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Inorganica Chimica Acta 350 (2003) 283–288

Inorganica Chimica Acta

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Palladium nitrosyl carboxylate complexes X-ray structures of $Pd_4(\mu\text{-}NO)_2(\mu\text{-}OCOCMe_3)_6$ and $Pd_3(NO)_2(\mu\text{-}OCOCF_3)_4 \cdot 2C_6H_5Me$

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Received 26 June 2002; accepted 24 October 2002

This paper is dedicated to Professor Pierre Braunstein in honor of his celebrated career

Abstract

Two types of palladium nitrosyl carboxylate complexes were synthesized and their structures were characterized by several methods including an X-ray diffraction analysis. The tetranuclear complexes $Pd_4(\mu\text{-}NO)_2(OCOR)_6$ (R = CMe_3, Me, Ph, $CHMe_2$, CH_2Cl, **IIa**–**e**, respectively) were synthesized by the reaction of Pd(NO)Cl with silver carboxylates Ag(OCOR). The structure of **IIa** was determined by a single crystal X-ray diffractometry. Crystals of **IIa** are monoclinic, space group $P2_1/n$, $a = 12.104(7)$, $b = 23.970(8)$, $c = 15.495(4)$ Å, $\beta = 90.30(4)^\circ$, $V = 4496(4)$ Å^3. The least-square structure refinement on F^2 was converged to $R = 0.0714$ for 6228 reflections $[I > 2\sigma(I)]$. In **IIa** the palladium atoms form near regular rectangle Pd_4, with the edges bridged by the ligands. Two bridging NO groups occupying the opposite sides of the rectangle are in the *cis*-positions with respect to the Pd_4 plane. These groups are symmetric, with the Pd–N–O angles ranging from 120.4(5) to 121.8(5)°. The coordination polyhedrons of the Pd atoms are close to square planar ones. The reaction of the $Pd_4(CO)_4(OCOCF_3)_4$ clusters with nitrogen monoxide leads to a substitution of the carbonyl groups and formation of the low stable complex $Pd_4(NO)_4(OCOCF_3)_4$ (**III**) that was characterized by the spectroscopic and analytical data. The transformation of **III** during slow recrystallization from toluene gives $Pd_3(NO)_2(OCOCF_3)_4 \cdot 2C_6H_5Me$ (**IV**) and palladium black. The structure of **IV** was determined by an X-ray diffraction analysis. Crystals of **IV** are monoclinic, space group $P2_1/n$, $a = 9.2340(2)$, $b = 9.2859(2)$, $c = 18.0460(4)$ Å, $\beta = 92.339(1)^\circ$, $V = 1546.08(6)$ Å^3. The least-square refinement on F^2 was converged to $R = 0.0205$ for 3209 reflections $[I > 2\sigma(I)]$. In the linear tri-nuclear molecule of **IV**, any adjacent metal atoms are linked with a couple of the CF_3CO_2 ligands and are separated by 3.0755(2) Å. Additionally, the terminal Pd atoms bear the NO and the η^2-toluene ligands. The configuration of the N atoms corresponds to the ideal sp^2-hybridization. The Pd–N–O angle is 117.2(2)°. The N atoms form short contacts with the aromatic rings. The distance between the center of the ring and the nitrogen atom is 2.70 Å. Complex **IV** is the first example of the Pd complex with the terminal nitrosyl ligand. The scheme of transformation of complex **III** to complex **IV** was proposed.

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Keywords: Palladium complexes; Nitrosyl; Carboxylate; Crystal structures

1. Introduction

The palladium complexes containing the coordinated nitrosyl groups are very rare. Such compounds were identified as intermediates in some reactions where nitrate ions, nitrite ions or nitrogen oxide participate as reactants or co-catalysts. For example, the complex $Pd_4(NO)_2(OAc)_6$ (**I**) was obtained as a by-product upon oxidation of ethylene by dioxygen in acetic acid to ethylene glycol monoacetate in the presence of the $Pd(OAc)_2/LiNO_3$ catalyst [1]. The formation of the palladium nitrosyl complex was detected mainly by the spectroscopic data in allylic acetoxylation of alkenes in

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doi:10.1016/S0020-1693(02)01575-X

the presence of $Pd(OAc)_2$–$Fe(NO_3)_3$ as a catalyst [2], or in the reduction of NO to N_2O on the $PdCl_2$–CuCl catalyst [3].

