

Crystal structure of a palladium metallacyclic complex: A key-intermediate in the carbonylation of nitrobenzene to isocyanates and carbamates

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Abstract

The metallacyclic complexes (N-N)PdCON(Ph)OCO have been obtained under mild reaction conditions with different bidentate nitrogen-donor chelating ligands, starting both from nitrobenzene and nitrosobenzene; the crystal structure of PdCON(Ph)OCO is reported. © 1997 Elsevier Science S.A.

The catalytic reductive carbonylation of nitroaromatic compounds to isocyanates and carbamates is currently of great interest both in academic and industrial field [1]. Up to now the most active and selective catalytic systems are based on palladium(II) salts modified by bidentate nitrogen-donor chelating ligands as 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen) and their substituted derivatives [2–7].

In 1990 Leconte et al. [8] reported the isolation of a yellow solid starting from [Pd(MeCO₂)₂], phen in nitrobenzene/ethanol solution at 80°C and 30 bar of CO pressure. On the basis of spectroscopic data, they formulated it as a metallacyclic complex of structure I (Fig. 1). The metallacycle was proposed as 'a key-intermediate' in the reductive carbonylation reaction of nitrobenzene. Although in a footnote of a successive paper (1993) they stated that an X-Ray determination confirmed the assigned structure I [9], no crystal structure has been reported up to now.

In a recent review Ragaini and Cenini reported that all the structurally characterized metallacyclic complexes containing the –N(R)–(CO₂)– moiety have the carbon atom of the CO₂ fragment bound to the nitrogen and not to the metal center [1]. Therefore they proposed structure II 'as more plausible' (Fig. 1) and stated that

this structure is also consistent with the spectroscopic data reported by Leconte [8]; consequently the proposed catalytic cycle was also questioned.

We have recently found that the yellow solid can be obtained under mild reaction conditions (room temperature and 1 atm of CO), starting from [Pd(phen)(MeCO₂)₂] in nitrobenzene/alcohol mixture using standard Schlenk techniques. In fact, when [Pd(phen)(MeCO₂)₂] (1 mmol) is dissolved in a nitrobenzene (4 ml) — methanol (12 ml) mixture in presence of free phen (1 mmol) and placed under CO atmosphere at room temperature, the color of the solution turns from yellow to red–orange and after 2 days the yellow solid precipitates in low yield (5%). Spectroscopic data are in agreement with those reported by Leconte [8] and in particular ¹H-NMR spectrum points out the formation of one isomer only.

The yield in the complex markedly increases with the CO pressure (from 5% to 90% yield from 1 to 40 atm¹ after 48 h) and going from methanol (10% after 4 h) to ethanol (35%), *n*-butanol (45%) and *i*-propanol (65%).

¹ At high pressure the reaction is carried out in a Berghof stainless steel autoclave (100 ml), equipped with a Teflon liner and magnetic stirrer; under these reaction conditions the formation of aniline, *N,N'*-diphenylurea and *N*-phenylurethane in low yield is also observed.

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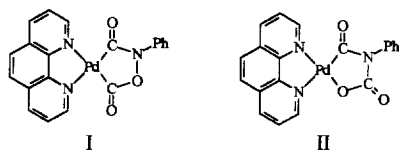


Fig. 1. Proposed structures for the metallacyclic complex [1,8].

Under these experimental conditions any decomposition to palladium metal does not occur. Interestingly, with methyl-substituted phenanthrolines (4,7-dimethyl-1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline) the metallacycle is obtained as a white solid at high CO pressure (40 atm) only. On the other hand, with bipy it is obtained both at atmospheric and high CO pressure, but in this last case decomposition to palladium metal is also observed. Particularly, at low CO pressure it precipitates as yellow solid under stirring and as orange crystals on standing.

Orange crystals, suitable for X-ray analysis, are also obtained when the yellow solid with phen is recrystallized from nitrobenzene. $^1\text{H-NMR}$ spectrum of orange crystals presents the same pattern of that of the yellow solid (both phen and bipy), except for the signals of free nitrobenzene.

The molecular structure ² has been resolved and it is given in Fig. 2. It confirms the structure I for the metallacycle, which therefore represents the first example of a fully characterized metallacyclic complex containing the $-\text{N(R)}-(\text{CO}_2)-$ moiety with the carbon atom of the CO_2 fragment bound to the metal.

The crystals consist of square planar palladium complexes I and uncoordinated nitrobenzene molecules. The overall molecule is essentially planar within $\pm 0.024(7)$ Å, if the phenyl ring bound to N(3) is excluded. The metal is slightly displaced (0.026 Å) from the mean N_2C_2 co-ordination plane. The Pd–N and Pd–C bond lengths are 2.128(4), 2.130(4) Å and 1.939(6), 1.928(5) Å, respectively. The strong *trans* influence of the C atoms *trans* to the N-chelating ligand is reflected in a significant increase of about 0.1 Å in the Pd–N dis-

