Transformations of arenes and nitrogen oxide in the coordination sphere of a linear palladium cluster giving aromatic amines and carbazoles

R. E. Podobedov,[a,b] T. A. Stromnova,[a,b] † and I. P. Stolyarov[b]

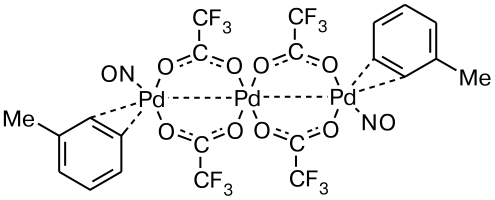
[a]M. V. Lomonosov Moscow State Academy of Chemical Technology,
86 prosp. Vernadskogo, 119571 Moscow, Russian Federation
[b]N. S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences,
31 Leninskii prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 954 1279. E-mail: bambryounger@gmail.com

Thermal transformations of linear trinuclear nitrosyl carboxylate complex $Pd_3(NO)_2(\mu\text{-}OCOCF_3)_4(\eta^2\text{-}C_6H_5Me)_2$ (**1**) in aromatic solvents (benzene or toluene) were studied. According to GLC and GLC/MS analyses, thermolysis of **1** in air and under NO atmosphere gives rise to an unusual set of organic compounds: aromatic diarylamines and carbazoles. A possible pattern of formation of the organic products was proposed.

Key words: palladium clusters, thermolysis, template reactions, biaryls, nitrosoarene, diarylamines, carbazoles, nitrogen monoxide, NO insertion.

Metal clusters with organic ligands are considered as convenient models for studying particular steps of catalytic transformations of organic compounds on metal catalysts. Although morphologically, polyhedral clusters resemble most closely nanosized metal particles, clusters with a metal-chain core open up new opportunities of template transformations of ligands. This is predetermined by combination of the "electron reservoir" function inherent in the clusters and the minimum steric hindrance at terminal metal atoms in the chain.

The purpose of this work is to study the products of template ligand transformations in aromatic solvents for the unusual linear cluster $Pd_3(NO)_2(\mu\text{-}OCOCF_3)_4(\eta^2\text{-}C_6H_5Me)_2$ (**1**) obtained previously and studied by X-ray diffraction.[1—3] In complex **1**, the η^2-arene and corner terminal NO groups are coordinated to the terminal metal atoms.



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Experimental

Complex **1** was prepared according to a previously described procedure[3] by the reaction of palladium(II) trifluoroacetate with gaseous NO in toluene.

The solvents, benzene and toluene (chemically pure grade), were used as received.

Gaseous nitrogen monoxide was prepared by a standard procedure[4] from sodium nitrite and potassium iodide in the presence of sulfuric acid.

GLC analysis of the organic fraction was carried out on a GC-17A Shimadzu chromatograph (Japan) with an XE-60 capillary column (25×0.2) and helium as the carrier gas.

GLC/MS analysis of the organic phase was carried out on a 5973 Agilent Technologies GLC/MS spectrometer (USA). The spectra were run in the electron impact mode.

Thermolysis of 1 in benzene or toluene (in air). The complex $Pd_3(NO)_2(\mu\text{-}OCOCF_3)_4(\eta^2\text{-}C_6H_5Me)_2$ (0.25 g, 0.25 mmol) dissolved in toluene or benzene (10 mL) was placed in a one-necked flask connected to a reflux condenser. The reaction mixture was refluxed for 6 h, cooled to room temperature and filtered through a Schott filter 40. The filtrate was concentrated on an oil pump to ~2 mL. The organic fraction was analyzed by gas liquid chromatography and gas chromatography/mass spectrometry. The composition of the organic phase: in benzene, CF_3CO_2Ph (traces), C_6H_5Ph (0.05 mmol), PhC_6H_4Me (0.04 mmol), PhNO (traces), PhNHPh (0.01 mmol), $C_6H_3NHC_6H_3$ (traces); in toluene, $CF_3CO_2C_6H_4Me$ (traces), $MeC_6H_4C_6H_4Me$ (0.19 mmol), MeC_6H_4NO (traces), $MeC_6H_4NHC_6H_4Me$ (0.4 mmol), $MeC_6H_3NHC_6H_3Me$ (0.01 mmol).