Thus, the palladium and platinum nitrosyl complexes are of high interest not only as traditional objects of coordination chemistry of noble metals but also as possible intermediates (or their models) of industrially important catalytic processes.

This paper describes new methods for the synthesis of palladium nitrosyl carboxylate complexes and study their structures by several methods including an X-ray diffraction analysis.

2. Experimental

All organic solvents and liquid organic reagents were purified and dried according to the standard procedures [4].

$PdCl_2$, $AgNO_3$, $NaNO_2$, and pivalic, benzoic, monochloroacetic, and trichloroacetic acids were commercially supplied by Reakhim (Russia), Aldrich, and Merck.

The elemental C, H, N analysis were conducted on an Analyzer CHNS-OEA 1108 (Carlo Erba Instruments, Italy).

The IR spectra were obtained with Spectrometer SPECORD M-80 in Nujol.

The X-ray structural data were collected on NONIUS CAD-4 and Bruker SMART CCD diffractometers.

2.1. Pd(NO)Cl

Pd(NO)Cl was prepared by the modified method [5].

In a two-neck flask, $PdCl_2$ (1.77 g, 10 mmol) and $NaNO_2$ (0.69 g, 10 mmol) were dissolved in 100 ml of H_2O containing 2 ml of concentrated H_2SO_4 The flask was evacuated and filled with propene; the later was bubbled until the color of the solution changed from bright-orange to dark-brown and a lustrous-black precipitate formed. The precipitate was filtrated off and washed by water, dried in vacuum, and kept under inert atmosphere. Yield of Pd(NO)Cl is equal 1.63 g (83% per Pd). IRS: ν_{NO} 1712, 1764 cm^{-1}. *Anal*. Calc. for NOClPd: N, 8.14. Found: N, 8.27%.

The product is insoluble in THF, benzene, toluene and CH_2Cl_2, soluble in HCl.

2.2. Preparation of silver carboxylates

2.2.1. AgOCOMe

To saturated solution of $AgNO_3$ (2.55 g, 15 mmol) in water acidified with several drops of HOAc was added a saturated water solution of NaOAc (1.47 g, 18 mmol). White residue that formed was filtered off, washed with small portions of water, methanol, and hexane and dried in vacuum. Yield is 90–92%.

2.2.2. $AgOCOCHMe_2$

A solution of NaOH (0.72 g, 18 mmol) in small excess of iso-butiric acid was added to a saturated aqueous solution of $AgNO_3$ (2.55 g, 15 mmol). White (or light gray) residue was filtered off, washed with water, MeOH, and hexane and dried in vacuum. Yield is 85–90%.

2.2.3. $AgOCOCM_3$, $AgOCOCH_2Cl$, AgOCOPh

NaOH (0.72 g, 18 mmol) was dissolved in minimum amount of water, the solution was acidified by several drops of acetic acid, and 20 mmol of the corresponding acid (pivalic, monochloroacetic, or benzoic) was added. The solution was added to a saturated aqueous solution of $AgNO_3$ (2.55 g, 15 mmol). The residue was filtered off, washed and dried in vacuum. Yields is 80–95%.

Note: all the operations should be conducted in the darkness to avoid the decomposition of silver carboxylates.

2.3. Synthesis of palladium nitrosyl carboxylates from Pd(NO)Cl

All the reactions with Pd(NO)Cl were carried out under inert atmosphere.

*2.3.1. Synthesis of $Pd_4(NO)_2(OCOCMe_3)_6$ (**IIa**)*

In two-neck flask, Pd(NO)Cl (0.17 g, 1 mmol), $AgOCOCMe_3$ (0.31 g, 1.5 mmol), and THF (10 ml) were stirred during ~ 1 h. The initial uncolored solution acquired dark-red color. The reaction mixture was filtered, and washed by THF. Than the filtrate was evaporated to dryness and recrystallized from mixture CH_2Cl_2–hexene.

Reddish-brown powder, soluble in THF, benzene, toluene, $CHCl_3$, CH_2Cl_2, and ethanol, insoluble in hexane. Yield: 0.25 g (92% on Pd). IRS: ν_{NO} 1568 cm^{-1}. *Anal*. Calc. for $Pd_2C_6H_9O_7N$: C, 32.98; H, 4.95; N, 2.57. Found: C, 33.35; H, 5.35; N, 2.67%.

