Isolation and Characterisation by *X*-Ray Studies of Palladium μ_2-Nitrosyl Clusters in the Reduction of Nitric Acid by Carbon Monoxide mediated by Palladium Acetate

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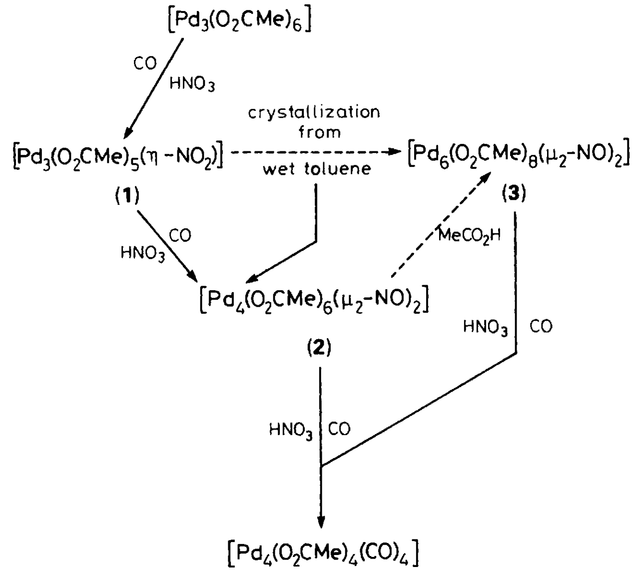
In the reduction by CO of HNO_3 to NO, mediated by $[Pd_3(O_2CMe)_6]$ in acetic acid, $[Pd_3(O_2CMe)_5(\eta^2\text{-}NO_2)]$ (**1**) is formed first, but is converted under the reaction conditions into the known cluster $[Pd_4(O_2CMe)_6(\mu_2\text{-}NO)_2]$ (**2**); slow crystallization of (**1**) from wet benzene and pentane gives (**2**) and $[Pd_6(O_2CMe)_8(\mu_2\text{-}NO)_2]$ (**3**), the structures of (**1**) and (**3**) having been determined by *X*-ray crystallography.

We recently reported the ready reduction by CO of HNO_3 to NO catalysed by $[Pd_3(O_2CMe)_6]$.[1] Reduction to metallic palladium does not occur; $[Pd_3(O_2CMe)_6]$ is transformed finally under the reaction conditions into the known cluster $[Pd_4(O_2CMe)_4(CO)_4]$ which is catalytically inactive.[2]

However by working under controlled conditions (10—15 °C and CO pressures between 1 and 2.5 atm) we have isolated palladium-containing intermediates corresponding to different steps of the reduction of HNO_3 (see Scheme 1). The first step produces a brown-red crystalline compound (**1**) together with minor products.† The *X*-ray crystal structure of (**1**) (Figure 1)‡ shows that the trimeric arrangement of the



Scheme 1

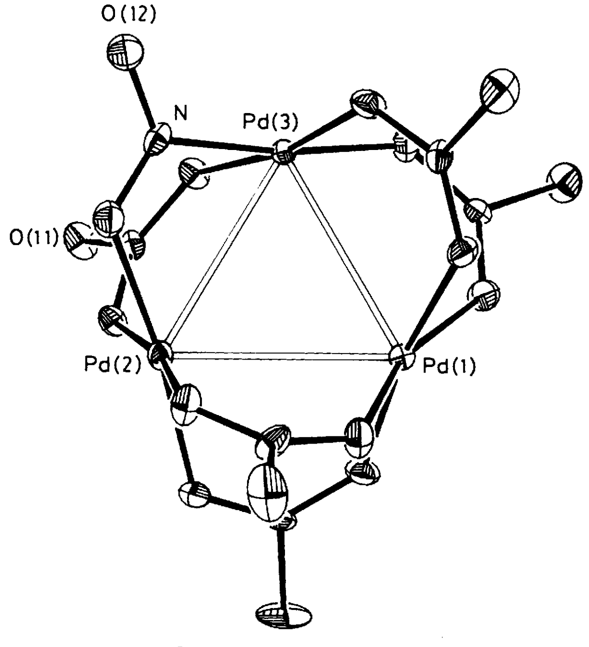


Figure 1. A view of the $[Pd_3(O_2CMe)_5(\eta_2\text{-}NO_2)]$ molecule. Relevant parameters are Pd(1)···Pd(2) 3.085(1), Pd(1)···Pd(3) 3.121(1), Pd(2)···Pd(3) 3.118(2); N–Pd(3) 1.97(1), N–O(11) 1.24(2), N–O(12) 1.23(1), O(11)–Pd(2) 2.00(1) Å; Pd(3)–N–O(11) 120.3(9), Pd(2)–O(11)–N 116.3(9), Pd(3)–N–O(12) 122(1), and O(11)–N–O(12) 118(1)°.

