Cluster Compounds

Ligand-Induced Formation of an Adamantanoid Hexanuclear (π-Allyl)Pd^{II}(μ_3-Hydroxo) Cluster Stacked as Hydrogen-Bonded Double Strands

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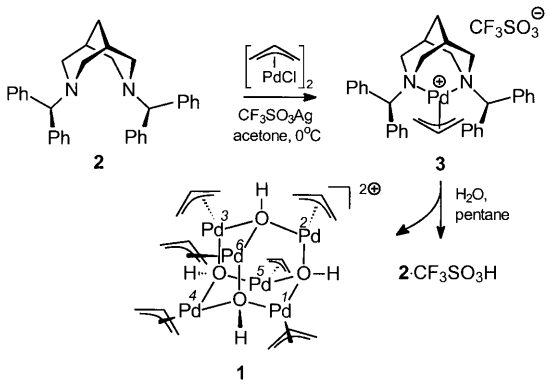
Hydroxo complexes of transition metals are of interest in materials science as precursors for intricate metal oxides,[1] and as intermediates in metal-mediated or -catalyzed processes. Hydroxopalladium intermediates have been postulated in some palladium-catalyzed reactions,[2] and they may explain the unexpected stability of some palladium catalysts in the presence of water.[3] In most of its hydroxo complexes, palladium is coordinated to further heteroatom ligands containing P and/or N atoms. Notable exceptions are (μ_2-hydroxo)bis(η^2,η^2-cyclooctadiene)dimethyldipalladium(II) hexafluoroantimonate[4a] and bis(tetrabutylammonium)-bis[(μ_2-hydroxo)bis(pentafluorophenyl)palladium],[4b] which contain palladium coordinated to η^2-alkene or σ-C ligands, respectively.

Isolated hydroxopalladium complexes usually display polynuclearity.[5] The formation of a trinuclear palladium complex was attributed to the presence of traces of water during purification.[6] Trinuclear, mixed-metal complexes were obtained by reaction between hydroxopalladium and metal hydride complexes.[7] Larger clusters of Pd atoms with predominantly carbon monoxide ligands are known, and non-hydroxopalladium clusters of catalytic interest have been studied.[8] A mixed-metal cluster (Pd/Cu) with an adamantanoid Pd–oxygen substructure (hexanuclear in Pd) but without organic ligands on the Pd atoms has been described.[9]

Herein, we report an organometallic, homonuclear hydroxo(π-allyl)Pd cluster **1**, [{(1,3-η^3-propenyl)Pd}$_6$(μ_3-OH)$_4$](CF$_3$SO$_3$)$_2$, without further heteroatom (P or N) ligands. The cluster has a distorted adamantanoid geometry, and the crystal lattice consists of clusters linked into double strands by hydrogen bonds via bridging counterions.

Cluster **1** was obtained during the attempted complexation of the sterically hindered bispidine ligand *N*,*N*′-bis(diphenylmethyl)-3,7-diazabicyclo[3.3.1]nonane (**2**) with a (π-allyl)palladium species, from which we expected to obtain complex **3** (Scheme 1). The formation of **3** was proven by ^{1}H NMR spectroscopy.[10] However, when trying to isolate solid **3** from the acetone solution, we observed the initial formation of colorless, needle-shaped crystals of the protonated ligand salt, **2**·CF$_3$SO$_3$H. Upon further undisturbed standing, the precipitation of yellow, rhomboid crystals was observed in experiments using technical-grade solvent. Under dry conditions, Pd black precipitated. The yellow crystals



Scheme 1. Ligand-induced formation of cluster **1** via complex **3**. The Pd$_6$(OH)$_4$ subunit is emphasized. The trifluorosulfonate ions are omitted for clarity.

were stable for several days at refrigerator temperature (below 4 °C) while covered by the crystallization solvent. Isolated crystals were reasonably stable in air at ambient temperature for several hours. To our surprise, the yellow crystals were not of the expected complex **3**, but of the adamantanoid (π-allyl)Pd^{II} cluster **1** with bridging hydroxo ligands. To the best of our knowledge, this is the first example of an organometallic cluster of palladium of this type.[11,14]

The Pd···C distances in cluster **1** (Figure 1) vary between 2.048 and 2.082 Å (propenyl C-2) and between 2.093 and 2.115 Å (propenyl C-1 and C-3). These distances are shorter

