kukushkin and Y. V. Murashkin, *Izv. Vyssh. Uchebn. Zaved.*, 1976, **19**, 1749.