*2.3.2. Synthesis of $Pd_4(NO)_2(OCOCH_3)_6$ (**IIb**)*

Synthesis of $Pd_4(NO)_2(OCOCH_3)_6$ (**IIb**) was provided analogously to the synthesis of $Pd_4(NO)_2(OCOCMe_3)_6$, using Pd(NO)Cl (0.35 g, 0.2 mmol), AgOCOMe (0.60 g, 3 mmol), and THF (20 ml). Reaction time was 1.5 h. Yield: 0.35 g (85% based on Pd). IRS: ν_{NO} 1616 cm^{-1}. *Anal*. Calc. for $Pd_2C_6H_9O_7N$: C, 17.15; H, 2.14; N, 3.34. Found: C, 17.63; H, 2.50; N, 3.74%.

*2.3.3. Synthesis of $Pd_4(NO)_2(OCOPh)_6$ (**IIc**)*

Synthesis of $Pd_4(NO)_2(OCOPh)_6$ (**IIc**) was provided analogously to the synthesis of $Pd_4(NO)_2(OCOMe_3)_6$, using Pd(NO)Cl (0.17 g, 0.1 mmol), AgOCOPh (0.34 g, 1.5 mmol), and THF (10 ml). Reaction time was1 h.

After evaporation a solution by half, several drops of hexane was added to avoid the formation of oil and the evaporation was continued to dryness. Yield: 0.19 g (86% based on Pd). IRS: ν_{NO} 1544 cm^{-1}. *Anal*. Calc. for $Pd_2C_{21}H_{15}O_7N$: C, 41.39; H, 2.47; N, 2.31. Found: C, 40.97; H, 2.96; N, 2.45%.

Analogously the complexes $Pd_4(NO)_2(OCOCHMe_2)_6$ (**IId**) and $Pd_4(NO)_2(OCOCH_2Cl)_6$ (**IIe**) were prepared with good yields:

IId: *Anal*. Calc. for $C_{12}H_{21}NO_7Pd_2$: C, 28.38; H, 4.17; N, 2.87. Found: C, 27.95; H, 3.89; N, 3.14%. IRS: ν_{NO} 1572 cm^{-1}.
IIe: *Anal*. Calc. for $C_6H_6NO_7Cl_3Pd_2$: C, 13.76; H, 1.15; N 2.67. Found: C, 14.28; H, 1.11; N, 2.82%. IRS: ν_{NO} 1588 cm^{-1}.

2.4. Synthesis of $Pd_4(NO)_4(OCOCF_3)_4$ (III)

Complex $Pd_4(CO)_4(OCOCF_3)_4$ (0.8 g, 0.81 mmol) prepared according to [6] was dissolved in 50 ml of toluene and solution was stirred under NO during 1.5 h at room temperature (r.t.). The color of the solution was changed from light-yellow to dark-red. The solution was evaporated, and reddish-brown residue was recrystallized from a mixture CH_2Cl_2–hexane. Yield: 0.75 g (93% on Pd). IRS: ν_{NO} 1516 cm^{-1}. *Anal*. Calc. for $C_2NO_3F_3Pd$: C, 19.82; H, 0.00; N, 5.61. Found: C, 10.31; H, 0.00; N, 5.59%.

2.5. Synthesis of $Pd_3(NO)_2(OCOCF_3)_4 \cdot 2TolH$ (IV)

During slow recrystallization of $Pd_4(NO)_4(OCOF_3)_4$ from toluene solution the lustrous black crystals were formed. The composition and structure of this substance were determined from the X-ray structure data.

2.6. X-ray diffraction study

The crystal data, data collection, and structure solution and refinement parameters for compounds **IIa** and **IV** are presented in Table 1. In the structure of **IIa**, all the methyl carbon atoms were refined isotropically. The t-Butyl group attached to C(26) was found to be disordered over two positions with approximately equal occupancies. All hydrogen atoms were placed in the calculated positions and refined using a riding model. As for the structure of **IV**, all non-hydrogen atoms were refined with the anisotropic thermal parameters. All hydrogen atoms were found from the difference Fourier synthesis and refined isotropically.

