Palladium ketonyl carboxylate complexes – potential models of polynuclear intermediates in olefin oxidation: formation and X-ray structure of $Pd_6(\mu\text{-Cl})_{2+x}(\mu\text{-CF}_3CO_2)_4(\mu,\kappa^2\text{-CH}_2C(O)CMe_3)_{6-x}$ ($x = 0, 2$)†

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Reactions of $Pd_4(NO)_4(CF_3CO_2)_4$ with olefins were studied, this Pd-cluster was shown to promote the oxidation of olefins into ketones, which were found as ketonyl ligands in complex products of the reaction; 6-nuclear palladium clusters with carboxylate and ketonyl ligands $Pd_6(\mu\text{-Cl})_x(\mu\text{-CF}_3CO_2)_4(\mu,\kappa^2\text{-CH}_2C(O)CMe_3)_{6-x}$ were characterized by XRD analysis.

Oxidation of olefins by molecular oxygen with transition metal complexes as catalysts is of great importance for organic synthesis. The Wacker process and its lab scale modification – the Wacker–Tsuji oxidation – are among the most important processes.[1] $PdCl_2/CuCl_2$ is a traditional catalytic system for the reaction and a number of studies have dealt with the mechanism.[2] At the same time there are many examples of applications of palladium acetate and its derivatives in the selective oxidation of olefins.[3] However, the information about mechanisms of the reaction in the presence of palladium carboxylates is very limited[4] and contribution of polynuclear species has never been considered. Palladium carboxylate complexes can react with olefins in three ways:

1 Direct coordination of olefin molecules by palladium.
2 Reactions of olefin molecules with other organic ligands.
3 Coordination of olefin molecules in allyl form.

Thus, complex $Pd_2(\mu\text{-SO}_3H)_2(MeCO_2)_2(\eta^2\text{-CH}_2{=}CHPh)_2$ was obtained by saturation of palladium acetate solution in glacial acetic acid in the presence of styrene with SO_2.[5] According to XRD data Pd atoms are connected by two bridging SO_3H-groups and every Pd atom also coordinates a styrene and an acetate group.

Binuclear complex $Pd_2(\mu\text{-MeCO}_2)_2(\eta^3\text{-C}_{11}H_{17})$ ($C_{11}H_{17}$ is 2-methyl-3-norbornyl-anion) was obtained in the reaction of $(\eta^3\text{-C}_3H_4)PdMeX$ (X = Cl, Br, I) with norbornene followed by treatment of formed $(C_{11}H_{17})PdX$ with NaOAc.[6] According to XRD data Pd atoms are connected by bridging acetate groups and every Pd atom binds the 2-methyl-3-norbornyl-anion by σ,π-type.

Palladium acetate $Pd_3(\mu\text{-MeCO}_2)_6$ reacts with monoolefins (propene, *cis*-pent-2-ene, cyclohexene, hex-1-ene, *cis*-hex-2-ene, octa-1-ene and 2,3,3-trimethylbut-1-ene) in glacial acetic acid to give 3-nuclear complexes $Pd_3(\mu\text{-MeCO}_2)_2(\eta^3\text{-allyl})_2$, which later transform into binuclear complexes $Pd_2(\mu\text{-MeCO}_2)_2(\eta^3\text{-allyl})_2$.[7] Their structures were set from NMR-spectroscopic data.

In summary, when palladium carboxylate complexes react with olefins formation of olefin or allyl complexes is observed. There are no examples when the palladium carboxylate complex contains a coordinated small molecule (like NO, for instance) or when olefin coordinates in the oxidized form.

Herein we continue our investigation on the reactions of the palladium nitrosyl carboxylate clusters with olefins.[8] Earlier we have described a reaction of 3-nuclear linear cluster $Pd_3(\mu\text{-CF}_3CO_2)_4(\eta\text{-NO})_2(\eta^2\text{-TolH})_2$ (**I**) with styrene and neohexene. The first stage of the reaction is a substitution of arene ligands by olefin molecules giving $Pd_3(\mu\text{-CF}_3CO_2)_4(\eta\text{-NO})_2(\eta^2\text{-olefin})_2$ (**II**). Complex **II** is rather unstable in solution in the presence of an excess of the olefin and transforms to tetrahedral cluster $Pd_4(\mu\text{-CF}_3CO_2)_4(\mu\text{-NO})_2(\eta^2\text{-olefin})_4$ (**III**) with bridging NO-groups and unusual asymmetrically coordinated carboxylate groups (Scheme 1).

