The substitution of arene by alkenes in linear trinuclear palladium complex Pd$_3$(NO)$_2$(μ-CF$_3$CO$_2$)$_4$(η^2-C$_6$H$_5$CH$_3$)$_2$. X-ray structure of Pd$_3$(NO)$_2$(μ-CF$_3$CO$_2$)$_4$(η^2-CH$_2$CHPh)$_2$ and Pd$_4$(μ-NO)$_2$(μ-CF$_3$CO$_2$)$_4$(η^2-CH$_2$CHPh)$_4$

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ABSTRACT

An interaction of Pd$_3$(NO)$_2$(μ-CF$_3$CO$_2$)$_4$(η^2-C$_6$H$_5$Me)$_2$ (**I**) with alkenes has been studied. A replacement of η^2-coordinated arene by various olefins has been found to result in complexes of different nuclearity, Pd$_3$(NO)$_2$(μ-CF$_3$CO$_2$)$_4$(η^2-L)$_2$ (L = Me$_3$CCH=CH$_2$ (**III**), CH$_2$CHPh (**IV**)), Pd$_4$(μ-NO)$_2$(μ-CF$_3$CO$_2$)$_4$(η^2-CH$_2$CHPh)$_4$ (**V**). Complexes **IV** and **V** have been characterized by an X-ray diffraction analysis. Molecule **IV** is constituted of a linear trinuclear metal core bearing η^2-coordinated molecules of styrene, terminal nitrosyl and bridging carboxylate groups, whereas, complex **V** has a tetrahedral core, with η^2-coordinated styrene molecules and half-bridging nitrosyl and carboxylate groups. Complex **V** represents a new type of nitrosyl carboxylate tetrahedral palladium cluster.

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1. Introduction

Complexes of transition metals containing η^6-coordinated benzene molecule or its derivatives are widely known, whereas, the examples of complexes with η^2- or η^3-coordinated molecule of arenes are few in number. Only several palladium complexes of this kind that may be divided into two groups are described.

The first group consists of the complexes with Pd–Pd unit sandwiched between two arene molecules. These dimeric complexes have a total composition Pd$_2$(arene)$_2$X$_2$, with the anionic ligands occupying the axial positions. In the case when the Pd–Pd bond is parallel to the planes of arene rings, each of the Pd atoms is bounded to three carbon atoms of both arene rings (arene = benzene, X = Al$_2$Cl$_7$) [1,2]. In the case when the Pd–Pd bond is non-parallel to the planes of arene rings, each Pd atom is bounded to two or three carbon atoms of each arene ring (arene = benzene, X = GaCl$_4$, Ga$_2$Cl$_7$ or GaBr$_4$; arene = toluene, X = GaCl$_4$ or GaBr$_4$; arene = p-xylene, X = GaCl$_4$ or GaBr$_4$) [3,4].

The palladium complexes earlier synthesized by us, with η^2-coordinated arene molecule [5–7] belong to the second group. These substances are of the common composition Pd$_3$(NO)$_2$(μ-RCO$_2$)$_4$(η^2-arene)$_2$ (R = CF$_3$, arene = toluene (**I**), R = CCl$_3$, arene = benzene (**II**)). Both molecules have a trinuclear linear metal core, with the Pd–Pd–Pd angle equal to 180° in **I** and **II** (Fig. 1).