Table 1
Crystal data, data collection, structure solution and refinement parameters for **IIa** and **IV**

Empirical formula	$C_{30}H_{54}N_2O_{14}Pd_4$ **IIa**	$C_{22}H_{16}F_{12}N_2O_{10}Pd_3$ **IV**
Formula weight	1092.35	1015.57
Color, habit	Brown block	Dark brown block
Crystal size (mm)	0.20 × 0.10 × 0.10	0.20 × 0.20 × 0.10
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	12.104(7)	9.2340(2)
b (Å)	23.970(8)	9.2859(2)
c (Å)	15.495(4)	18.0460(4)
β (°)	90.30(4)	92.339(1)
V ($Å^3$)	4496(3)	1546.08(6)
Z	4	2
D_{calc} ($g\ cm^{-3}$)	1.614	2.182
Absorption coefficient (mm^{-1})	1.629	1.853
$F(000)$	2176	976
Diffractometer	Enraf-Nonius CAD4	Bruker SMART CCD
Temperature (K)	293(2)	120.0(2)
Radiation (λ/Å)	Graphite-monochromated Mo Kα (0.71073)	
θ Range (°)	2.13–29.96	2.26–27.50
Index ranges	$-11 \le h \le 0$, $-33 \le k \le 32$, $-21 \le l \le 21$	$-11 \le h \le 11$, $-10 \le k \le 12$, $-23 \le l \le 22$
Reflections collected	8757	8872
Independent reflections	8054 [$R_{int} = 0.0629$]	3518 [$R_{int} = 0.0154$]
Absorbtion correction	none	empirical [7]
Min./max. transmission		0.7082 and 0.8364
Solution method	Direct methods (SHELX-86) [8]	
Refinement method	full-matrix least-squares on F^2 (SHELXL-93) [9]	
Data/restraints/parameters	8054/0/389	3518/0/255
Reflections with $I > 2\sigma(I)$	6228	3209
Goodness-of-fit on F^2	1.067	1.068
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0507$, $wR_2 = 0.1478$	$R_1 = 0.0205$, $wR_2 = 0.0535$
R indices (all data)	$R_1 = 0.0714$, $wR_2 = 0.1570$	$R_1 = 0.0233$, $wR_2 = 0.0547$
Extinction coefficient	0.0009(2)	
Largest difference peak and hole (e $Å^{-3}$)	1.005 and −0.719	0.688 and −0.620

3. Results and discussion

The first palladium nitrosyl complex Pd(NO)Cl (**V**) has been synthesized more than 40 years ago by the reaction of $PdCl_2$ with $NaNO_2$ in water in the presence of alkene [5]. The dissolution of Pd(NO)Cl in concentrated HCl followed by the addition of phosphonium or arsonium salts produces the anionic complex $[Pd_2Cl_4(NO)_2]^{2-}$ [10]. Later, the palladium nitrosyl complexes $(C_5R'_2R''_3)Pd(NO)$ (**VI**), where $R' = R'' = H$,

