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Palladium nitrosoarene complexes in reductive carbonylation of nitroarenes

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The reactions of carbon monoxide with the palladium nitrosoarene complexes $Pd_2(\mu\text{-}OCOR)_2(—CH_2C_6H_4NO)_2$ (**1**, R = Me, CF_3, Bu^t, or Ph) and $Pd_2(\mu\text{-}OCOR)_2(PhNC_6H_4NO)_2$ (**2**, R = Me, CF_3, Bu^t, or Ph) were studied. Complexes **1** contain the *o*-nitrosotoluene molecule metallated at the methyl group. In complexes **2**, the phenyl-*o*-nitrosophenylamide ligand coordinated *via* two nitrogen atoms can be considered as a nitrosobenzene derivative bearing the NPh group in the *ortho* position of the Ph ring. It all cases, carbonylation of the complexes afforded the corresponding aryl isocyanates Ar—N=C=O or the products of their further transformations. The mechanism of reductive carbonylation of nitroarenes catalyzed by palladium compounds and the role of palladium nitrosoarene complexes as possible intermediates in this process are discussed.

Key words: palladium, reduction, reductive carbonylation, nitroarenes, nitrosoarenes, aryl isocyanates, phenyl isocyanate.

As part of our continuing studies of the reactivities of palladium complexes containing the nitrosoarene ligands, we examined the reactions of $Pd_2(\mu\text{-}OCOR)_2(—CH_2C_6H_4NO)_2$ (**1**) and $Pd_2(\mu\text{-}OCOR)_2(PhNC_6H_4NO)_2$ (**2**) (R = Me, CF_3, Bu^t, or Ph), which we have synthesized previously,[1—3] with carbon monoxide under mild conditions.

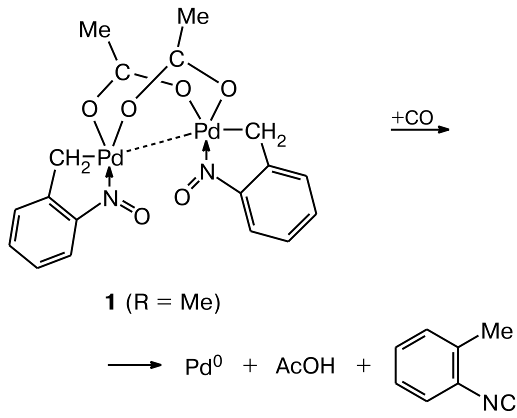
Complexes **1** bear the *o*-nitrosotoluene molecule metallated at the Me group as a bidentate chelating ligand. Complexes **2** contain the phenyl-*o*-nitrosophenylamide ligand coordinated *via* two N atoms, which can also be considered as a nitrosobenzene derivative bearing the NPh group in the *ortho* position of the Ph ring. Such complexes containing the coordinated nitrosoarene molecule were postulated[4—7] as active intermediates in the palladium-catalyzed reductive carbonylation of nitroarenes, which has promise as an industrial procedure for the preparation of aromatic isocyanates, carbamates, and urea derivatives.

Results and Discussion

Previously,[8] it has been found that complexes **1** and **2** are readily reduced with different reducing agents (H_2, $NaBH_4$, or alcoholic solutions of alkali) under mild conditions. Our experiments demonstrated that these complexes react with CO in a solution in benzene or toluene under mild conditions (~20 °C, p_{CO} = 1 atm, τ = 10—15 h). Under the reaction conditions, the palladium atom in these complexes is reduced to metal and the nitrosoarene ligands are transformed into the expected reductive carbonylation products.

The reaction of complex **1** (R = Me) with CO afforded acetic acid and tolyl isocyanate along with palladium black (Scheme 1).

Scheme 1



Tolyl isocyanate was obtained in 8—12% yields with respect to the amount of the complex used (~0.2 mol of tolyl isocyanate per mole of the complex), whereas acetic acid was produced in a nearly stoichiometric yield (~2 mmol of acetic acid per mole of the complex). Apparently, tolyl isocyanate was obtained in such a low yield because of high reactivities of aryl isocyanates, particularly, in the presence of palladium compounds. It is believed that under the reaction conditions, tolyl isocyanate either undergoes dimerization, trimerization, and poly-

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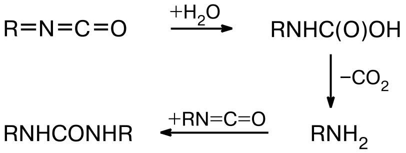
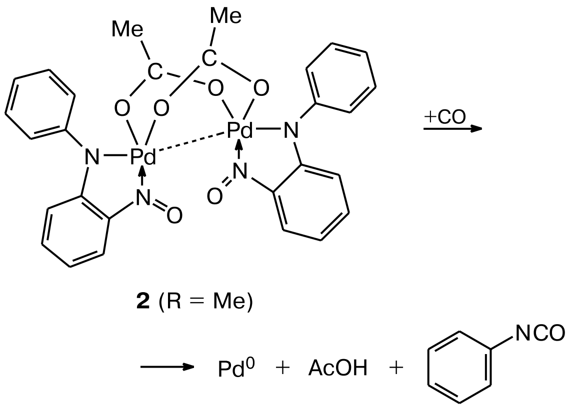
merization or reacts with water that is present in the solvent (Scheme 2) to give high-boiling products, which are difficult to identify.[9,10]