The arene molecules are linked to each terminal Pd atoms through a couple of carbon atoms. The plane of each arene molecule is perpendicular to the nearest Pd–(OC(R)O)$_2$–Pd plane. Two Pd–C bonds are nearly equal (average distance is 2.417 Å for **I** and 2.420 Å for **II**). The rest of the Pd–C distances with the arene molecules are much longer and vary within 3.096–3.691 Å for **I** and 3.175–3.732 Å for **II**. Therefore, the coordination of arene molecules
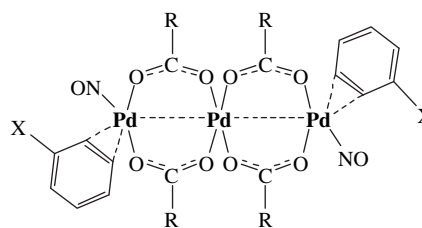
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Fig. 1. Structure of complexes **I** (R = CF$_3$, X = Me) and **II** (R = CCl$_3$, X = H).
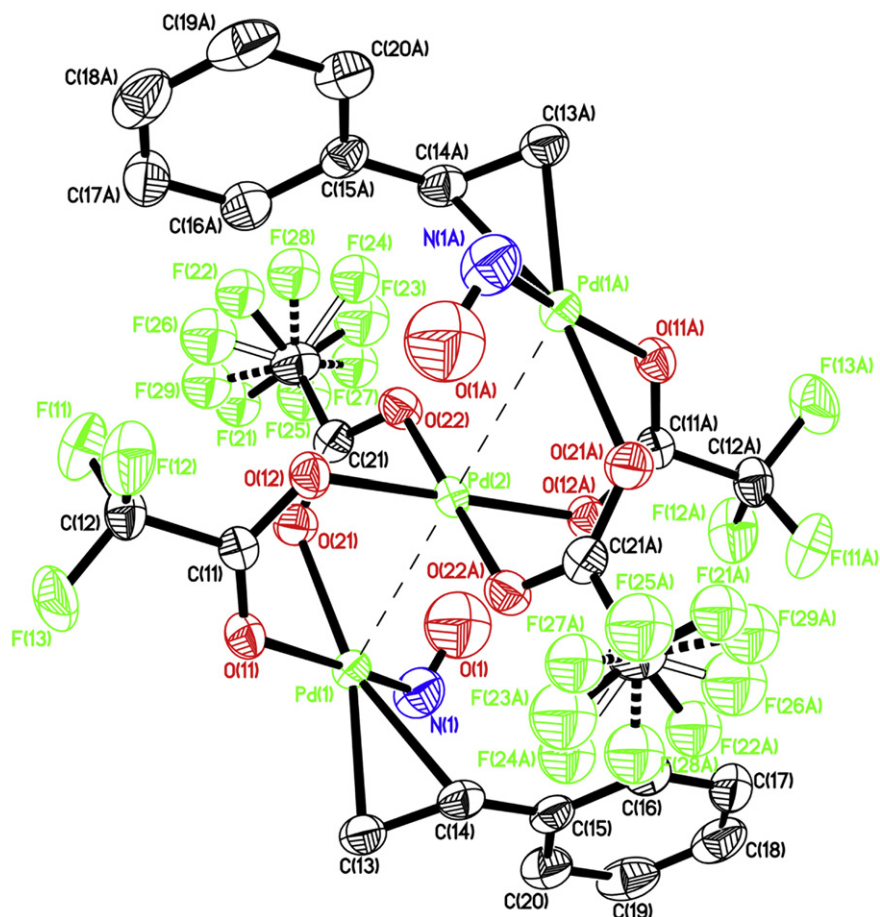
Fig. 2. The molecular structure of **IV**. Only one independent molecule is presented. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level. Dashed lines denote short intramolecular Pd...Pd contacts (3.0195(5) and 3.1686(5) Å).

is best described as η^2 type interaction. The phenyl rings are planar and shown no significant elongations of the coordinated C–C bond. It was found that in complex **I**, the coordinated toluene molecule is not replaced even on recrystallization from non-aromatic solvents. Unlike complex **I**, complex **II** decomposes under the same conditions. Thus the Pd(μ-RCO$_2$)$_2$Pd(μ-RCO$_2$)$_2$Pd fragment in complex **I** is stable enough to remain under conditions of the replacement of η^2-coordinated toluene molecule to another ligand.

This Pd$_3$-fragment is a well-known building block for a design of oligomeric palladium carboxylate complexes. In these complexes three palladium atoms form a Pd(μ-RCO$_2$)$_2$Pd(μ-RCO$_2$)$_2$Pd chain (R = Me, CCl$_3$, CF$_3$), in which the terminal palladium atoms are coordinated by ancillary ligands. In such linear molecules, a distortion of the square-planar coordination around the central metal atom is far less pronounced than in the complexes with the bent metal chain. Only a few compounds with the linear metal chain are known [8]. The Pd–Pd distances in these compounds range within 2.86–3.08 Å depending on the nature of the substituent R in the carboxylate group and the ancillary ligand. In this paper we report interactions of trinuclear palladium carboxylate complex **I** with alkenes.

2. Results and discussion

2.1. Reaction of I with ethylene and propylene

A treatment of **I** in CH$_2$Cl$_2$ solution with ethylene or propylene for some hours at ambient temperature leads to the complete decomposition of **I** to palladium black. The products of alkene oxidation (acetaldehyde in the case of ethylene and propionaldehyde in the

case of propylene) in solution were recorded by the GC–MS (together with vinyltrifluoroacetate and allyltrifluoroacetate). Our attempts to separate any Pd-containing compounds from the reaction mixtures failed.

2.2. Reaction of I with neohexene (3,3-dimethyl-1-butene)

An addition of solution of neohexene in CH$_2$Cl$_2$ to the solution of **I** in CH$_2$Cl$_2$ leads to the formation of a new complex of the composition Pd$_3$(NO)$_2$(CF$_3$CO$_2$)$_4$(Me$_3$CCH=CH$_2$)$_2$ (**III**). The IR spectrum of **III** displays the presence of terminal NO-groups (ν(NO) = 1680 cm^{-1}). This value is significantly lower than that in **I** (1730 cm^{-1}), apparently, due to the higher electron donor capability of neohexene as compared with that of toluene. The ^{1}H NMR spectrum of **III** contains singlet (δ = 1.13 ppm) from protons of ^{t}Bu-group, doublet (δ = 4.90 ppm, Me$_3$CCH=C$\underline{H_2}$), and multiplet (δ = 5.90 ppm, Me$_3$CC$\underline{H}$=CH$_2$).

