NO-disproportionation, promoted by Pd-cluster: formation and X-ray structure of $Pd_8(\mu\text{-}CO)_4(\mu\text{-}OOCCMe_3)_8[\mu\text{-}N(=O)O\text{–}]_4$†

Tatiana A. Stromnova,*[a] Oleg N. Shishilov,[a] Andrei V. Churakov,[a] Lyudmila G. Kuz'mina[a] and Judith A. K. Howard[b]

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Interaction of Pd-clusters $[Pd(CO)(OCOR)]_n$ with NO was investigated, these Pd-clusters were found to promote the NO disproportionation into N_2 and NO_2^- in mild conditions; an eight-nuclear palladium cluster $Pd_8(\mu\text{-}CO)_4(\mu\text{-}OOCCMe_3)_8(\mu\text{-}NO_2)_4$ with a new type of structure and an uncommon set of ligands was characterized by X-ray diffraction analysis.

Transformations of nitric monoxide that take place within the coordination sphere of transition metal complexes and that afford different species, such as NO_2, N_2, N_2O, are of great importance for biological and environmental processes. All NO disproportionation reactions resulting in NO_2 and N_2O or NO_2 and N_2 species, are thermodynamically permissible:

$$3NO \rightarrow N_2O + NO_2\text{: } \Delta G^0 = -104.2 \text{ kJ mol}^{-1}$$

$$4NO \rightarrow N_2 + NO_2\text{: } \Delta G^0 = -121.8 \text{ kJ mol}^{-1}$$

However, these reactions are very slow at room temperature. It is known that these reactions can be promoted by transition metal complexes.[1] Any mechanism for catalytic NO disproportionation involving several NO molecules is rather complicated and the reaction is assumed to proceed through the formation of dinitrosyl complexes containing an N–N bond.[2] Usually, the investigation of these reactions have been concentrated on nitrite complexes formed by NO oxidation, while the products of the NO reduction frequently escaped detection. The only recorded product of the NO reduction frequently was found to be N_2O rather than N_2.[3–5] Only a few studies are known where both products of the disproportionation, nitrite complexes and N_2O, were detected.

If M(TC-5,5)[3a,b] (M = Mn, Fe, TC-5,5 = bivalent tropocoronand ligand) interact with the stoichiometric amount of NO, the M(NO)(TC-5,5) complexes are generated. However, the interaction of M(TC-5,5) with an excess of NO proceeds very differently. In the case of Mn(TC-5,5), the resultant product is $Mn(NO_2)$(TC-5,5)[3a] and, in the case of Fe(TC-5,5), Fe(NO)(TC-5,5-NO_2) was formed.[3b] In both cases, N_2O was recorded as a product of the NO reduction. The interaction of $CuTp^{R2}$(THF) (Tp^{R2} = disubstituted tris(pyrazolyl)borate) with NO leads to the formation of $CuTp^{R2}(NO_2)$ complexes and N_2O evolution.[3c] It was also shown that the reaction between the Ru(Por)(CO) complexes and NO results in the formation of the Ru(Por)(NO)(ONO) complexes and N_2O.[4] In related investigations carried out for the f-elements Sm, Eu, Yb, again N_2O escaped detection.[5]

In summary, when transition metal complexes interact with NO, the formation of the nitric or nitrosyl–nitric complexes and N_2O are commonly observed. However, there are few examples of N_2 formation during the course of the NO disproportionation reaction which is shown to be promoted by transition metal complexes.

Herein we continue our investigation of the interaction of the palladium carbonyl carboxylate clusters *cyclo*-$[Pd_2(\mu\text{-}CO)_2(\mu\text{-}OOCR)_2]_n$ (**I**, R = CF_3, CCl_3, CH_2Cl, Me, Ph, Pr, *i*-Bu, *t*-Bu, *n*-Bu, *n*-C_5H_{11}; *n* = 2 or 3) with nitrogen monoxide. Clusters **I** have a cyclic metal core with near coplanar metal atoms, short Pd–Pd distances and alternating pairs of the bridging carbonyl and carboxylate ligands.[6]

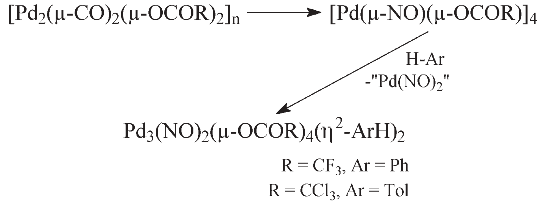
Three types of interaction between coordinated CO group in cluster **I** and NO are possible:

(i) the simple substitution of CO by NO,

(ii) the interaction of NO with CO to lead to formation of CO_2 and products of NO reduction,

(iii) NO disproportionation promoted by **I**.