Thermolysis of 1 in toluene (under NO). The complex $Pd_3(NO)_2(\mu\text{-}OCOCF_3)_4(\eta^2\text{-}C_6H_5Me)_2$ (0.2 g, 0.2 mmol) dissolved in toluene (10 mL) was placed in a two-necked flask connected to a reflux condenser and a U-shaped gas seal. The reaction mixture was stirred at reflux for 4 h under NO. The solution color changed from dark-brown to black-green. The organic fraction was isolated and analyzed similarly to the previous one. The composition of the fraction: $CF_3CO_2C_6H_4Me$ (traces), $MeC_6H_4C_6H_4Me$ (0.15 mmol), MeC_6H_4NO (traces), $MeC_6H_4NHC_6H_4Me$ (0.02 mmol), $MeC_6H_3NHC_6H_3Me$ (0.04 mmol).

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† Deceased.

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Results and Discussion

Previously, it was shown by TGA[5] that crystalline cluster **1** decomposes in the temperature range of 65—390 °C losing successively toluene molecules and trifluoroacetate and nitrosyl groups. Weakly bound arene molecules were removed in the range of 65—120 °C, three of the four trifluoroacetate groups were lost at 120—180 °C, a nitrosyl ligand and the last trifluoroacetate ligand, possibly, as $NO^+CF_3COO^-$, were eliminated at 180—225 °C, and the last nitrosyl ligand was eliminated at 225—390 °C. Since the weakly bound arene ligands are the first to be eliminated, one could hardly expect the formation of any new organic products upon the solid-phase thermal decomposition of **1**. Much more favorable conditions for inner-sphere transformations of the arene ligands of the cluster are created by performing the thermolysis in aromatic solvents, *viz.*, toluene and benzene. Obviously, in aromatic solvents, η^2-coordinated toluene **1** molecules can be replaced by coordinated solvent molecules, so the latter can participate in the inner-sphere ligand transformations.

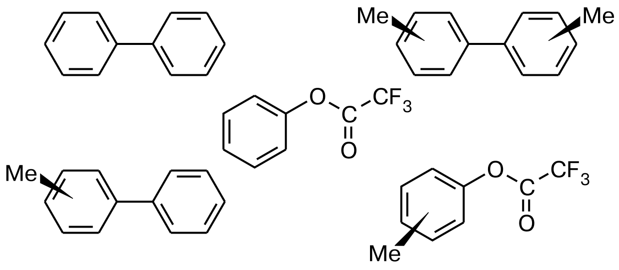
Thermolysis of **1** was carried out for 4—6 h in boiling benzene and toluene in a nitrogen oxide atmosphere or in air, the organic reaction products were identified by GLC/MS. Usually, aromatic compounds react with palladium carboxylates to give oxidative coupling products, namely, bi- and polyaryls, and oxidative esterification products, aryl carboxylates[6,7] (Scheme 1).

Scheme 1

$$2\,ArH + Pd(OCOR)_2 = Ar{-}Ar + 2\,RCOOH + Pd^0$$

$$ArH + Pd(OCOR)_2 = ArOCOR + RCOOH + Pd^0$$

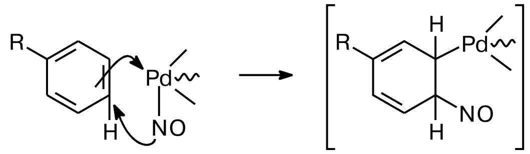
These compounds were found among the products of thermolysis of **1**. The reaction carried out in benzene yields diphenyl and its methyl derivatives, and phenyl trifluoroacetate, and the reaction in toluene affords bitolyl isomers and *o*- and *p*-cresyl trifluoroacetate.