2.3. Reaction of I with styrene

The first stage of the interaction of styrene with **I** is analogous to the reaction with neohexene. It results in fast (for 1 h) formation of a new complex Pd$_3$(NO)$_2$(CF$_3$CO$_2$)$_4$(CH$_2$CHPh)$_2$ (**IV**). As in the case of complex **I**, the IR spectrum of **IV** contains the band at 1720 cm^{-1} attributed to the terminal NO-groups.

The structure of **IV** was confirmed by the X-ray diffraction analysis (see Fig. 2). The asymmetric unit contains two crystallographically independent molecules with the close geometric parameters. The molecules are situated at the symmetry centres and
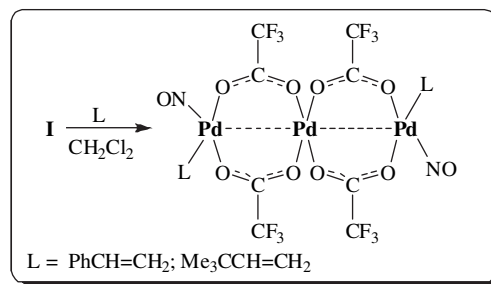
Table 1
Selected bond lengths (Å) and angles (°) for **IV**.[a]

Pd(1)–Pd(2)	3.0195(5)	Pd(3)–Pd(4)	3.1686(5)
Pd(2)–O(12)	1.995(3)	Pd(3)–O(31)	2.248(3)
Pd(2)–O(22)	2.012(3)	Pd(3)–O(41)	2.265(3)
Pd(1)–O(11)	2.285(3)	Pd(4)–O(32)	1.997(3)
Pd(1)–O(21)	2.210(3)	Pd(4)-O(42)	2.000(3)
Pd(1)–C(13)	2.232(5)	Pd(3)–C(33)	2.221(5)
Pd(1)–C(14)	2.381(5)	Pd(3)–C(34)	2.343(5)
Pd(1)–N(1)	1.938(5)	Pd(3)–N(2)	1.910(5)
C(13)–C(14)	1.362(7)	C(33)–C(34)	1.353(7)
C(14)–C(15)	1.478(7)	C(34)–C(35)	1.473(7)
N(1)–O(1)	1.147(7)	N(2)–O(3)[b]	1.068(9)
		N(2)–O(4)[b]	1.129(13)
Pd(1)–N(1)–O(1)	112.8(5)	Pd(3)–N(2)–O(3)[b]	132.9(6)
		Pd(3)–N(2)–O(4)[b]	118.8(8)
C(13)–C(14)–C(15)	126.6(5)	C(33)–C(34)–C(35)	126.0(5)

[a] Two independent molecules.
[b] Major and minor components of disorder.

have strictly linear trinuclear metal core. Both terminal Pd atoms are linked to the central one by a couple of bridging carboxylate ligands. Two Pd–(OC(R)O)$_2$–Pd fragments are virtually orthogonal. The Pd–Pd distances are equal to 3.0195(5) and 3.1686(5) Å. These values lie within the range 2.821–3.428 Å reported for Pd$_2$(μ-RCO$_2$)$_2$ units in the Cambridge Structural Database [9] (ver. 5.30, 156 refcodes, 243 fragments). In both molecules, the central Pd atom has a square-planar coordination environment, with the O–Pd–O

Scheme 1. Interaction **I** with alkenes.

angles varying within a narrow range 88.6(1)–91.4(1)°(Table 1). To the best of our knowledge, the linear arrangement of three Pd atoms is rather rare. This was previously observed in a few palladium carboxylates **I** [6], [Pd$_3$(μ-OCOCH$_3$)$_4$(η^3-C$_3$H(COOCMe$_3$)$_2$)] [10], and [Pd$_3$(μ-OCOCH$_3$)$_4$(C$_6$H$_3$Me$_2$)$_2$(S(CH$_2$CHMe$_2$)$_2$)$_2$] [11].