The reactivity of cluster **I** was found to be affected by the nature of the carboxylate ligands. According to our data,[7] the reaction of **I** containing electron-withdrawing substituents R in the carboxylate group (R = CF_3, CCl_3, *n* = 2), with NO, leads to the complete replacement of CO by NO during 5–10 min to give the $[Pd_2(\mu\text{-}NO)_2(\mu\text{-}OOCR)_2]_n$ complex (**II**). Complex **II** is rather unstable in solution and transforms to $Pd_3(\mu\text{-}OOCR)_4(NO)_2(\eta^2\text{-}ArH)_2$, with a linear metal chain, bent terminal NO groups and an η^2-coordinated benzene or toluene molecule:



A dramatically different result is observed of the same reaction for **I**, if **I** contains electron donor substituents (R = *n*-Bu, *i*-Bu, *t*-Bu) on the carboxylate ligand. All the CO groups of the initial complex turned out to be too stable for replacement by NO under a NO atmosphere, even at prolonged exposure (*i.e.* from several hours up to several weeks).

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[a] *N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Science, Leninsky pr., 31, Moscow, 119991, Russian Federation. E-mail: strom@igic.ras.ru; Fax: 74959541279; Tel: 74959554805*
[b] *Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE*

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We studied the reaction of cluster **I** (R = *tert*-Bu, $n = 3$) with NO in further detail. CO_2, N_2 and traces of N_2O were recorded in the gas phase above the reaction mixture.‡ Free carbon monoxide was not detected. The presence of this particular set of gases may be explained by the two following general reactions:

$$CO + 2NO \rightarrow CO_2 + N_2O$$

$$2CO + 2NO \rightarrow N_2 + 2CO_2$$

It was found that the total amount of gases after 72 h are the following: 0.15–0.16 mol CO_2/mol Pd, 0.03–0.035 mol N_2O/mol Pd, 1.1–1.3 mol N_2/mol Pd. Thus, the contribution of the first reaction in total reaction of coordinated CO oxidation is about 20% and the contribution of the second reaction is about 80%, respectively. In that case the amount of N_2 formed in the second reaction must be about 0.06 mol/mol Pd while its actual amount ranges from 1.1 to 1.3 mol/mol Pd. Probably, the excess N_2 is formed as a result of NO disproportionation promoted by the palladium cluster:

$$4NO \xrightarrow[\text{Cluster}]{\text{Pd}} N_2 + 2NO_2$$

It could be expected that the products of NO oxidation should also occur in the system, however such products were found in the complex in the form of the $[NO_2^-]$ ligand only. This complex was separated from the reaction solution as a mixture of a deep red powder and dark deep red crystals. Both powder and crystals are insoluble in common organic solvents. The IR spectra of the powder and crystals have similar frequency sets and contain the following bands: ν_{CO} 1936 cm^{-1}, $\nu_{N=O}$ 1624 cm^{-1}, $\nu_{COO\ asym}$ 1544 cm^{-1}, $\nu_{COO\ sym}$ 1412 cm^{-1}, ν_{N-O} 1338 cm^{-1}. The structure of complex $Pd_8(NO_2)_4(CO)_4(OCOCMe_3)_8$ **III** was determined by X-ray diffraction analysis (see Fig. 1).

The molecular structure of **III** consists of two bent four-membered palladium chains, Pd(1)–Pd(4) and Pd(5)–Pd(8) (Fig. 1). Both metal chains are planar within 0.057 Å and almost perpendicular to each other (91.0°). In the chains, the central metal pairs Pd(2)–Pd(3) and Pd(6)–Pd(8) are linked by two approximately symmetrical μ_2-CO ligands forming nearly planar $Pd_2(CO)_2$ fragments, while the terminal palladium atoms are linked to central atoms by μ_2-pivalato groups. The coordination environment of each Pd atom is square-planar. The geometry of $Pd_2(\mu_2\text{-}CO)_2$ and $Pd_2(\mu_2\text{-}O_2CMe_3)_2$ frames are close to that found previously in the structures of parent carbonyl acetate Pd clusters.[6,7] The ends of the independent metal chains are connected by four nitrito groups forming the "Pd_8" cluster. All nitrito groups are coordinated by central nitrogen atoms to one metal chain and by terminal oxygen atoms to the other one. Meanwhile, all terminal Pd atom capture one N and one O atom from different bridging nitrito-*N*,*O* ligands. Pd–Pd distances range from 2.664 to 2.666 Å for the $Pd(\mu\text{-}CO)_2Pd$ unit and from 2.845 to 2.883 Å for the $Pd(\mu\text{-}OCOR)_2Pd$ unit. One might assume that the difference in Pd–Pd distances is the result of the fact that the central Pd atoms have formal oxidation state +1 and terminal Pd atoms may be regarded as +2. However, this explanation is contrary to the fact that the same difference is observed in carbonyl carboxylate clusters $Pd_n(\mu\text{-}CO)_n(\mu\text{-}OCOR)_n$, where all Pd atoms have formal oxidation state +1.[6c] The formal oxidation state of Pd atoms in **III** equals +1.5.