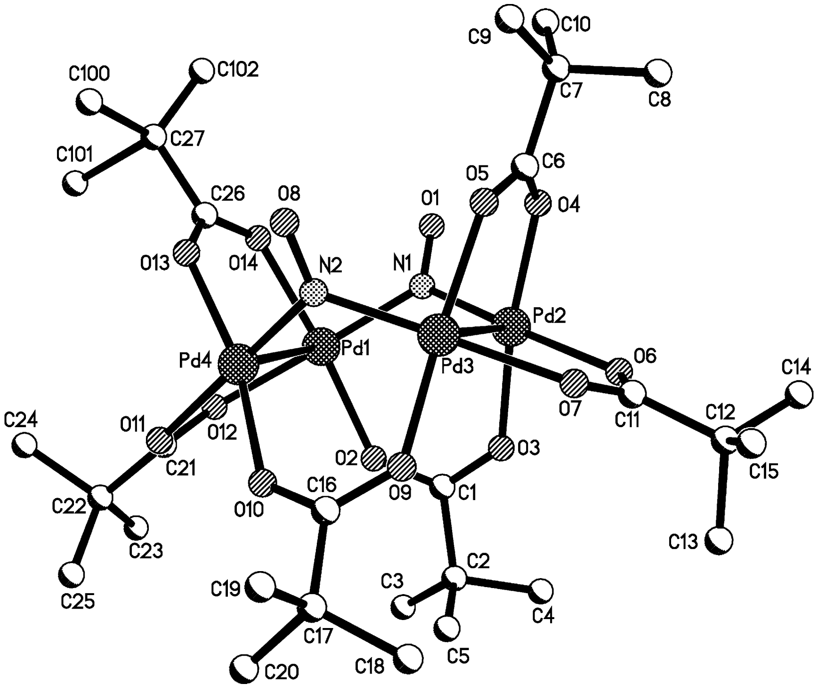


Fig. 1. Molecular structure of complex **IIa**. Hydrogen atoms are omitted for clarity.

Ph or *p*-tolyl; or R′ = Et, R″ = Ph, have been prepared by the treatment of initial salts with NO gaseous [11].

It is essential that none of the complexes under consideration have been characterized by an X-ray diffraction analysis and their structures are not clear up-to-date. For example, complexes **VI** were proposed [12,13] to have a geometry of ‘one-legged piano-stool’ by analogy to the corresponding nickel compounds. However, the frequency ν_{NO} (around 1750 cm^{-1}) in the IR spectra of complexes **VI** also allows one to assume the bridging coordination of the nitrosyl groups and a dimer structure of the complexes.

Two palladium nitrosyl complexes have been characterized by an X-ray diffractometry. The first compound, $Pd_4(\mu\text{-}NO)_2(\mu\text{-}OCOCH_3)_6$ (**I**), was isolated as an intermediate (or by-product) with a very low yield in the process of ethylene oxidation [see above, [1]]. The second complex, $Pd_6(\mu\text{-}NO)_2(\mu\text{-}OAc)_8$ (**VII**), was isolated in a low yield from the reaction of palladium(II) acetate with carbon monoxide in the nitric acid medium [14]. Hence, no efficient methods for the preparation of palladium nitrosyl complexes were available up-to-date.

In our search for feasible methods for the preparation of palladium nitrosyl complexes, we studied the reactions of Pd(NO)Cl with potential acceptors of Cl anions.

Our experiments showed that the reaction of Pd(NO)Cl with silver carboxylates AgOCOR (R = CMe_3, Me, Ph, $CHMe_2$, CH_2Cl, CCl_3, CF_3) (THF, room temperature, molar ratio Pd–Ag = 1/1.5) occurs almost completely in 0.5–3.0 h (depending on the nature of silver carboxylate) and leads to the formation of dirty-white precipitate of AgCl and a dark-brown solution. The analytical and spectroscopic data for the products isolated from THF as a brown or reddish-brown powder or oil allow us to formulate these complexes as $Pd_2(NO)(OCOR)_3$ (**II**). The IR spectra of complexes **II** contain a middle-intensity band in the region of 1560–1620 cm^{-1}, which can be attributed to the bridging nitrosyl group. The stability of complexes **II** decreases in the series $CMe_3 \sim CHMe_2 > Ph \sim Me > CH_2Cl \gg CCl_3 > CF_3$. Therefore, we have managed to characterize the complexes **II** except those containing CCl_3COO and CF_3COO groups.

We solved the structures of complexes **II** (**IIa**, R = CMe_3; **IIb**, R = Me) using an X-ray diffraction analysis.

The structure of complex **IIa** is shown in Fig. 1. The selected geometrical parameters for **IIa** are given in Table 2. In the molecule of **IIa**, the palladium atoms

Table 2
Selected bond lengths (Å) and angles (°) for complex **IIa**

Pd(1)–Pd(4)	2.994(1)	Pd(2)–Pd(3)	3.000(1)
Pd(1)–N(1)	1.903(6)	Pd(3)–N(2)	1.916(5)
Pd(1)–O(2)	2.009(6)	Pd(3)–O(9)	2.008(5)
Pd(1)–O(14)	2.019(6)	Pd(3)–O(5)	2.021(5)
Pd(1)–O(12)	2.043(6)	Pd(3)–O(7)	2.063(5)
Pd(2)–N(1)	1.909(6)	Pd(4)–N(2)	1.917(6)
Pd(2)–O(3)	2.011(6)	Pd(4)–O(10)	1.999(6)
Pd(2)–O(4)	2.016(5)	Pd(4)–O(13)	2.021(5)
Pd(2)–O(6)	2.029(5)	Pd(4)–O(11)	2.056(5)
N(1)–O(1)	1.184(8)	N(2)–O(8)	1.188(7)
O(1)–N(1)–Pd(1)	120.4(5)	O(8)–N(2)–Pd(3)	121.8(5)
O(1)–N(1)–Pd(2)	120.7(5)	O(8)–N(2)–Pd(4)	121.0(5)
Pd(1)–N(1)–Pd(2)	118.9(3)	Pd(3)–N(2)–Pd(4)	117.2(3)