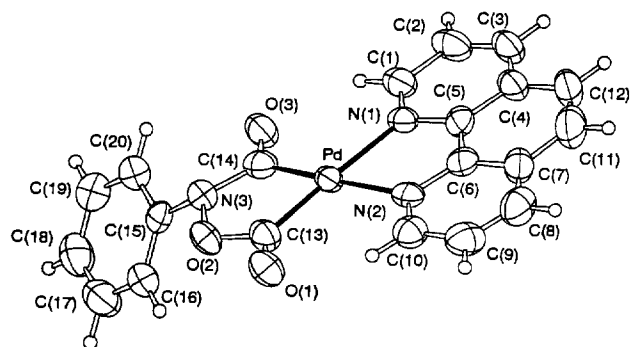


Fig. 2. ORTEP drawing (50% probability thermal ellipsoids) of the PdCON(Ph)OCO with labelling scheme. Selected bond lengths (Å) are as follows: Pd–N(1) 2.128(4), Pd–N(2) 2.130(4), Pd–C(13) 1.939(6), Pd–C(14) 1.928(5), O(1)–C(13) 1.203(7), O(2)–N(3) 1.425(6), O(2)–C(13) 1.403(7), O(3)–C(14) 1.223(7), N(1)–C(1) 1.321(7), N(1)–C(5) 1.369(7), N(2)–C(6) 1.366(7), N(2)–C(10) 1.316(7), N(3)–C(14) 1.410(7), N(3)–C(15) 1.416(7). Selected bond angles ($^\circ$): N(1)–Pd–N(2) 77.6(2), N(1)–Pd–C(13) 177.2(2), N(1)–Pd–C(14) 100.4(2), N(2)–Pd–C(13) 99.9(2), N(2)–Pd–C(14) 177.5(2), C(13)–Pd–C(14) 82.0(2), N(3)–O(2)–C(13) 112.8(4), Pd–N(1)–C(1) 128.1(4), Pd–N(1)–C(5) 113.7(3), C(1)–N(1)–C(5) 118.1(5), Pd–N(2)–C(6) 113.9(3), Pd–N(2)–C(10) 128.6(4), C(6)–N(2)–C(10) 117.6(5), O(2)–N(3)–C(14) 113.7(4), O(2)–N(3)–C(15) 112.1(4), C(14)–N(3)–C(15) 24.1(5), Pd–C(13)–O(1) 131.6(5), Pd–C(13)–O(2) 115.9(4), O(1), C(13)–O(2) 112.5(5), Pd–C(14)–O(3) 128.0(4), Pd–C(14)–N(3) 115.4(4), O(3)–C(14)–N(3) 116.6(5).

tances with respect to those found in $[\text{Pd(N-N)(MeCO}_2)_2]$, (N–N = phen and bipy), where they range from 2.002(3) to 2.036(5) Å [10]. On the other hand, the co-ordination distances are comparable with those detected in the complex bis(carbomethoxy)Pd(bipy) [11]. In the latter, the Pd–N and Pd–C distances are 2.118(6) and 1.989(9) Å, respectively.

The phenyl ring forms a dihedral angle of $44.4(2)^\circ$ with the chelating fragment $\text{NO}(\text{CO})_2$ with a O(2)–N(3)–C(15)–C(16) torsional angle of $22.9(7)^\circ$ (see Fig. 2).

The interesting feature of the crystal structure is the packing of the complex molecules stacking along the crystallographic *c* axis. The metals are arranged approximately in a straight line with Pd \cdots Pd' distances of 3.251(5) and 3.527(5) Å, being related alternatively by a center of inversion and a two-fold axis. The uncoordi-

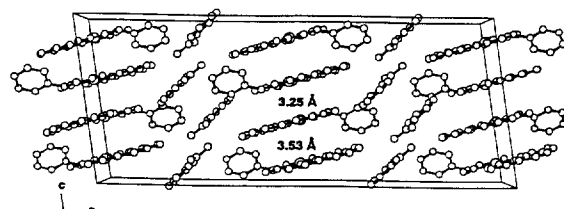


Fig. 3. A perspective view of the molecular packing along the crystallographic *c* axis.

² Crystal data for PdCON(Ph)OCO at 298 K: crystal sealed in a glass capillary with a drop of solvent, formula $\text{PdO}_5\text{N}_4\text{C}_{26}\text{H}_{18}$, $M = 572.86$, monoclinic, space group $C2/c$, (No. 15), $a = 31.920(8)$, $b = 10.799(2)$, $c = 13.433(3)$ Å, $\beta = 98.69(1)^\circ$, $U = 4577(2)$ Å³, $Z = 8$, $D_c = 1.66$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 8.44$ cm⁻¹, $F(000) = 2304$, 2θ max = 52° , total data collected, 4956; unique data, 4496, data with $I \geq 3\sigma(I)$, 2213; number of variables 325. An empirical absorption correction based on ψ scans was applied to the data. Structure solved with conventional Fourier methods, final $R(\text{on } F) = 0.029$, $R'(\text{on } F) = 0.030$. Programs from the Enraf-Nonius SDP-Plus package were run on a micro Vax 2000 computer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC).

nated nitrobenzene molecules lie in between the pile of complexes (Fig. 3).

According to structure **I** the metallacycle is also obtained starting from nitrosobenzene under high CO pressure, suggesting the formation of two four-membered metallacyclic intermediates, $(\text{PdN}(\text{Ph})\text{OCO}$ **1** and $\text{PdON}(\text{Ph})\text{CO}$ **2**.

The complex **2** has been already reported as an intermediate of the catalytic cycle [8].

The structure **I**, proposed by Leconte for the metallacyclic complex, has been confirmed by X-ray analysis; consequently the proposed catalytic cycle may remain a reasonable hypothesis of mechanism for the reductive carbonylation of nitrobenzene, although the formation of other intermediates can not be excluded.

Moreover, on the basis of our data, the transformation of nitrobenzene to isocyanate, although still being part of a cycle, easily occurs at room temperature. These results open the possibility to carry out the reductive carbonylation of nitroaromatic compounds under very mild reaction conditions and the ring opening becomes the main problem to solve.

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