The Pd$_2$(μ-RCO$_2$) fragments are planar within 0.229(2) Å. The CF$_3$ groups in three of four carboxylate ligands display a high level of the rotational disorder. Each terminal Pd atom bears a terminal NO-group and π-coordinated styrene molecule. The Pd–N–O angles lie within 112.8(5)–132.9(6)° in two independent molecules, which corresponds to the sp^2 hybridization of nitrogen atom. Therefore, the NO ligands present the monoanionic form. The PhC$^\alpha$H=C$^\beta$H$_2$ double bonds of the nearly planar styrene molecules are η^2-bonded
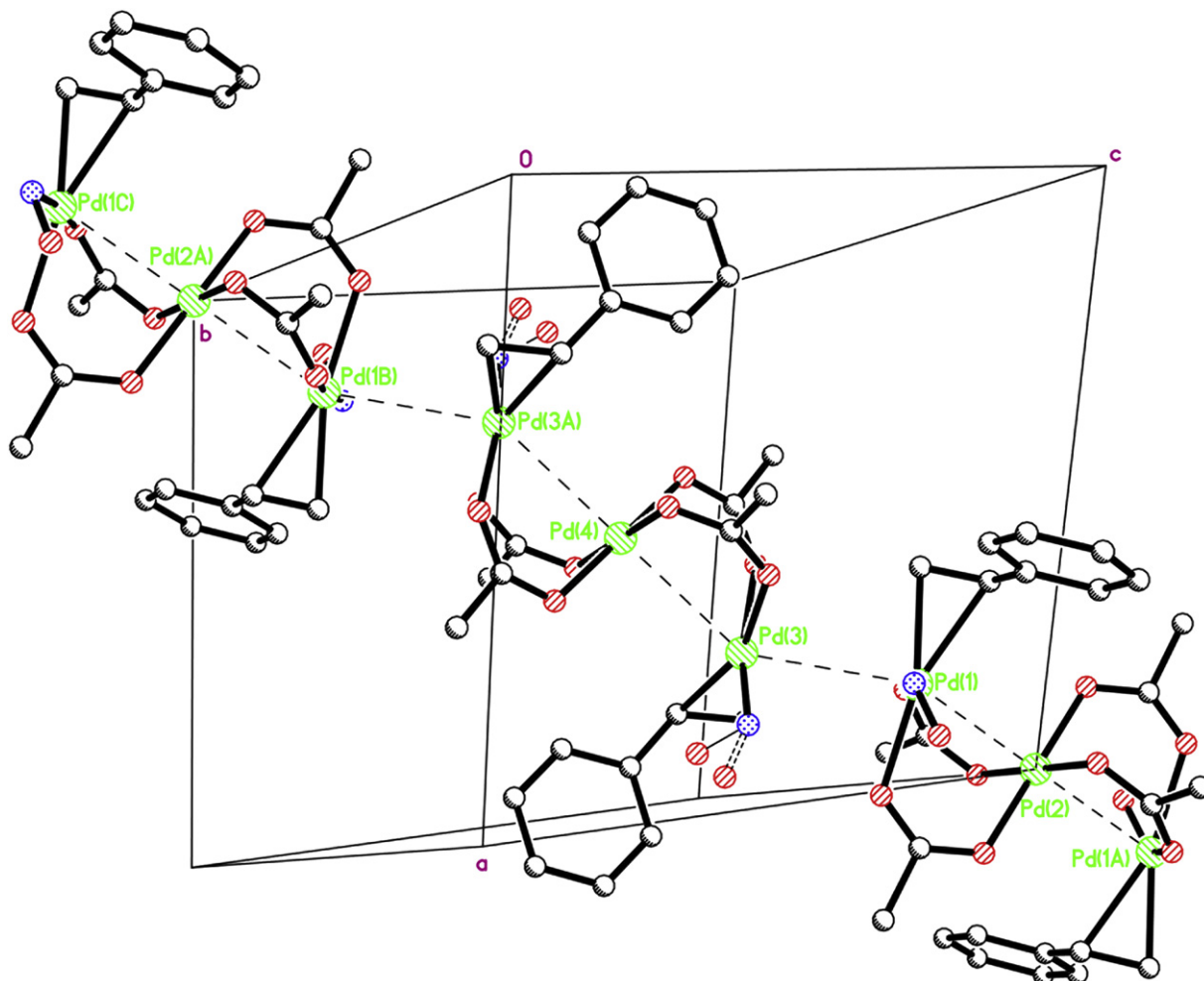