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† The mass spectrum (*m/z* 661; expected isotopic pattern for Pd_3) is in agreement with the formula $[Pd_3(O_2CMe)_5(NO_2)]$; the IR [Nujol; $\nu(NO_2)$ 1514 and 1195 cm^{-1}][3] and ^1H NMR spectra ($CDCl_3$; δ 2.07, 2.06, 2.03, 1.99, and 1.95, 5 × Me, 1:1:1:1:1 ratio) suggest the presence of five non-equivalent bridging acetato ligands and of one nitro ligand.

‡ *Crystal data for* (**1**): $C_{10}H_{15}NO_{12}Pd_3$, $M = 660.4$, orthorhombic crystals from tetrahydrofuran–pentane, space group $P2_1cn$ (non-standard setting of No. 33), $a = 10.125(2)$, $b = 11.662(2)$, $c = 15.923(4)$ Å, $Z = 4$, $D_c = 2.33$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.71073$ Å, $\mu(\text{Mo-}K_\alpha) = 28.6$ cm^{-1}. 2330 Intensity data were collected on an Enraf-Nonius CAD4 diffractometer within the limits $3 < \theta < 27°$. Refinement by full-matrix least-squares, on the basis of 1562 significant $[I > 3\sigma(I)]$ unique data led to final values of $R = 0.040$ and $R_w = 0.052$ for the correct enantiomorph. For (**3**): $C_{16}H_{24}N_2O_{18}Pd_6$, $M = 1170.8$, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.688(4)$, $b = 14.858(5)$, $c = 15.655(5)$ Å, $\alpha = 115.89(3)$, $\beta = 93.22(3)$, $\gamma = 101.49(3)°$, $Z = 2$, $D_c = 2.21$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 30.33$ cm^{-1}. 6161 Intensity data were collected on a Enraf-Nonius CAD4 diffractometer within the limits $3 < \theta < 25°$. Refinement by full-matrix least-squares on the basis of 2337 significant $[I > 5\sigma(I)]$ unique data led to R and R_w values of 0.061 and 0.080, respectively.

The crystal structure consists of a disordered assembly of $Pd_6(O_2CMe)_8(\mu_2\text{-}NO)_2$ molecules held together by van der Waals interactions. The structure is affected by a non-crystallographically imposed disorder consisting of the sharing of the same volume by two enantiomeric $[Pd_6(O_2CMe)_8(\mu_2\text{-}NO)_2]$ molecules, with an occupancy ratio 0.69:0.31 as determined by refining the multiplicity of the disordered heavy atoms.

The two enantiomers are related by the reflection of Pd(3), Pd(4), and their connected atoms with respect to the Pd(5), Pd(1), Pd(2), Pd(6) plane. This operation, which interchanges the unbridged and the μ_2-NO bridged Pd–Pd edges, leaves the atoms on the surface of the molecule, *i.e.* those involved in the packing interactions, common to the two molecules but leads to disorder of those in the core. Nitrosyl groups in particular are poorly defined and the presence of an intermolecular interaction of 2.28 Å between the oxygen atoms of two adjacent molecules is a measure of their bad definition.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

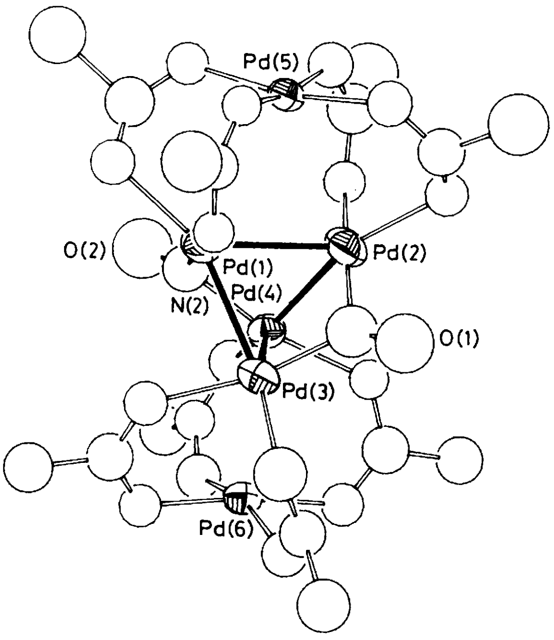

Figure 2. A view of the $[Pd_6(O_2CMe)_8(\mu_2\text{-}NO)_2]$ molecule. Relevant parameters are: Pd(1)–Pd(2) 2.680(2), Pd(1)–Pd(3) 2.568(2), Pd(1)···Pd(4) 2.952(2), Pd(1)···Pd(5) 3.044(2), Pd(2)···Pd(3) 2.966(2), Pd(2)–Pd(4) 2.562(2), Pd(2)···Pd(5) 3.063(2), Pd(3)–Pd(4) 2.704(2), Pd(3)···Pd(6) 3.090(2), Pd(4)···Pd(6) 3.036(2) Å; mean Pd–N–Pd 102(1)°.