Scheme 2



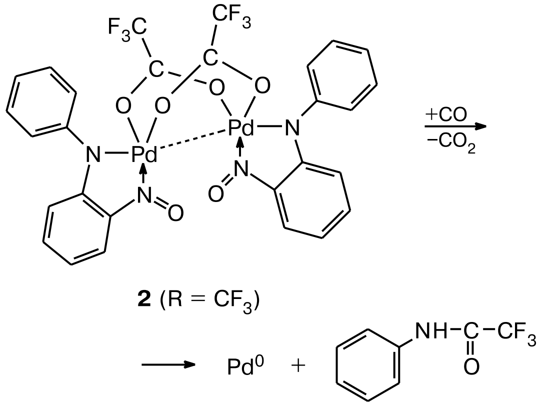
Complexes **2** (R = Me or CF_3) react with CO under the same conditions. The reaction of complex **2** (R = Me) afforded acetic acid and phenyl isocyanate (Scheme 3). It should be noted that the yield of phenyl isocyanate generated in this reaction, like that obtained in the above-considered process, was much lower than the stoichiometric value (10—15% from the starting complex).

Scheme 3



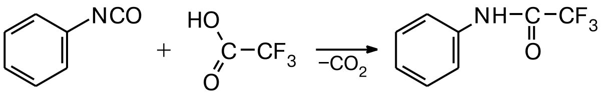
The reaction of CO with complex **2** containing the trifluoroacetic ligands gave *N*-phenyltrifluoroacetamide PhNHC(=O)CF_3 along with palladium black (Scheme 4).

Scheme 4



It is believed that *N*-phenyltrifluoroacetamide is formed in the reaction of trifluoroacetic acid, which is generated by reduction of the complex, with phenyl isocyanate (Scheme 5). Such a reaction with strong carboxylic acids is typical of aryl isocyanates.[9,10]

Scheme 5



Hence, our study showed that the reactions of CO with palladium complexes containing the coordinated nitrosoarene molecules afford aryl isocyanates ArN=C=O, *i.e.*, the products of reductive carbonylation of nitroarenes, which occurs according to the overall equation

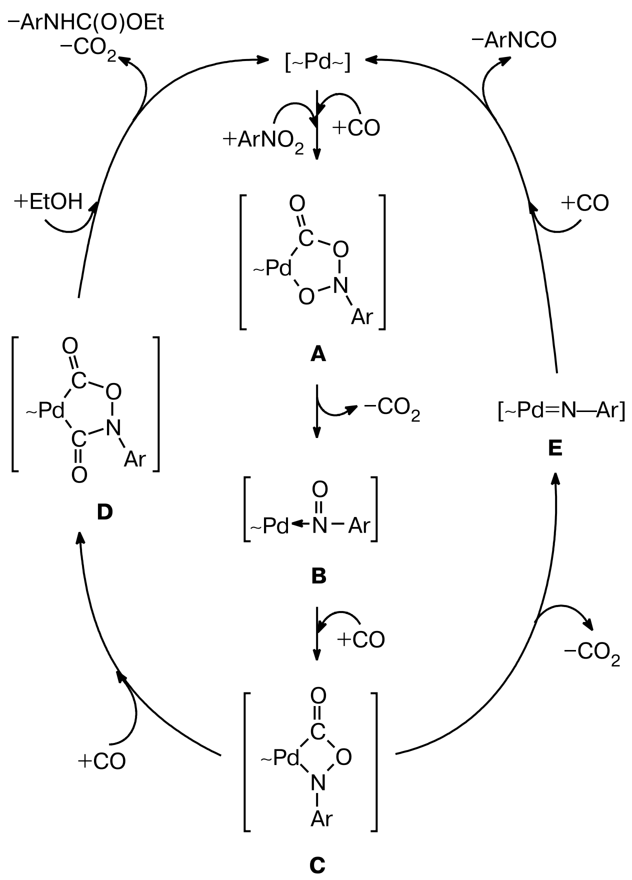
$$ArNO_2 + 3\,CO \longrightarrow 2\,CO_2 + ArNCO.$$

The mechanism of reductive carbonylation of nitroarenes catalyzed by noble metal (Ru, Rh, Pd) compounds has been the subject of prolonged discussion. Most researchers assumed[11,12] that this reaction involves a series of successive carbonylation—decarbonylation steps (Scheme 6). The carbonylation step produces five- or six-membered metallocycles whose decarboxylation affords coordinated nitrosoarenes. The coordination of the nitrosoarene ligand in the intermediate **B** can give rise to both the three-membered Pd—N—O— metallocycle and a complex with the donor-acceptor Pd←N bond. The subsequent steps afford the coordinated arylnitrene ligands [ArN:]. Depending on the substrate, the subsequent steps yield either aryl isocyanate or carbamate.