form almost rectangular Pd_4 skeleton with the pair of bridging ligands on each side of the rectangle. Two opposite shortest sides of the rectangle are bridged by two pairs of the carboxylate ligands. Another two sides are linked by the carboxylate and the nitrosyl bridges each. The two NO groups have *cis*-arrangement with respect to the Pd_4 plane. The Pd(1)–Pd(4) and Pd(2)–Pd(3) bond lengths are 2.994(1) and 3.000(1) Å, while Pd(1)–Pd(2) and Pd(3)–Pd(4) distances are longer than 3.27 Å and they may be considered as non-bonded. The coordination polyhedrons of all Pd atoms are close to the square-planar ones. The NO bridges are approximately symmetric, with the Pd–N–O angles ranging within 120.4(5)–121.8(5)°.

We found that complexes **IIa** and **IIb** have the analogous structure, which turned out to be close to the structure of complex **I** [1]. In complex **I**, the palladium atoms form the tetrahedron strongly distorted towards the parallelogram; the deviations from the Pd_4 plane do not exceed 0.17 Å). The angles in the parallelogram are close to 90°. All other peculiarities of the structures under consideration are identical. It is of interest that the platinum analog $Pt_4(NO)_2(OCOCH_3)_6$ (**VIII**) is of almost the same structure, that is, four metal atoms form a rectangle with the bridging nitrosyl and acetate groups [15]. Complex **VIII** was isolated as a by-product in the synthesis of $Pt_4(OCOCH_3)_8$ from platinum(II) salts in the presence of nitric acid [16]. These facts suggest that as in the case of complex **I**, the NO ligands originates from nitric acid.

It is noteworthy that three complexes, **I**, **II**, and **VIII**, prepared by different methods, have almost the same structures. It is possible to suggest that, in each case, the source of the NO ligands ([Pd(NO)Cl] or the product of NO_3^- reduction) supplies the nitrosyl groups in the form of NO^-.

We also found another method for preparation of palladium nitrosyl complexes, which includes replacement of the coordinated CO ligands to the NO ones. The reaction of the $Pd_4(\mu\text{-}CO)_4(\mu\text{-}OCOR)_4$ tetranuclear clusters with nitrogen monoxide was found to afford the palladium nitrosyl carboxylate complexes. The structures of the prepared nitrosyl carboxylate complexes is similar to those of the initial Pd carbonyl carboxylate clusters that have a rectangular metal core and bridging carbonyl and carboxylate ligands.

Complex $Pd_4(NO)_4(OCOCF_3)_4$ (**III**) was synthesized by the reaction of $Pd_4(\mu\text{-}CO)_4(\mu\text{-}OCOCF_3)_4$ with NO in benzene solution. Comparative analysis of the IR spectra of the initial and the prepared complexes showed no changes in the bands related to the carboxylate groups. The absence of IR absorption in the region of 2000–1900 cm^{-1} (ν_{CO} bridging) and the appearance of a new band at 1516 cm^{-1} (ν_{NO} bridging) indicate full replacement of the μ-CO groups to the μ-NO groups. Therefore, the structure of complex **III** seems to be very close to that of the initial Pd complex. During the reaction, the replacement of the CO groups to the NO groups was accompanied by the oxidation of Pd(+1) to Pd(+2) and the reduction of the neutral NO molecules to anions NO^-. Complex **III** is unstable. Our attempts to grow the single crystals of **III** suitable for an X-ray Structural Analysis from toluene solution resulted in complex $Pd_3(NO)_2(OCOCF_3)_4 \cdot 2C_6H_5CH_3$ (**IV**) together with palladium black. The structure of complex **IV** was characterized by the X-ray diffraction data (see Fig. 2). Selected geometrical parameters for complex **IV** is given in Table 3.