parent compound[4] $[Pd_3(O_2CMe)_6]$ is maintained with substitution of one bridging acetato ligand with a NO_2 ligand which bridges two palladium atoms *via* an η^2-NO bond. Both oxygen and nitrogen are co-ordinated to palladium as in the oxime ligand of the related trimer $[Pd_3(O_2CMe)_3(ONCMe_2)_3]$.[5]

When the reaction is continued for more than 4—5 h or if it is carried out at 20 °C and under 2.5 atm of CO for a shorter time, a violet-red compound (**2**) separates in good yields.§ *X*-Ray crystallography confirmed the formula $[Pd_4(O_2CMe)_6(NO)_2]$; the same compound, with a different clathrate solvent, was obtained by a different route and crystallographically characterized by a Russian group.[8]

The rectangular shape of the Pd_4 core with two μ_2-NO ligands is structurally related to that of the platinum compound $[Pt_4(O_2CMe)_6(\mu_2\text{-}NO)_2]$, isolated as a by-product in the synthesis in acetic acid of $[Pt_4(O_2CMe)_8]$ from platinum salts in the presence of nitric acid;[9] as in our case, the nitric acid is the origin of the NO ligand.

Compound (**2**) is also formed in minor amounts together with metallic palladium and a few crystals of the hitherto unknown brown-red product (**3**) by very slow crystallization in air of (**1**) from wet benzene and pentane. Product (**3**) shows two methyl ^1H NMR signals in $CDCl_3$ at δ 2.14 and 1.99 (1 : 1 ratio), but is not sufficiently volatile for its mass spectrum to be determined; its IR spectrum (Nujol) has a broad and relatively weak band at 1653 cm^{-1} which suggests the presence of μ_2-NO ligands.[6] The *X*-ray crystal structure of (**3**),‡ although not highly accurate because of the poor quality of the crystals, is sufficiently accurate to confirm the structure $[Pd_6(O_2CMe)_8(\mu_2\text{-}NO)_2]$; an ORTEP view is in Figure 2. The structure, which is in agreement with the spectroscopic data, is based on a Pd_4 distorted tetrahedral core with D_{2d} idealized symmetry. Acetato bridges link two isolated Pd atoms on opposite edges of the tetrahedron, thus affording two lateral triangular wings (the overall idealized symmetry is C_2). The Pd–Pd distances are in four groups: (i) the four edges of the lateral wings, mean 3.058 Å; within the tetrahedral core, (ii) the two edges bridged by the μ_2-NO ligands, mean 2.959 Å; (iii) the two edges supporting the lateral wings, mean 2.692 Å; (iv) the two unbridged edges, mean 2.565 Å.

The Pd–Pd interactions of classes (iii) and (iv) are shorter than those found in other Pd_3, Pd_4, or Pd_{10} clusters.[10,11] Compound (**3**) corresponds to a new kind of cluster arrangement of six metal atoms; even the structure of the internal Pd_4 fragment is unusual with a distorted butterfly arrangement with two bonds lengthened instead of one. This kind of distortion is probably due to the presence of two μ_2-NO ligands, which are known to bridge the wing-tips of butterfly clusters such as in $H_3Os_4(CO)_{12}(\mu_2\text{-}NO)$.[12] Both the N–O distances and the metal–N–metal angles are similar in compounds (**2**) and (**3**) and are in good agreement with those found in $[Pt_4(O_2CMe)_6(\mu_2\text{-}NO)_2]$.[9]

All the palladium μ_2-nitrosyl clusters are inactive in the reduction of nitric acid by carbon monoxide; they react slowly with carbon monoxide to produce the well characterised and stable cluster $[Pd_4(O_2CMe)_4(CO)_4]$ with displacement of the NO ligands by CO.

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§ $[Pd_4(O_2CMe)_6(NO)_2]$ (*m/z* 810; isotopic distribution expected for a Pd_4 system, $M^+ - NO$). The ^1H NMR spectrum in $CDCl_3$ (δ 2.25, 1.63, and 1.33, 1 : 1 : 1 ratio) and the absence of IR absorptions in the regions 2000—1650 and 1300—900 cm^{-1}, together with the presence of a broad band at 1615 cm^{-1}, suggest the presence of three different acetato ligands and of μ_2-NO or bent NO ligands[6,7] and the absence of both NO_2^- or linear NO^+ type ligands.[3,7]

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