Fig. 3. The chains in the structure of **IV** formed by intermolecular Pd…Pd interactions. Fluorine and hydrogen atoms are omitted for clarity.
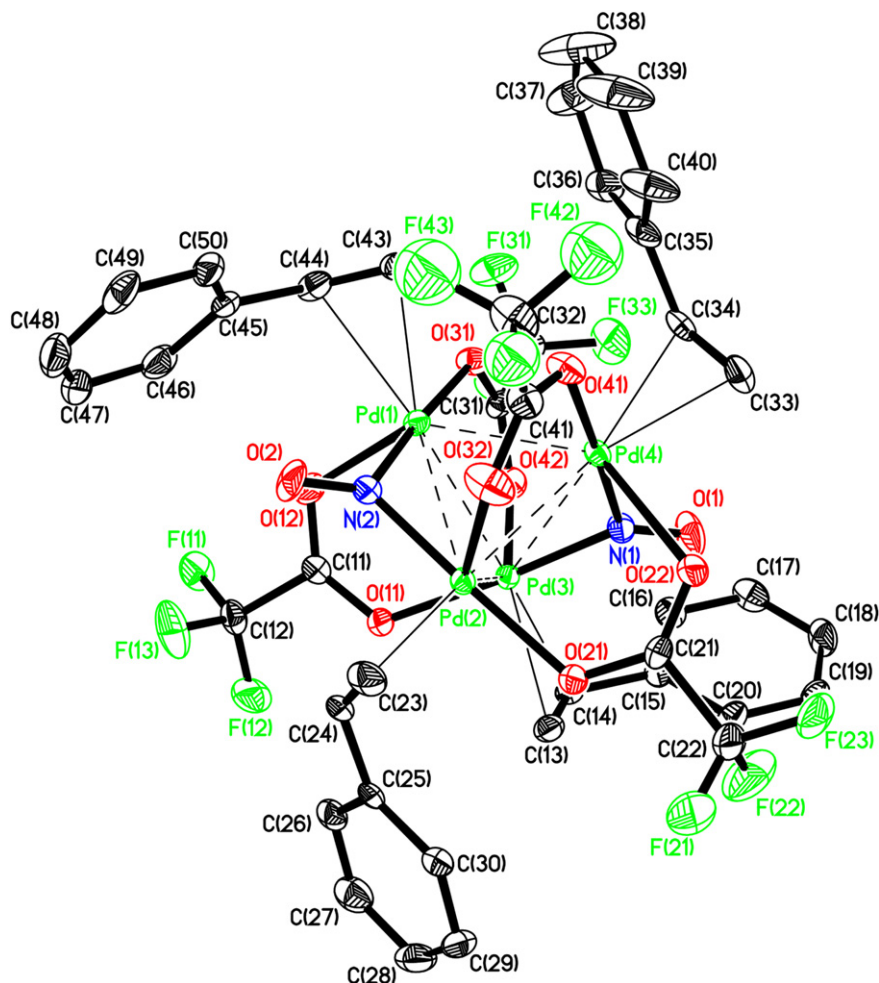
Fig. 4. The molecular structure of **V**. Hydrogen atoms is omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

to the Pd atoms. A significant difference in Pd–C$^\alpha$ and Pd–C$^\beta$ distances was observed (2.232(5), 2.221(5) vs 2.381(5), 2.343(5) Å, respectively). The metal coordination resulted in a noticeable elongation of the C=C bonds (1.353(7) and 1.362(7) Å) in comparison to the value found in crystalline styrene (1.325(2) Å) [12] . Within the molecule, two styrene ligands possess *transoid* mutual arrangement [6]. The cluster has a total electron count of 48 electrons (=10 × 3 (Pd) + 3 × 4 (carboxylate) + 1 × 2 (nitrosyl) + 2 × 2 (styrene); monoanionic terminal nitrosyls are considered as 1 electron donors). This corresponds to the 3-Pd 16-e cluster without any metal–metal bonds.

In contrast to well-known the *extended metal atom chain* complexes (EMACs) of Ni [13,14] and Co [15,16], the terminal palladium atoms in **IV** do not bear any axial ligands. Thus, the terminal Pd atoms may form additional intermolecular contacts. Actually, in crystal of **IV**, the adjacent molecules are combined into chains spread along the cell diagonal by weak Pd…Pd interactions (3.3490(6) Å) (Fig. 3). Thus, the first step of the interaction of **I** with alkenes (neohexene, styrene) completely suits (Scheme 1).

However, after crystals of **IV** were separated, the residual reaction mixture was concentrated (up to the oil formation) and kept in a fridge. Two days later, the black crystals formed. Their elemental analysis was in a good agreement with the total composition [Pd$_2$(NO)(CF$_3$CO$_2$)$_2$(CH$_2$CHPh)$_2$]$_n$ (**V**). The IR spectrum of **V** does not contain the band at 1650–1730 cm^{-1} attributed to the terminal NO-group, but contains the band 1544 cm^{-1} (ν(NO) for bridging group). In the ^{1}H NMR spectrum of **V**, two symmetrical doublets (δ = 5.28 and 5.80 ppm,

C$_6$H$_5$CH=C**H$_2$**), quadruplet (δ = 6.73 ppm, C$_6$H$_5$C**H**=CH$_2$), and multiplet (δ = 7.42 ppm, C$_6$**H$_5$**CH=CH$_2$) were observed. In comparison with the free styrene molecule, all the signals in **V** are shifted by 0.1–0.2 ppm to the low field, which confirms the coordination of styrene molecule.

Table 2
Selected bond lengths (Å) and angles (°) for **V**.