A dramatically different result is observed in the same reaction for the complex $Pd_4(\mu\text{-NO})_4(\mu\text{-CF}_3CO_2)_4$ (**IV**). All the transformations of complex **IV** are accompanied by oxidation of olefins that leads to compounds containing corresponding enolate ligands. At the first stage the metal core of complex **IV** doesn't change in the reaction with styrene or 3,3-dimethylbut-1-ene and 4-nuclear *enolate* complexes $Pd_4(\mu\text{-NO})_4(\mu\text{-CF}_3CO_2)_3(\mu,\kappa^2\text{-CH}_2C(O)R)$ (R = Ph – **Va**, R = CMe₃ – **Vb**) form.
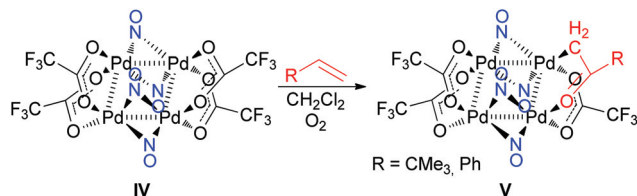
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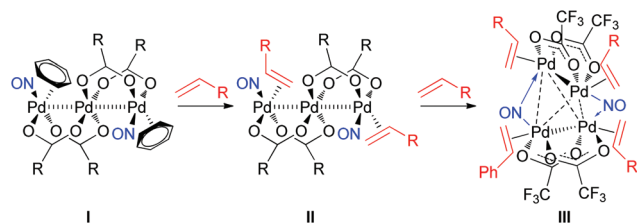
Scheme 1   Reactions of $Pd_3(\mu\text{-}CF_3CO_2)_4(\eta\text{-}NO)_2(\eta^2\text{-}TolH)_2$ with olefins.

Scheme 2   The first stage of the reaction of complex **IV** with olefins.

Complexes **V** are products of substitution of the CF_3CO_2 ligand by corresponding enolates formed as a result of olefin oxidation (Scheme 2).

IR-spectroscopic data confirm bridging coordination of trifluoroacetate and nitrosyl ligands. Bands of asymmetric and symmetric stretching vibrations of trifluoroacetate groups lie at 1644 and 1460 cm^{-1} for complex **Va** and at 1642 and 1469 cm^{-1} for complex **Vb**. Bands of stretching vibrations of nitrosyl groups are observed at 1519 and 1520 cm^{-1}, correspondingly. Bands of enolate ligands are significantly overlapped with $\nu_{as}(CO_2)$ and $\nu(NO)$, which makes assignation difficult.

On increasing the time of the reaction between complex **IV** and 3,3-dimethylbut-1-ene we succeeded in obtaining a new 6-nuclear cluster $Pd_6(\mu\text{-}Cl)_2(\mu\text{-}CF_3CO_2)_4(\mu,\kappa^2\text{-}CH_2C(O)CMe_3)_6$ (**VIa**), which was characterized by X-ray diffraction analysis (Fig. 1). In centrosymmetric structure **VIa** all six palladium atoms possess a square-planar coordination environment. The molecule **VIa** contains two well-known binuclear dicarboxylate fragments $Pd_2(\mu\text{-}CF_3CO_2)_2$ which came from parent compound **IV**. Their geometries are close to those previously determined for the wide series of Pd carboxylates.[8–10] The $Pd_2(\mu\text{-}CF_3CO_2)_2$ clusters are combined by bridging $Pd[\mu\text{-}CH_2C(O)CMe_3]_3(\mu\text{-}Cl)$ units into a six-membered metallocycle. The structural features of enolate-containing fragments $Pd(\mu\text{-}CH_2C(O)CMe_3)$ are similar to those previously observed in the structure of $Pd_4(\mu\text{-}CF_3CO_2)_4(\mu,\kappa^2\text{-}CH_2C(O)CH_3)_2(\eta^3\text{-}CH_2C(OH)CH_2)_2$.[11]