Intermediates **A**, **B**, and **C** were isolated and structurally characterized (see Scheme 6) in the studies of ruthenium-[13,14] or rhodium-based catalysts for reductive carbonylation.[15—17] In some cases, subsequent transformations of these intermediates gave rise to aryl isocyanates or carbamates. In the investigations of palladium-based catalytic systems, a possible intermediate (**D**, see Scheme 6) was isolated and structurally characterized only once.[12,18] However, the products of subsequent transformations of this complex provide only indirect evidence that this complex can be involved in carbonylation of nitroarenes.

Data on reactions of palladium complexes containing the nitrosoarene ligands (intermediates or models of intermediates of type **B** in Scheme 6) with carbon monoxide are lacking in the literature. Apparently, the formation of phenyl isocyanate and tolyl isocyanate in the reactions of palladium nitrosoarene complexes with carbon monoxide is evidence that reductive carbonylation of nitroarenes in the presence of palladium compounds proceeds through the formation of coordinated nitrosoarenes.

Scheme 6



Experimental

Nitrosoaromatic compounds o-R′C_6H_4NO (R′ = H or Me) were prepared according to a general procedure[19] by the oxidation of phenylhydroxylamine with sodium bichromate in aqueous H_2SO_4 (R′ = H) or by the reduction of the corresponding nitro compound (R′ = Me). The resulting nitrosoarenes were isolated from the reaction mixture by azeotropic steam distillation under atmospheric or reduced pressure. The purities of the compounds were checked by the TLC on Silufol and melting points. Because the nitroso group in nitrosoaromatic compounds is readily oxidized by atmospheric oxygen, nitrosoarenes were stored over a short period of time in Schlenk vessels under argon in a refrigerator, and all reactions with these compounds were carried out under an inert atmosphere (N_2 or Ar).

Palladium complexes with nitrosoarene ligands $Pd_2(OCOR)_2(CH_2C_6H_4NO)_2$ (1) and $Pd_2(OCOR)_2(PhNC_6H_4NO)_2$ (2) (R = Me, CF_3, Bu^t, or Ph) were prepared according to procedures described previously[1,2] from tetranuclear palladium carbonyl carboxylates $Pd_4(\mu\text{-}CO)_4(\mu\text{-}OCOR)_4$ (R = Me, CF_3, Bu^t, or Ph) and the corresponding nitrosoaromatic compounds.

The organic solvents were purified according to standard procedures.[20]

The GLC analysis of the liquid products was carried out on a 3700 chromatograph (OV-101 on Chromaton for analyses of high-boiling reaction products and Reoplex for analyses of low-boiling organic products).

The GLC-MS analyses of organic products were carried out on an Automass 150 instrument (Delsi Nermag, France). The recording conditions were as follows: EI, 70 eV, capillary columns with PEG-20M phases for analyses of low-boiling organic products and Silicon SE-30 for analyses of high-boiling reaction products.

Reactions of complexes 1 and 2 with carbon monoxide were carried out at 20 °C and CO pressure of 1 atm. in a two-neck flask equipped with a magnetic stirrer, a sampler with a rubber diaphragm, and a system for evacuation and gas supply. A weighed sample of the complex (0.25 mmol; 0.14 g of complex **1**; 0.18 or 0.21 g of complex **2** for R = Me and CF_3, respectively) was placed in a flask and the solvent (benzene or toluene, 2 mL) was added. The system was evacuated, CO was supplied, and the reaction mixture was stirred. The liquid reaction products were analyzed by GLC and GLC-mass spectrometry.

Carbonylation of complex **1** (R = Me) afforded tolyl isocyanate as the major product; the yield was 8—12% with respect to the amount of the complex used. MS, m/z (I_{rel} (%)): 133 $[M]^+$ (92), 132 $[M - H]^+$ (25), 105 $[M - CO]^+$ (42), 104 $[M - HCO]^+$ (100), 91 $[M - CH_2CO]^+$ or $[M - CO - N]$ (13), 78 $[M - CO - NCH]^+$ (38), 77 $[M - HCO - NCH]^+$ (21), 63 $[M - NCO - C_2H_4]^+$ (8). The yield of AcOH was *ca.* 100% from the complex used.

Carbonylation of complex **2** (R = Me) produced phenyl isocyanate as the major product; the yield was 10—15% from the complex used. MS, m/z (I_{rel} (%)): 119 $[M]^+$ (100), 91 $[M - CO]$ (39), 64 $[M - CO - NCH]^+$ (87), 63 $[M - HCO - NCH]^+$ (39). The yield of AcOH was *ca.* 100% from the complex used.

Carbonylation of complex **2** (R = CF_3) afforded *N*-phenyltrifluoroacetamide. MS, m/z (I_{rel} (%)): 189 $[M]^+$ (84), 120 $[M - CF_3]^+$ (58), 92 $[M - CF_3 - CO]$ (61), 77 $[M - CF_3 - NHCO]^+$ (100), 65 $[M - CF_3 - CO - NCH]^+$ (54).

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