

m41.p37

## Detailed characterization of new Pd-based cluster compounds

Bernard Tinant<sup>a</sup>, Christopher Willocq,<sup>b</sup> Sophie Hermans<sup>b</sup>, Michel Devillers<sup>b</sup>

<sup>a</sup>Unité de Chimie Structurale et des Mécanismes Réactionnels. <sup>b</sup>Unité de Chimie des Matériaux Inorganiques et Organiques, Université Catholique de Louvain, Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium. E-mail: tinant@chim.ucl.ac.be

**Keywords:** clusters, palladium, gold

In recent years, the synthesis of carbonyl phosphine clusters has received a lot of interest. They can be used as nanoscopic building blocks for a variety of applications including supported catalysts. Once incorporated onto a matrix of interest, the ligands sheath can be removed selectively to yield nanoparticles of controlled size and composition. In particular, we are interested in the synthesis of gold-palladium clusters to produce bimetallic nanoparticle catalysts for applications in selective oxidations. The chosen strategy to reach this goal was to start from palladium clusters, or their reduced form, and to react them with Au<sup>+</sup> fragments. Here, we wish to report the synthesis of the starting Pd clusters and their reactivity towards reducing agents. In addition, the direct reaction of Pd compounds with [Au(PPh<sub>3</sub>)Cl] was also explored. In a first step, a new cluster, [Pd<sub>10</sub>(CO)<sub>12</sub>(PPh<sub>3</sub>)<sub>6</sub>], was prepared by reacting [Pd<sub>2</sub>(dba)<sub>3</sub>] with one equivalent of PPh<sub>3</sub> under a CO atmosphere. It was fully characterised by NMR, IR and X-ray crystallography. The metal framework of this cluster was shown to consist in a palladium octahedron with four edges bridged by additional palladium atoms. The CO ligands adopt a  $\eta^2$  coordination mode on Pd-Pd edges, as expected from the CO stretching frequencies observed in the IR spectrum. By varying the amount of PPh<sub>3</sub> in the synthesis (0.5 to 3 eq.), clusters of different nuclearities were obtained. In a second step, the clusters [Pd<sub>12</sub>(CO)<sub>17</sub>(PBU<sup>n</sup><sub>3</sub>)<sub>5</sub>], [Pd<sub>10</sub>(CO)<sub>12</sub>(PBU<sup>n</sup><sub>3</sub>)<sub>6</sub>] and [Pd<sub>10</sub>(CO)<sub>12</sub>(PPh<sub>3</sub>)<sub>6</sub>] were reduced using NaBH<sub>4</sub>. For example, when [Pd<sub>12</sub>(CO)<sub>17</sub>(PBU<sup>n</sup><sub>3</sub>)<sub>5</sub>] was reacted with NaBH<sub>4</sub>, the mono-anionic compound (NEt<sub>4</sub>)[Pd<sub>12</sub>H<sub>x</sub>(CO)<sub>12</sub>(PBU<sup>n</sup><sub>3</sub>)<sub>6</sub>] (x = 0 or 1) was obtained. The success of the synthesis was established by IR and NMR, and confirmed by X-ray crystallography. The crystal structure comprised the reduced cluster and its counter-ion in a 1:1 ratio. Finally, when reacting different Pd compounds with [Au(PPh<sub>3</sub>)Cl], Pd clusters or positively charged Au complexes were obtained in all cases except one where a mixed-metal cluster was isolated.

m41.p38

## How complicated can it get: Diprotonated meso-tetra (5'-methylthien-2'-yl) porphyrin as its bistriflate salt

Matthias Zeller<sup>a</sup>, Allen D. Hunter<sup>a</sup>, Christian Brückner<sup>b</sup>, Paul C.D. Foss<sup>b</sup>, James O. Sullivan<sup>c</sup>, Ryan Peltó<sup>c</sup>, Robert R. Birge<sup>c</sup>, Guy Crundwell<sup>c</sup>

<sup>a</sup> Department of Chemistry, Youngstown State University, One University Plaza, Youngstown OH 44555-3663, U.S.A. <sup>b</sup> Department of Chemistry, University of Connecticut, Storrs, CT 06269-3060, U.S.A. <sup>c</sup> Department of Chemistry, Central Connecticut State University, New Britain, CT 06050-2490, U.S.A.

**Keywords:** pseudo-merohedral twinning, disorder, pseudosymmetry

The diprotonated triflate salt of meso-tetra (5'-methylthien-2'-yl) porphyrin, C<sub>40</sub>H<sub>28</sub>N<sub>4</sub>S<sub>4</sub>•(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>, was synthesized as part of an investigation into the origin of the bathochromically shifted optical spectra of meso-tetrathienylporphyrins as compared to meso-tetraphenylporphyrin. It crystallizes in a metrically tetragonal setting and but initial attempts to solve the structure in this setting failed. Close inspection of the collected data suggested a combined racemically and pseudo-merohedrally twinned monoclinic setting in the space group C2. To better resemble the metrically tetragonal setting the alternative inner-centered setting in I2 with the tetragonal cell parameters was chosen for the refinement. In this setting, there are two cations and four F<sub>3</sub>C-COO<sup>-</sup> anions in the asymmetric unit. The cations are located on a two fold crystallographic axis and their porphyrin cores could be also described in the orthorhombic space group I2mm. For the whole unit cell this higher symmetry is broken by the arrangement of the thienyl substituents and the trifluoroacetate anions. The 3-methylthienyl substituents are flip disordered, and due to the steric demands of the methyl substituents the orientation of the thienyl groups on one independent porphyrin molecule is dependent on those of the other. All four trifluoroacetate anions are disordered around the two fold crystallographic axis of the unit cell, and two different types coordination modes of the anions are observed. Due to the pronounced disorder and the degree of twinning and pseudosymmetry observed a range of constraints was required in order to achieve a stable refinement. Despite this substantial application of restraints the overall quality of the structure with an R1 value for all data of 7.8 % and a goodness-of-fit of 1.162 allows a solid description of the molecular geometry of the protonated tetrathienylporphyrin.