The mechanism of formation of these compounds has been studied in detail by the example of reactions of arenes with palladium carboxylates.[6] In both cases, the reactions involve the intermediate formation of σ-aryl Pd^{II} complexes. However, apart from these regular products of transformation of arene and trifluoroacetate ligands of cluster **1**, the reaction mixture was found to contain nitrogen-containing aromatic compounds: nitrosoarenes PhNO (**2**), *o*- and *p*-MeC_6H_4NO (**3**), diphenylamine derivatives $C_6H_4RNHC_6H_4R$ (**4**), and carbazole $C_6H_3RNHC_6H_3R$ (**5**) (R = H or Me). It is of interest that thermolysis of **1** proceeds in the same way in air and in the nitrogen oxide atmosphere, so all nitrogen-containing products come only from the coordinated NO present in initial cluster **1**.

The formation of compounds **4** and **5** may include the addition of Pd—NO fragment to the arene C=C bond with simultaneous cleavage of the Pd—N bond as the key step (Scheme 2). The initial π-arene complex is converted to an intermediate with σ-bonded cyclohexadienyl ligand.

Scheme 2

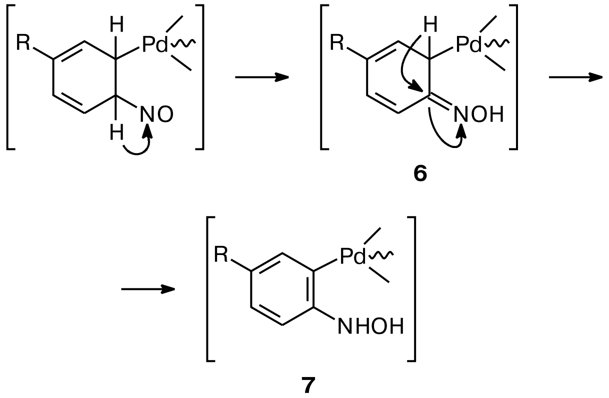


R = H, Me

Nitroso compounds **2** and **3** found in the reaction mixture may have resulted from decomposition of the intermediate with the σ-bonded cyclohexadienyl ligand.

The subsequent intramolecular migration of hydrogen atoms yields successively σ-bonded oxime **6** and hydroxylamine **7**, which are products of NO insertion into the C—H bond of the coordinated arene (Scheme 3).

Scheme 3

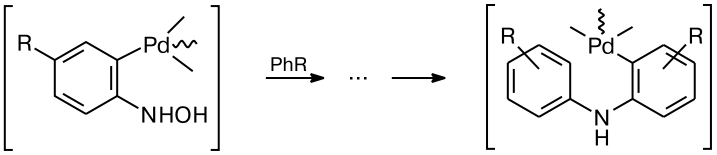


R = H, Me

The reaction of **7** with the solvent, benzene or toluene, leads to *ortho*-metallated diarylamine (**8**) (Scheme 4).

The reactions of substituted hydroxylamines with aromatic compounds in the presence of trifluoroacetic acid to

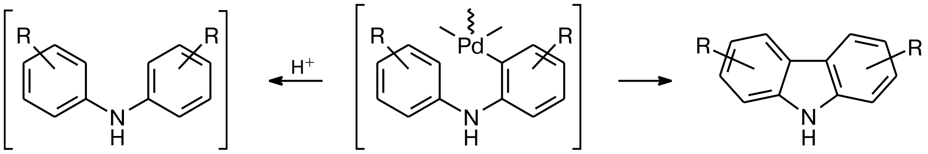
Scheme 4



7 **8**

R = H, Me

Scheme 5



4 **8** **5**

R = H, Me

give diarylamines were described previously.[8] The presence of coordinated μ-$OCOCF_3$ groups in the initial complex **1** allows the formation of CF_3COOH in the system. The subsequent transformations of metallated diarylamine afford free diarylamine and carbazole (Scheme 5).

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