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Reduction of nitrosoarene ligands in binuclear palladium(II) complexes

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Reduction of the binuclear Pd^{II} complexes $Pd_2(OCOR)_2(o\text{-}CH_2C_6H_4{-}NO)_2$ (**1**) and $Pd_2(OCOR)_2(o\text{-}PhN{-}C_6H_4{-}NO)_2$ (**2**) (where R = Me, CF_3, Bu^t, or Ph) by sodium borohydride, an ethanolic solution of KOH, or molecular hydrogen was examined. The first stage of reduction was demonstrated to afford metallic palladium and aromatic amines, *viz.*, *o*-toluidine $o\text{-}Me{-}C_6H_4{-}NH_2$ from complex **1** and aniline $Ph{-}NH_2$ from complex **2**. The reactions with molecular hydrogen involve deeper stages to yield cyclic ketones (*o*-methylcyclohexanone and cyclohexanone) and then cycloalkanes (methylcyclohexane and cyclohexane, respectively). The latter reactions are accompanied by elimination of N_2. The mechanism of reduction of complexes **1** and **2** with molecular hydrogen was proposed.

Key words: palladium, reduction, nitrosoarenes, aromatic amines.

The reactivities of palladium complexes containing nitrosoarene ligands attract interest primarily because these complexes are formed and undergo subsequent conversions (primarily, reductive) in industrially important processes involving reduction of nitroarenes catalyzed by transition metal compounds.[1—5]

The data on the reactivities of nitrosoarene palladium complexes, which are of considerable interest for both the coordination chemistry of transition metals and metal-complex catalysis, are scarce.

With the aim of studying the reactivities of compounds of this type, we examined the behavior of the complexes $Pd_2(OCOR)_2(CH_2C_6H_4NO)_2$ (**1**) [6] and $Pd_2(OCOR)_2(PhNC_6H_4NO)_2$ (**2**) [7,8] (where R = Me, CF_3, Bu^t, or Ph), which we have synthesized previously, under the conditions of thermal decomposition and in reductive media.

Results and Discussion

Binuclear complexes **1** and **2**, in spite of particular structural differences (**1** involves the Me-metallated *o*-nitrosotoluene molecule, whereas **2** includes the phenyl-*o*-nitrosophenylamide ligand), contain the nitroso group, which is bound to the phenyl ring and is coordinated to the Pd atom through the Pd←N donor-acceptor bond. It is the behavior of the coordinated nitroso group in reductive media that is of prime interest.

The differential thermal analysis (DTA/TGA) demonstrated that decomposition of the complexes in the absence of solvents (dry thermolysis) under an Ar atmosphere started at 160 °C for complex **1** and at 195 °C for complex **2** and was accompanied by a substantial exothermic effect and sharp weight loss within a narrow temperature range (162—220 °C for **1**) (Fig. 1). In this case, palladium is reduced to Pd^0.

Thermolysis of complexes **1** (R = CF_3, Me, or Ph) in organic solvents (benzene, toluene, or *m*-xylene) at temperatures higher than 150 °C afforded metallic Pd, toluidine $Me{-}C_6H_4{-}NH_2$, and acetic acid or benzoic acid, respectively.

Complexes **1** and **2** were reduced to metallic palladium by sodium borohydride, an ethanolic solution of KOH, or molecular hydrogen even at ~20 °C.

The reactions of complexes **1** (R = Me, CF_3, or Ph) with $NaBH_4$ afforded the corresponding carboxylic acid or its salt, Pd^{II} was reduced to Pd^0, and the metallated nitroso ligand was reduced to *o*-toluidine in ~90% yield (Scheme 1).

Complexes **1** (R = CF_3) were reduced to metallic Pd and *o*-toluidine also under the action of an ethanolic

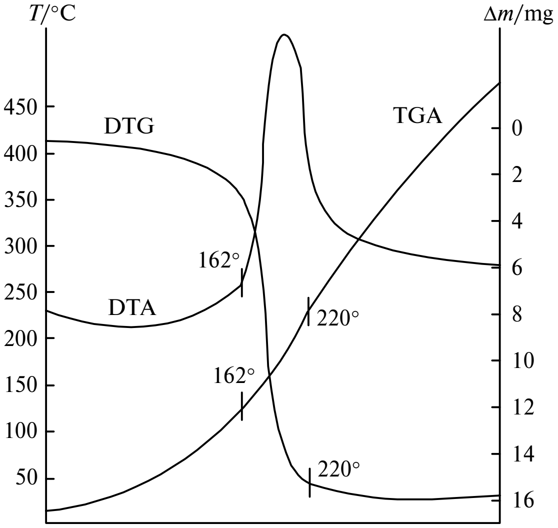

Fig. 1. DTA/TGA data for complex **1** (weighted sample 23.8 mg, total mass loss 14.5 mg (60.9%), resudue 9.3 mg (39.1%)).