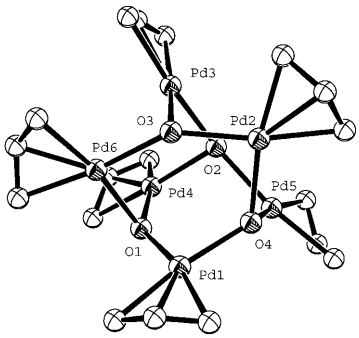


Figure 1. Molecular structure of cluster **1** (counterions omitted for clarity).

than those in the chloro dimer bis[(1,3-η^3-propenyl)palladium chloride] (2.121 Å for C-2, 2.108–2.123 Å for C-1 and C-3),[12] and in (*N*,*N*′-diphenyl-1,5-dimethyl-3,7-diazabicyclo[3.3.1]-nonane-9-one)(1,3-η^3-propenyl)palladium trifluoromethanesulfonate (2.128 Å for C-2 and 2.125–2.126 Å for C-1 and C-3),[15] most likely because of the small *trans* influence of μ_3-hydroxo ligands on the Pd–C bond compared to that of Cl or N ligands.

The Pd···O distances in cluster **1**, which range from 2.133 to 2.179 Å, are shorter than those in the only other reported Pd–(μ_3-OH) cluster, [{Pd(8-methylquinoline)}$_3$(μ_3-Ph$_2$PCH-COOC$_2$H$_5$)(μ_3-OH)]PF$_6$, which are between 2.144 and 2.281 Å.[4] In comparison with a series of μ_2-OH complexes, the Pd···(μ_3-OH) distances in **1** are similar to[16a] or signifi-

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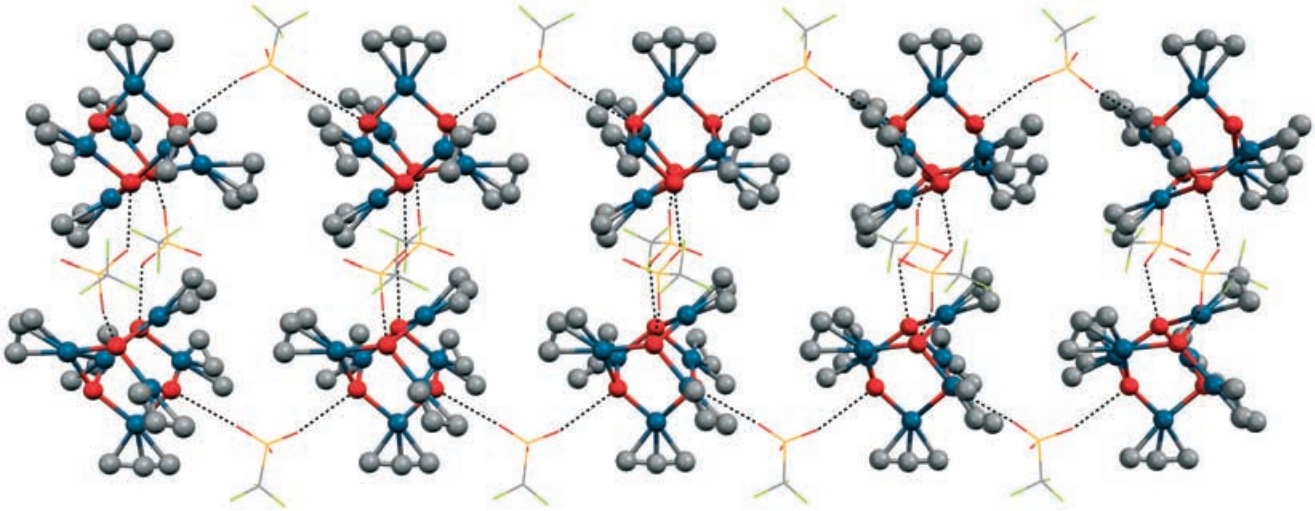

Figure 2. Double strands of clusters of **1**. Cluster pairs bonded via two $CF_3SO_3^-$ ions are linked into strands via two other $CF_3SO_3^-$ ions. Hydrogen bonds are indicated (••••, hydrogen atoms omitted for clarity). The lattice contains one acetone molecule per cluster (not shown).

cantly longer than[4,16b–e] those in the μ_2-OH complexes, where a common feature is that the Pd–(μ_2-O) bond experiences significantly less *trans* influence from other ligands than that exerted by the η^3-propenyl ligands in **1**.

The dicationic clusters of complex **1** are grouped into pairs, linked by two $CF_3SO_3^-$ ions hydrogen-bonded to the hydroxy ligands (connecting O3···O4′ and O4···O3′). These pairs are then linked into double strands of clusters by two more $CF_3SO_3^-$ ions connecting O1···O2′ and O2···O1′, respectively (Figure 2). Hydrogen-bond lengths are shorter between pairs than in the chains of clusters, with CF_3SO_3···(μ_3-H*O*) distances at 2.839 and 2.872–2.921 Å, respectively. Thus, each cluster is surrounded by four shared anions, which leads to a regular crystal lattice composed of double strands.