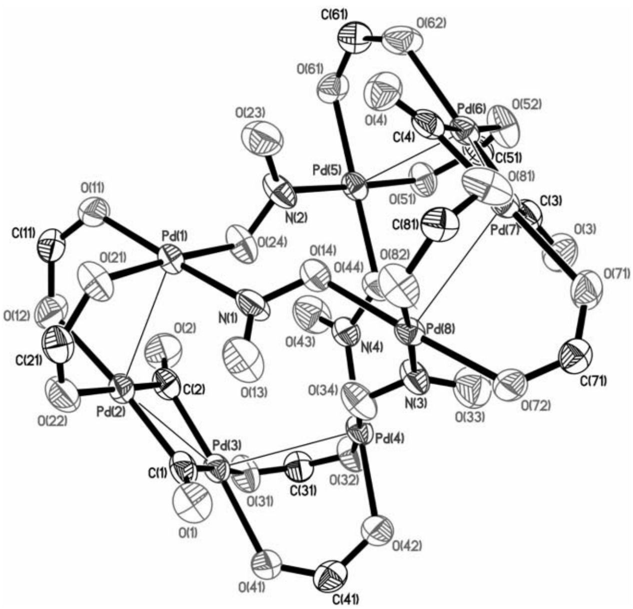


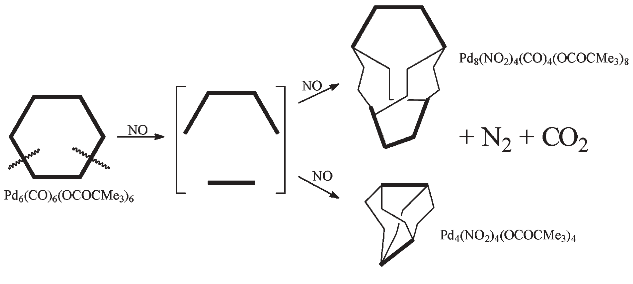
Fig. 1 The molecular structure of $Pd_8(\mu\text{-}CO)_4(\mu\text{-}OOCCMe_3)_8(\mu\text{-}NO_2)_4$. Hydrogen atoms and *t*-Bu groups are omitted for clarity. Selected bond lengths (Å): Pd(1)–N(1) 1.977(5), Pd(1)–O(24) 2.014(4), Pd(1)–Pd(2) 2.8471(5), Pd(2)–C(2) 1.958(6), Pd(2)–C(1) 1.974(6), Pd(2)–Pd(3) 2.6664(6), Pd(3)–C(2) 1.975(6), Pd(3)–C(1) 1.976(6), Pd(3)–Pd(4) 2.8730(6), Pd(4)–N(4) 1.986(5), Pd(4)–O(34) 2.022(4), Pd(5)–N(2) 1.984(4), Pd(5)–O(44) 2.009(4), Pd(5)–Pd(6) 2.8833(6), Pd(6)–C(4) 1.970(6), Pd(6)–C(3) 1.974(5), Pd(6)–Pd(7) 2.6642(6), Pd(7)–C(4) 1.969(5), Pd(7)–C(3) 1.982(6), Pd(7)–Pd(8) 2.8454(5), Pd(8)–N(3) 1.968(5), Pd(8)–O(14) 2.036(4).

To the best of our knowledge, **III** is the first example of Pd cluster containing both carbonyl and nitrito ligands.

One can assume that the formation of $Pd_8(NO_2)_4(CO)_4(OCOCMe_3)_8$ includes the intramolecular rupture of two $Pd(\mu\text{-}CO)_2Pd$ bonds of the initial hexanuclear cluster under the action of NO. Nitrogen monoxide and CO-ligand transformation to N_2 and CO_2, occurs on the terminal Pd atoms of the generated Pd_2 and Pd_4 fragments. Further dimerization of such fragments using NO_2 groups leads to the formation of the described Pd_8-cluster and hypothetical Pd_4-cluster according to Scheme 1.