There are two examples in the literature describing complexes $Zn(phen)LCl$ (L = $PhC(S)NP(O)(O^iPr)^-$)[12] and $Pd_2(\mu\text{-}Cl)(PhCH_2N{=}C(COPh)C_6H_4)_2$[13] with chloride ligands, which were proved to come from dichloromethane itself. In those cases dichloromethane was specially purified and all the traces of hydrochloric acid were removed. Since we didn't remove the hydrochloric acid in our first experiments, we suggested that chloride ligands can come from the acid. We carried out the reactions in purified CH_2Cl_2 after removing all
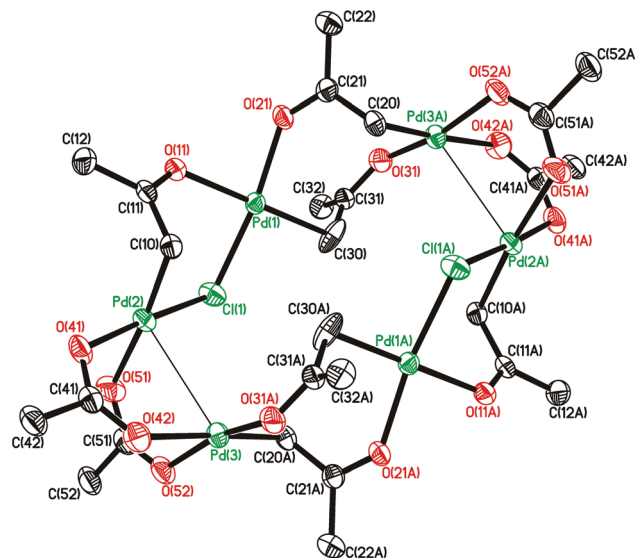

Fig. 1   Molecular structure of complex **VIa**. Methyl groups and fluorine atoms are omitted for clarity. Displacement ellipsoids are shown at 50% probability level.
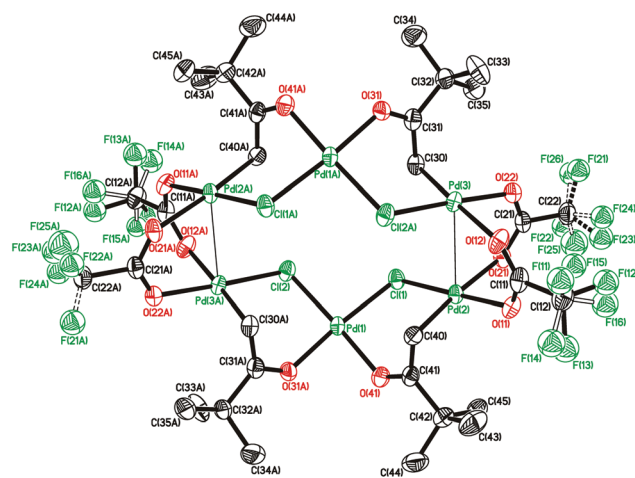

Fig. 2   Molecular structure of complex **VIb**. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at 50% probability level.

the HCl, but in those cases only complexes **V** could be isolated. However, taking into account the low yields of 6-nuclear ketonyl complexes in all the experiments it doesn't necessarily mean that the complexes don't form at all in this case. Also it should be noted that under the formation of complexes **VI** Cl-anions substitute trifluoroacetate groups, so the presence of such a strong acid as HCl can be favorable itself, since the acid protonates trifluoroacetate anions.

More convincing proof that Cl-anions come from hydrochloric acid is a result of the reaction in the presence of an excess of hydrochloric acid. The reaction proceeds in a similar way but complex $Pd_6(\mu\text{-}Cl)_4(\mu\text{-}CF_3CO_2)_4(\mu,\kappa^2\text{-}CH_2C(O)CMe_3)_4$ (**VIb**) with more chloride ligands formed. The molecular structure of **VIb** is similar to that of **VIa** (Fig. 2) taking into account

that two enolate ligands are substituted by bridging chloride anions.

Both complexes **VI** do not contain nitrosyl groups, although it's difficult to confirm one can assume that nitrosyl can provide oxidation of olefins. Earlier we showed that nitrogen monoxide can oxidize, for instance, CO in the presence of palladium compounds.[13] On the other hand, NO is a potential transfer agent for oxygen, as was shown by An and co-workers.[14] Further investigations of properties of nitrosyl compounds are required for understanding the nature of these processes.