Pd(1)–N(2)	1.883(4)	Pd(3)–N(1)	1.878(4)
Pd(2)–N(2)	1.889(4)	Pd(4)–N(1)	1.892(4)
N(2)–O(2)	1.173(5)	N(1)–O(1)	1.177(5)
Pd(1)–Pd(2)	2.9894(4)	Pd(3)–Pd(4)	2.9859(4)
Pd(1)–Pd(3)	2.7594(4)	Pd(2)–Pd(4)	2.7084(4)
Pd(1)–Pd(4)	2.8495(4)	Pd(2)–Pd(3)	2.8320(4)
Pd(3)–O(11)	2.081(3)	Pd(1)–O(12)	2.420(3)
Pd(2)–O(21)	2.065(3)	Pd(4)–O(22)	2.507(3)
Pd(1)–O(31)	2.088(3)	Pd(3)–O(32)	2.402(3)
Pd(4)–O(41)	2.060(3)	Pd(2)–O(42)	2.554(3)
Pd(3)–C(13)	2.341(4)	Pd(3)–C(14)	2.457(4)
Pd(2)–C(23)	2.319(4)	Pd(2)–C(24)	2.455(4)
Pd(4)–C(33)	2.314(4)	Pd(4)–C(34)	2.444(4)
Pd(1)–C(43)	2.368(4)	Pd(1)–C(44)	2.466(4)
C(13)–C(14)	1.358(6)	C(14)–C(15)	1.473(6)
C(23)–C(24)	1.347(7)	C(24)–C(25)	1.474(6)
C(33)–C(34)	1.358(7)	C(34)–C(35)	1.470(7)
C(43)–C(44)	1.362(7)	C(44)–C(45)	1.464(6)
Pd(1)–N(2)–Pd(2)	104.84(17)	Pd(3)–N(1)–Pd(4)	104.75(18)
O(2)–N(2)–Pd(1)	128.1(3)	O(1)–N(1)–Pd(3)	128.2(3)
O(2)–N(2)–Pd(2)	127.1(3)	O(1)–N(1)–Pd(4)	126.8(3)
C(13)–C(14)–C(15)	125.1(4)	C(33)–C(34)–C(35)	125.7(4)
C(23)–C(24)–C(25)	126.8(5)	C(43)–C(44)–C(45)	124.2(4)
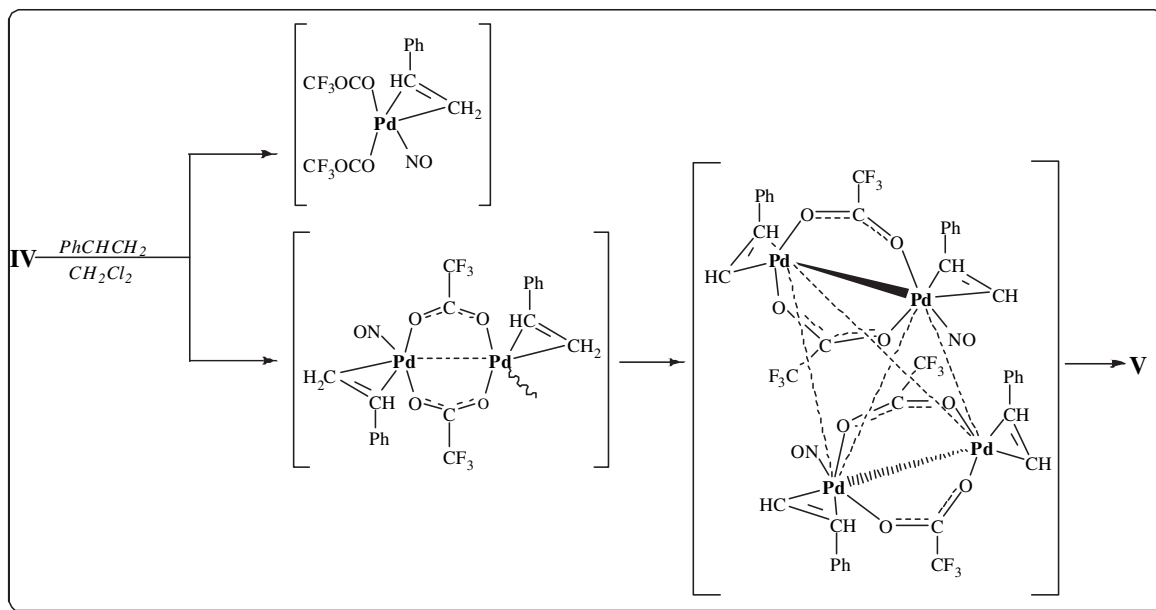
Scheme 2. Possible steps formation of cluster **V**.

The structure of **V** was determined by the X-ray diffraction analysis (Fig. 4). In **V**, the central metal core represents the tetrahedron with the Pd–Pd distances varying within the range 2.7084(4)–2.9894(4) Å. Two opposite edged of this tetrahedron are occupied by nearly symmetrical bridging NO ligands. The Pd–N bond lengths (1.878(4)–1.892(4) Å) are somewhat shorter than those we have earlier found for the square-planar complex $Pd_4(NO)_2(^tBuCO_2)_6$ (1.903(6)–1.917(6) Å) [5]. The two other edges of Pd_4 polyhedron are engaged by four nonsymmetrical bridging CF_3CO_2. In two formed $Pd_2(\mu\text{-}RCO_2)_2$ subunits, the Pd–Pd distances (2.7084(4) and 2.7594 (4) Å) are the shortest ones among the known Pd–Pd(carboxylate)₂. In all carboxylate ligands, the differences between the Pd–O($n1$) and Pd–O($n2$) distances ($n = 1$–4, Table 2) are longer than 0.3 Å. Of interest, all Pd–O($n1$) bonds lie opposite to the NO ligands in the coordination spheres of Pd atoms. As a result of this distortion, the $Pd_2(\mu\text{-}RCO_2)$ fragments are not planar and the O–Pd–Pd–O torsion angles vary from 16.0(1) to 22.3(1)°. The rest two edges of the Pd_4 tetrahedron (Pd(1)–Pd(4) and Pd(2)–Pd(3)) are not occupied by any bridging ligands. In **V**, the geometrical features of η^2-coordinated styrene molecule are similar to those found in structure **IV**.