We believe that the mixture of the deep red powder and dark-red crystals obtained in the reaction has the composition corresponding to an equimolar mixture of $Pd_4(NO_2)_4(OCOCMe_3)_4$ and $Pd_8(NO_2)_4(CO)_4(OCOCMe_3)_8$.

Thus, the reaction of NO in the presence of the palladium carbonyl pivalate cluster includes at least two independent reactions:



Scheme 1

(i) CO oxidation by nitrogen monoxide:

(ii) NO disproportionation promoted by palladium complex.

We believe that the reactions of this type are only feasible in a system containing polynuclear transition metal complexes. To the best of our knowledge, there are no examples of the formation of N_2 in any system where the NO disproportionation was promoted by mononuclear transition metal complexes.[8] We do not observe examples of the NO disproportionation promoted by polynuclear transition metal complexes and moreover, we could not find examples of NO disproportionation promoted by palladium and its complexes in the literature.

In summary, we describe the first example of NO disproportionation under mild conditions promoted by palladium clusters, and followed by N_2 formation. The reaction results in the formation of a Pd_8 cluster.

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Notes and references

‡ Gas chromatography was performed on a 3700 instrument for N_2O and CO_2 analysis equipped with Porapak Q packed column (l = 1 m) and LHM-80 instrument for N_2, CO and NO analysis equipped with molecular sieve packed column (l = 3 m). Both instruments were equipped with a thermal conductivity (TC) detector. The column flow rate of He carrier gas was 30 ml h^{-1} at 25 °C.

Synthesis of the mixture $Pd_8(NO_2)_4(CO)_4(OCOCMe_3)_8$ + $Pd_4(NO_2)_4(OCOCMe_3)_4$: 0.6 g $Pd_6(CO)_6(OCOCMe_3)_6$ was first dissolved in 100 ml benzene and filtered. The resulting solution was placed in a three-neck round-bottomed 250 ml flask and stirred by magnetic stirrer in NO atmosphere for 72 h. After this time NO was removed and the dark wine-red solution was filtered to remove small amounts of impurities. The filtrate was evaporated on an oil pump to 5–7 ml, and benzene or toluene and hexane were added leading to a wine-red powder. The crystals were obtained by storing the solution in a fridge at 4 °C. The mixture of powder and crystals was filtered off and dried under vacuum. The yield is 20–25% based on palladium. Elemental analysis: Found: C 25.24, H 2.76, N 3.81, Pd 42.58%. Calc. for an equimolar mixture $Pd_4(NO_2)_4(OCOCMe_3)_4$ + $Pd_8(NO_2)_4(CO)_4(OCOCMe_3)_8$ **III**: C 25.87, H 3.64, N 3.77, Pd 43.01%. IR-spectra of powder and crystals have similar frequency sets: 1936, 1624, 1544, 1412, 1338 cm^{-1}. Unfortunately, all attempts to record mass-spectra (MALDI TOF and ESI) of **III** and a mixture of $Pd_4(NO_2)_4(OCOCMe_3)_4$ + $Pd_8(NO_2)_4(CO)_4(OCOCMe_3)_8$ failed due to insolubility of both complexes in common organic solvents.

Single crystals of $Pd_8(NO_2)_4(CO)_4(OCOCMe_3)_8$ **III** were crystallized from toluene–benzene–hexane, mounted in inert oil and transferred immediately to the cold gas stream of a Bruker SMART diffractometer. *Crystal data*: $C_{63}H_{96}N_4O_{28}Pd_8$, M = 2208.64, monoclinic, space group $P2_1/n$, a = 20.2125(13), b = 19.3904(13), c = 23.8068(16) Å, β = 114.58(1)°, V = 8489.2(10) Å^3, T = 115 K, Z = 4, μ(Mo-Kα) = 1.727 mm^{-1}, 75538 reflections measured, 21499 unique (R_{int} = 0.047) which were used in further calculations. The structure was solved by direct methods[9] and refined[10] by full-matrix least squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms, except all methyl groups of the pivalate ligands and disordered solvate benzene molecules. Two of the eight pivalate ligands were found to be rotationally disordered with occupancy ratios of 0.71 : 0.29 and 0.53 : 0.47; six others showed high rotational thermal motion that prevented anisotropic refinement. The asymmetric unit contains two toluene, two benzene and one *n*-hexane molecule, of which two toluene and one benzene molecules were disordered over crystallographic inversion centres. All H atoms were placed in calculated positions and refined using a riding model. The final residuals were R_1 = 0.0513, wR_2 = 0.1270 for 14784 reflections with $I > 2\sigma(I)$ and 0.0814, 0.1394 for all data and 839 parameters. CCDC 653643. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b710230e

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