Conclusions

We describe reactions of palladium polynuclear nitrosyl carboxylate complexes with olefins accompanied by olefins oxidation and formation of carboxylate enolate palladium compounds. New 6-nuclear palladium clusters $Pd_6(\mu-Cl)_{2+x}$-$(\mu-CF_3CO_2)_4(\mu,\kappa^2-CH_2C(O)CMe_3)_{6-x}$ ($x = 0, 2$) can be considered as potential models of polynuclear intermediates of olefin oxidation in the presence of palladium carboxylate compounds. The following new ideas for future mechanistic investigations can be deduced from the formation of these complexes: (1) polynuclear compounds can take part in the reactions (as intermediates, as a result of catalyst deactivation or somehow else) and it is possible even under a quite high excess of olefins; (2) after oxidation of olefins a corresponding ketone or aldehyde can still be coordinated by palladium; (3) ketonyl groups are quite likely coordinated in bridging mode. Also these chloride carboxylate complexes look promising as starting materials for synthesis of palladium mixed carboxylate due to possibility of substitution of chloride ligands with other carboxylates under the action of silver carboxylates. Finally, the 6-nuclear clusters have quite big cavities in structure ~5.2 Å in diameter. This feature can be used for absorption of small molecules of organic solvents or gases.

Experimental

General techniques

All chemicals were obtained from commercial sources and used without further purifications. The palladium nitrosyl trifluoroacetate $Pd_4(NO)_4(CF_3CO_2)_4$ was prepared according to a literature procedure.[15] Elemental analyses were obtained with a EuroVector EA 1112 analyzator. IR-spectra were recorded in Nujol and hexachlorobutadiene with a Magna IR 750 spectrometer (Nicolet).

Synthesis of $Pd_4(\mu-NO)_4(\mu-CF_3CO_2)_3(\mu,\kappa^2-CH_2C(O)Ph)$. 200 mg of $Pd_4(NO)_4(CF_3CO_2)_4$ was dissolved in 25 ml of methylene chloride and 0.18 ml of styrene was added. The solution was stirred in air for 2 h at r.t. After that the solution was concentrated to 5 ml, then 10 ml of diethyl ether was added and a brown precipitate formed. The precipitate was filtered off, washed with diethyl ether (2 × 15 ml) and dried under

vacuum. The yield is 35% based on palladium. Element analysis: found: C 16.45, H 1.49, N 5.67%; calc. for $C_{14}H_7F_9N_4O_{11}Pd_4$: C 16.77, H 0.70, N 5.59%. IR-spectrum: $\nu_{as}(CO_2)$ 1644, $\nu_s(CO_2)$ 1460, $\nu(NO)$ 1519 cm^{-1}.

Synthesis of $Pd_4(\mu-NO)_4(\mu-CF_3CO_2)_3(\mu,\kappa^2-CH_2C(O)CMe_3)$. 200 mg of $Pd_4(NO)_4(CF_3CO_2)_4$ was dissolved in 25 ml of methylene chloride and 0.19 ml of 3,3-dimethylbut-1-ene was added. The solution was stirred in air for 2 h at r.t. After that the solution was concentrated to 5 ml, then 10 ml of hexane was added and a brown precipitate formed. The precipitate was filtered off, washed with hexane (2 × 15 ml) and dried under vacuum. The yield is 65% based on palladium. Element analysis: found: C 15.10, H 1.10, N 5.70%; calc. for $C_{12}H_{11}F_9N_4O_{11}Pd_4$: C 14.66, H 1.12, N 5.70%. IR-spectrum: $\nu_{as}(CO_2)$ 1642, $\nu_s(CO_2)$ 1460, $\nu(NO)$ 1520 cm^{-1}.

Obtaining crystals of $Pd_6(\mu-Cl)_2(\mu-CF_3CO_2)_4(\mu,\kappa^2-CH_2C(O)-CMe_3)_6$. 200 mg of $Pd_4(NO)_4(CF_3CO_2)_4$ was dissolved in 25 ml of methylene chloride and 0.19 ml of 3,3-dimethylbut-1-ene was added. The solution was stirred in air for 2 h at r.t. Then the solution was filtered and left in air for slow evaporation. After 5 days a dark orange oil and some red lamellar crystals formed.