In complex **V**, the PdO_2N fragments are T-shaped and point to square-planar, but the overall geometry of the Pd centres is very odd and difficult to classify. The Pd–Pd bonds would complete a typical 16-e configuration, but we have one additional ligand, the olefin. Therefore, the electron count at each individual Pd looks like 18 electrons. The cluster has the total electron count of 66 electrons (=10 × 4 (Pd) + 4 × 3 (carboxylate) + 2 × 3 (nitrosyl) + 4 × 2 (styrene); bridging nitrosyls are considered as 3 electron donors). This corresponds to a 4-Pd 18-e cluster with three Pd–Pd bonds in total (4 × 18−3 × 2). Although there are some differences in the Pd–Pd bonds, they all range within 2.7084(4)–2.9894(4) Å. Thus, it appears that they are similar in fact, and cluster **V** contains 6 equivalent Pd–Pd interactions each with the 0.5-bond order.

To the best of our knowledge, **V** is the first example of the tetrahedral carboxylate cluster formed by 10 groups metal.

Apparently, the formation of complex **V** includes the following steps: the action of excess styrene molecules leads to a splitting of trinuclear molecule **IV** into mononuclear fragment [(PhCH=CH₂) (NO)Pd(CF₃CO₂)₂] and binuclear fragment [(PhCH=CH₂)(NO)Pd(μ-CF₃CO₂)Pd(PhCH=CH₂)(μ-CF₃CO₂)] as the main building blocks. Steric hindrances in binuclear fragments resulted from styrene coordination requirements force these two fragments to be arranged perpendicularly. Finally, the transformation of the terminal NO-groups into the bridging ones yields complex **V** (see Scheme 2).

3. Conclusion

We have described the reactivity of the linear trimer $Pd_3(NO)_2(\mu\text{-}CF_3CO_2)_4(\eta^2\text{-}C_6H_5Me)_2$ (**I**) containing η^2-coordinated toluene molecule toward unsaturated hydrocarbons. The first step of the reaction of **I** with L (L = neohexene, styrene) includes the replacement of toluene to form the π complexes of general formula $Pd_3(NO)_2(\mu\text{-}CF_3CO_2)_4(\eta^2\text{-}L)_2$. The cluster $Pd_3(NO)_2(\mu\text{-}CF_3CO_2)_4(\eta^2\text{-}CH_2CHPh)_2$ (**IV**) was characterized by the X-ray diffraction analysis. It represents a trinuclear nitrosyl carboxylate complex. It was shown that under the excess of styrene, complex **IV** transforms to $Pd_4(\mu\text{-}NO)_2(\mu\text{-}CF_3CO_2)_4(\eta^2\text{-}CH_2CHPh)_4$ (**V**). According to the X-ray data, tetrahedral palladium cluster **V** is the first representative of a new type of nitrosyl carboxylate complexes.

Table 3
X-ray structure determination summary.

Compound	IV	V
Formula	$C_{24}H_{16}F_{12}N_2O_{10}Pd_3$	$C_{40}H_{32}F_{12}N_2O_{10}Pd_4$
M	1039.59	1354.28
Crystal system	Triclinic	Monoclinic
Space group	P-1	Cc
a/Å	12.2228(16)	11.2255(5)
b/Å	12.2745(16)	23.3335(11)
c/Å	12.6023(17)	17.6671(8)
α/°	86.123(2)	90
β/°	82.101(2)	94.549(1)
γ/°	60.811(2)	90
V/Å³	1635.0(4)	4613.0(4)
Z	2	4
μ/mm⁻¹	1.755	1.639
Data collected	16,992	20,772
Unique data (R_{int})	7869 (0.0244)	10,560 (0.0226)
R_1 [$I > 2\sigma(I)$]	0.0406	0.0281
wR_2 (all data)	0.1043	0.0695

4. Experimental

4.1. General techniques and procedures

All organic solvents and liquid organic reagents were purified and dried according to standard procedures. The unsaturated hydrocarbon and gaseous olefins were commercially supplied. Complex $Pd_3(NO)_2(\mu\text{-}CF_3CO_2)_4(\eta^2\text{-}C_6H_5Me)_2$ **I** was prepared according to a described procedure [7]. Microanalyses performed on Carlo Erba Analyzer CHND-OEA 1108. IR spectra of solid samples in a region of $400\text{–}4000\ cm^{-1}$ were recorded on a Zeiss SPECORD-M82 spectrophotometer. The samples of solid compounds were prepared as suspensions in Nujol. ^1H NMR spectra in CD_2Cl_2 were recorded on a Bruker AVANCE 400 spectrometer with working frequencies of 400.13 (^1H) and internal deuterium stabilization at room temperature. The chemical shifts of ^1H nucleus are given relative to TMS. GS–MS investigation was carried out on an Agilent Technologies model 5973 instrument equipped with capillary column HP-1 using helium as a carrier gas and temperature of vaporizer 250 °C. Spectra were recorded using electron impact method.