Hydroxo complexes of transition metals are usually formed by ligand exchange with water.[5b,17] We propose that this is also the case in the formation of cluster **1**. The sequence of steps leading to **1** is coupled to the dynamic process of apparent π-allyl rotation observed in (π-allyl)Pd complexes with chelating dinitrogen ligands.[18] Most likely, steric interactions between the organic ligands in complex **3** favor dissociation of one of its nitrogen atoms. Next, protonation of the basic nitrogen prevents reattachment to the palladium. Instead, the resulting coordinatively unsaturated complex is stabilized by coordination of hydroxy ions, generated by deprotonation of water by the strongly basic ligand **2**.[19] Involvement of η^3–η^1 isomerism of the π-allyl ligand is unlikely, since no exchange between *syn* and *anti* protons of complex **3** was detected by ^{1}H NMR spectroscopy.[10] Furthermore, the cluster **1** is not formed when bispidine ligands other than **2** are used.[15,18b,c]

In conclusion, ligand **2**, although itself not part of the cluster **1**, appears to be responsible for the formation of this new type of palladium complex.

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[10] Full characterization of **3** will be presented in a separate paper.
[11] Formation of **1** and **2**·CF_3SO_3H: Ligand **2**[12] (7.6 mg, 16.6 μmol) was dissolved in a mixture of acetone (0.3 mL) and $CHCl_3$ (0.2 mL) in a small test tube. After cooling to 0 °C a solution of bis[(1,3-η^3-propenyl)palladium chloride][13] (3.1 mg, 8.5 μmol) in acetone (0.2 mL) was added, followed by a solution of CF_3SO_3Ag (4.3 mg, 16.7 μmol) in acetone (0.2 mL). After stirring (30 s), the precipitated AgCl was separated by centrifugation. The clear, slightly yellow solution was transferred with a Pasteur pipette into a screw-cap vial, and carefully layered with the same volume of cold hexane, which became slightly cloudy. The closed vial was stored at 4 °C. After one day, colorless needles of **2**·CF_3SO_3H had formed. After two days, yellow rhomboid crystals of **1** appeared (yield ca. 0.1 mg, 4 %).
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[14] Crystal data for **1**: $C_{23}H_{40}F_6O_{11}Pd_6S_2$, $M_r = 1309.07$, yellow rhombohedra, crystal size $0.20 \times 0.18 \times 0.16$ mm^3, triclinic, space group $P\bar{1}$, $a = 10.321$, $b = 13.86770(10)$, $c = 14.531$ Å, $\alpha = 99.0800(10)$, $\beta = 107.3650(10)$, $\gamma = 94.5410(10)$°, $V = 1942.494(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.238$ g cm^{-3}, $\mu = 2.901$ mm^{-1},

$\theta = 2.09$–$32.89°$, $F(000) = 1256$, $T = 173(2)$ K, $R_1 = 0.0334$, $wR_2 = 0.0780$. Independent reflections = 13422 [R(int) = 0.0274], restraints = 240, parameters = 435. Crystal data for **2**·CF_3SO_3H: $C_{34}H_{35}F_3N_2O_3S$, $M_r = 608.70$, colorless needles, $1.00 \times 0.04 \times 0.04$ mm^3, monoclinic, space group $P2_1/n$, $a = 9.1585(2)$, $b = 14.3750(3)$, $c = 23.3428(5)$ Å, $\alpha = \gamma = 90$, $\beta = 90.073(1)°$, $V = 3073.16(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.316$ g cm^{-3}, absorption coefficient = 0.161 mm^{-1}, $\theta = 0.87$–$25.12°$, $F(000) = 1256$, $T = 173(2)$ K, $R_1 = 0.0519$, $wR_2 = 0.1078$. Independent reflections = 5418 [R(int) = 0.0823], restraints = 0, parameters = 424. Siemens SMART CCD area-detector diffractometer, $Mo_{K\alpha}$ radiation, wavelength = 0.71073 Å, multiscan, SADABS (Sheldrick, 2002). The structures were solved by direct methods, and refined with the SHELX software package and with full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure-factor calculations. The authors acknowledge Dr. V. Langer, Chalmers University of Technology, Goteborg (Sweden), for the data collection. CCDC-264283 (for **1**) and CCDC-264284 (for **2**·CF_3SO_3H) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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