Synthesis of $Pd_6(\mu-Cl)_4(\mu-CF_3CO_2)_4(\mu,\kappa^2-CH_2C(O)CMe_3)_4$. 200 mg of $Pd_4(NO)_4(CF_3CO_2)_4$ was dissolved in 25 ml of methylene chloride and 0.19 ml of 3,3-dimethylbut-1-ene was added. The solution was stirred in air for 2 h at r.t. After that 0.02 ml of concentrated HCl was added and the solution was stirred for 45 min. Then the solution was concentrated to 5 ml and 10 ml of hexane was added. The formed brown precipitate was filtered off and the filtrate was left in air for slow evaporation. After 2 days red lamellar crystals formed. The crystals were washed with hexane (2 × 15 ml) and dried under vacuum. The yield is 5% based on palladium. Element analysis: found: C 23.66, H 3.07%; calc. for $C_{32}H_{44}Cl_4F_{12}O_{12}Pd_6$: C 23.59, H 2.72%. IR-spectrum: $\nu_{as}(CO_2)$ 1656, $\nu_s(CO_2)$ 1454, $\nu(C-O_{enolate})$ 1512, $\nu(C-C_{enolate})$ 1280 cm^{-1}.

Single crystals of VIa and VIb. These were obtained from dichloromethane–hexane mixtures, mounted in inert oil and transferred immediately to the cold gas stream (173 K) of the Bruker SMART APEX II diffractometer. *Crystal data* (**VIa**): $C_{44}H_{66}Cl_2F_{12}O_{14}Pd_6$, $M = 1756.27$, monoclinic, $a = 25.986(4)$, $b = 14.314(2)$, $c = 19.812(3)$ Å, $\beta = 113.231(2)^\circ$, $V = 6771.9(16)$ Å^3, space group $C2/c$, $Z = 4$, μ(Mo-Kα) = 1.721 mm^{-1}, 22 515 reflections measured, 6641 unique (R_{int} = 0.0218). The structure was solved by direct methods and refined by full matrix least-squares on F^2 [16] with anisotropic thermal parameters for all non-hydrogen atoms, except disordered t-Bu and $-CF_3$ groups. One of three crystallographically independent t-Bu and both $-CF_3$ groups were found to be rotationally disordered over two or three positions and were refined isotropically with restrained C–C and C–F distances. All H atoms were placed in calculated positions and refined using a riding model. The structure contains voids with an approximate volume of 270 Å^3. Several irregular peaks with intensity ~0.6 e Å^{-3} were seen inside them. These peaks indicated the presence of a small amount of solvate CH_2Cl_2. The SQUEEZE procedure[17]

was used to discount this effect. The final residuals were R_1 = 0.0588, wR_2 = 0.1959 for 5518 reflections with $I > 2\sigma(I)$ and 0.0682, 0.2040 for all data and 344 parameters. (**VIb**): $C_{32}H_{44}Cl_4F_{12}O_{12}Pd_6$, M = 1628.87, monoclinic, a = 9.1569(14), b = 14.474(2), c = 19.072(3) Å, β = 95.500(2)°, V = 2516.0(7) Å^3, space group $P2_1/c$, Z = 2, μ(Mo-Kα) = 2.407 mm^{-1}, 17 558 reflections measured, 4932 unique (R_{int} = 0.0421). The structure was solved by direct methods and refined by full matrix least-squares on F^2 [16] with anisotropic thermal parameters for all non-hydrogen atoms, except disordered –CF$_3$ groups. Both crystallographically independent –CF$_3$ groups were found to be rotationally disordered over two positions with occupancy ratios of 0.52/0.48 and 0.61/0.39. Inevitably, all fluorine atoms were refined isotropically with restrained C–F distances. All H atoms were placed in calculated positions and refined using a riding model. The final residuals were R_1 = 0.0497, wR_2 = 0.1314 for 3722 reflections with $I > 2\sigma(I)$ and 0.0740, 0.1442 for all data and 298 parameters.

Acknowledgements

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