4.2. Reaction I with ethylene or propylene

0.4 g (0.04 mmol) complex **I** was dissolved in 20 ml CH_2Cl_2 at room temperature. Solution was placed in two-neck round-bottom 100 ml flask and stirred in C_2H_4 or C_3H_6 atmosphere for 12 h. The color changed from dark-vinous to pale-yellow and palladium black formation was observed. Palladium black was filtered off and organic products were identified by GS–MS.

4.3. Synthesis $Pd_3(NO)_2(\mu\text{-}CF_3CO_2)_4(\eta^2\text{-}CH_2CHCMe_3)_2$ (**III**)

0.2 g (0.2 mmol) of complex **I**, 20 ml CH_2Cl_2 and 0.4 ml (3.0 mmol) of neohexene were placed in round-bottom 50 ml flask. The color changed from dark-vinous to deep-brown. After 1 h a solution was evaporated on oil pump up to ~5 ml, 15 ml hexane was added and green precipitate formed. The precipitate was filtered, washed with hexane (15 ml) and dried under vacuum. The yield is 56% based on palladium. Element analysis: found: C 23.65, H 2.12, N 2.72%; calc. for $Pd_3(NO)_2(CF_3CO_2)_4(CH_2CHCMe_3)_2$: C 24.05, H 2.42, N. 2.81%. IR spectrum: 1680, 1656, 1408, 1196, 1152, 976, 844, 792, 728 cm^{-1} ^1H NMR (CD_2Cl_2): δ 1.13 (s, 9H, CH_3) 4.90 (dd, 2H, CH_2) 5.90 (m, 1H, CH).

4.4. Synthesis $Pd_3(NO)_2(\mu\text{-}CF_3CO_2)_4(\eta^2\text{-}CH_2CHPh)_2$ (**IV**)

0.2 g (0.2 mmol) complex **I**, 20 ml CH_2Cl_2, 0.35 ml (3.0 mmol) styrene were placed in a round-bottom 50 ml flask. The reaction mixture was stirred for 1 h. The color changed from dark-vinous to deep-brown. The resulting solution was concentrated on an oil pump up to 10 ml. After that 5 ml of hexane was added and yellow prism crystals were obtained. The crystals were filtered under Ar atmosphere. The yield is 25% based on palladium. Element analysis: found: C 27.62, H 1.46, N 2.83%; calc. for $Pd_3(NO)_2(CF_3CO_2)_4(CH_2CHPh)_2$: C 27.75, H 1.55, N 2.69%. IR spectrum: 1720, 1652, 1336, 1200, 1157, 820, 808, 728 cm^{-1}.

4.5. Synthesis $Pd_4(\mu\text{-}NO)_2(\mu\text{-}CF_3CO_2)_4(\eta^2\text{-}CH_2CHPh)_4$ (**V**)

After filtration of complex **V**, the saturated solution was placed in the fridge cell at −4 °C for two days and brown block crystals were obtained. Element analysis: found: C 35.51, H 2.47, N 2.12%; calc. for $Pd_4(NO)_2(CF_3CO_2)_4(CH_2CHPh)_4$: C 35.50, H 2.39, N 2.07%. IR spectrum: 1648, 1544, 1424, 1196, 1168, 1140, 940, 920, 848, 792, 728, 705 cm^{-1} ^1H NMR (CD_2Cl_2): δ 5.28 (dd, 1H, CH_2) 5.80 (dd, 1H, CH_2) 6.73 (dd, 1H, CH) 7.47 (m, 5H, C_6H_5).

4.6. X-ray crystallography

Crystal data and details of the X-ray analyses are given in Table 3. All experimental datasets were collected on a Bruker SMART APEX II diffractometer using graphite monochromatized Mo–Kα radiation ($\lambda = 0.71073$ Å) at 150 K. Absorption corrections based on measurements of equivalent reflections were applied. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms [17] (except disordered trifluoromethyl and nitrosyl groups). In **IV**, three CF_3 groups were found to be rotationally disordered over three positions with occupancy ratios 0.35/0.33/0.32, 0.60/0.25/0.15 and 0.52/0.28/0.20. One NO ligand is also rotationally disordered over two positions (0.53/0.47). All hydrogen atoms were placed in calculated positions and refined using the riding model.

Appendix A. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 772047 and 772048. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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