The linear tri-nuclear molecule of **IV** lies on the center of symmetry. The Pd(1) and Pd(2) atoms are linked by the two CF_3CO_2 bridging ligands and they are separated by 3.0755(2) Å. Additionally, Pd(1) and Pd(1A) atoms bear the NO and the η^2-toluene substituents. The configuration of the N(1) atom corresponds to the almost ideal sp^2-hybridization; the Pd(1)–N(1)–O(5) angle is 117.2(2)°. To the best of our knowledge, **IV** is the first example of the Pd complex with the terminal nitrosyl ligand. The N(1) atom forms a short contact with the aromatic ring. The distance between the center of the ring and the nitrogen atom is 2.70 Å.

One can assume that the unusual transformation of tetranuclear complex **III** containing bridging NO groups

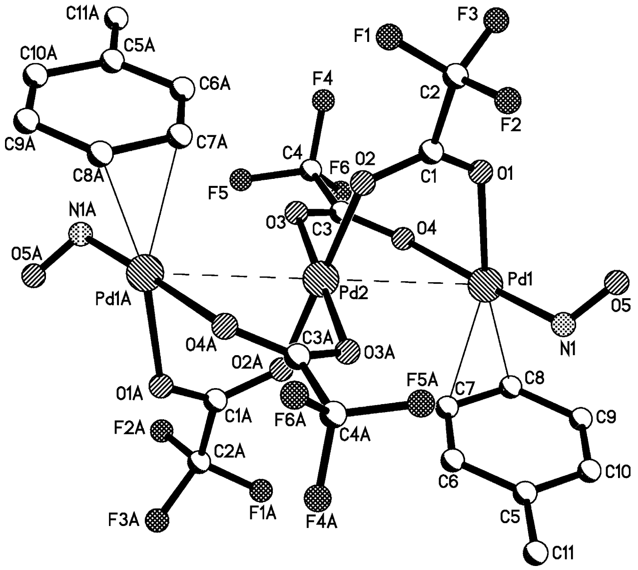


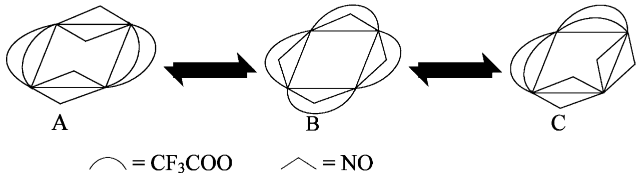
Fig. 2. Molecular structure of complex **IV**. Hydrogen atoms are omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) for complex **IV**

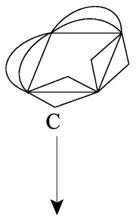
Pd(1)–N(1)	1.896(2)	Pd(1)–Pd(2)	3.0755(2)
Pd(1)–O(1)	2.229(2)	Pd(2)–O(3)	2.005(1)
Pd(1)–O(4)	2.237(2)	Pd(2)–O(2)	2.009(1)
Pd(1)–C(7)	2.405(2)	N(1)–O(5)	1.150(3)
Pd(1)–C(8)	2.428(2)	O(5)–N(1)–Pd(1)	117.2(2)

into trinuclear complex **IV** with terminal nitrosyl ligands includes an intramolecular migration of the bridging nitrosyl and trifluoroacetate groups through the metal core. Such a ligand migration is the well-known process in cluster chemistry [17,18].

It seems that complex **III** can exist in solution as a mixture of isomers with different arrangement of the ligands:



It seems that isomer C which contains two pairs of the identical ligands bind to the same metal atom is less stable compared with isomers A and B. The decomposition of isomer C produces the unstable $[Pd(NO)_2]$ species and trinuclear complex **IV**:



$[Pd\,(NO)_2]$ + ON-Pd $(\mu\text{-}OCOCF_3)_2$ Pd $(\mu\text{-}OCOCF_3)_2$ Pd-NO

The unstable $[Pd(NO)_2]$ species were detected finally as Pd black.

4. Supplementary material

The crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC Nos. 187780 and 187781. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Support from the Russian Foundation for Basic Research for LGK (grant number 01-03-32474) is gratefully acknowledged. A.V.C. thanks the Royal Society of Chemistry for the RSC Journal Grant for International Authors.

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