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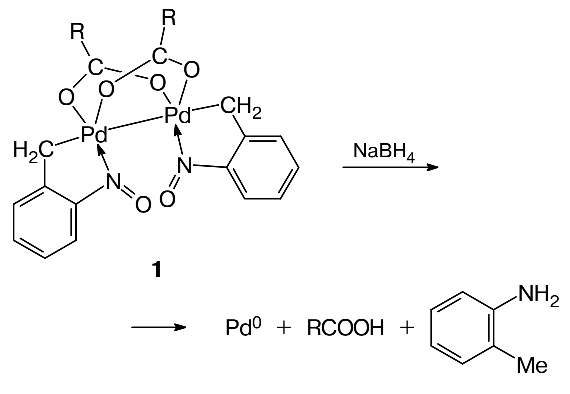
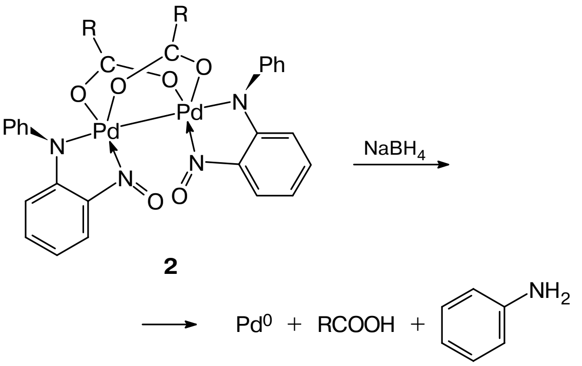
Scheme 1



solution of KOH. In this case, the amount of *o*-toluidine that formed was substantially lower than stoichiometric. Apparently, the starting organic substrates and those formed in the course of the reaction readily underwent condensation in a strongly alkaline medium to yield products, which were difficult to identify. The carboxylate groups present in the starting complexes were found as the KOOCR salts.

The reactions of complexes **2** (R = Me, CF_3, or Ph) with $NaBH_4$ also afforded metallic Pd and the corresponding carboxylic acid or its salt. The reactions gave rise to aniline instead of the expected products of reduction of the amide-containing nitroso ligand (*N*-(*o*-nitrosophenyl)-*N*-phenylamine or *N*-(*o*-aniline)-*N*-phenylamine). The yield of aniline was ~40% with respect to the starting complex (Scheme 2).

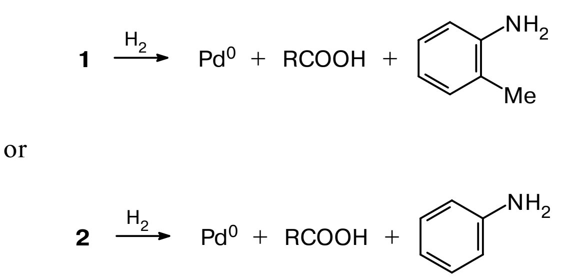
Scheme 2



Apparently, the reactions occurred with the cleavage of the PhN—C bond in the amide ligand accompanied by reduction both of the nitroso group and the phenylnitrene fragment to give aniline. Subsequent conversions of aniline, like those of toluidine in the above-considered reactions, in a reductive medium afforded products, which we failed to identify.

The reactions of complexes **1** and **2** with H_2 under mild conditions, like the reactions with $NaBH_4$, afforded initially metallic Pd and the corresponding aromatic amines (toluidine and aniline in 10—30% yields with respect to the starting complex) (Scheme 3).

Scheme 3



However, the latter reactions involved deeper stages. Upon subsequent hydrogenation of complex **1** (Fig. 2), the amount of toluidine decreased slowly and methylcyclohexanone (after 4—5 h) and then methylcyclohexane (after 45—50 h) were found in the reaction mixture; N_2 was detected in the gaseous phase (≤15% of the stoichiometric amount assuming that one N_2 molecule is formed from two nitroso groups). The total amount of methylcyclohexanone and methylcyclohexane was at most 15—20% with respect to the stoichiometry. We believe that the resulting toluidine was only partially consumed for the formation of methylcyclohexanone, which was subsequently reduced to methylcyclohexane.

The reactions of complexes **2** with H_2 proceeded analogously. The concentration of aniline first increased and then decreased in parallel with the increase in the concentrations of cyclohexanone and cyclohexane. In the gaseous phase, N_2 was also detected. The formation of methylcyclohexane upon hydrogenation of methylcyclohexanone and the generation of cyclohexane from cyclohexanone in the presence of palladium as a catalyst are readily explicable. However, the production of

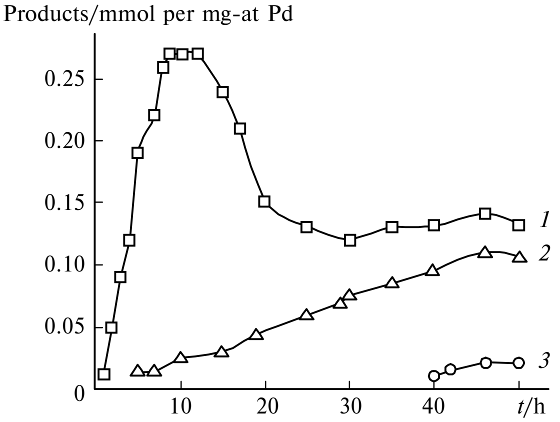
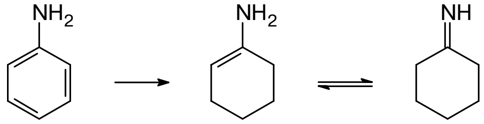


Fig. 2. Variation in time of the products of reaction of complex **1** with H_2: *1* — toluidine, *2* — methylcyclohexanone, *3* — methylcyclohexane.

methylcyclohexanone from toluidine as well as of cyclohexanone from aniline is unexpected. It can be suggested that either H_2O molecules or carboxylate groups serve as a source of O atoms in the formation of cyclic ketones. The ability of the coordinated carboxylate groups to act as donors of O atoms has been noted previously in a number of studies[9—12] on the chemistry of carboxylate palladium compounds.

The available data on hydrogenation of complexes **1** and **2** suggest that the formation of cyclic ketones, *viz.*, methylcyclohexanone from toluidine and cyclohexanone from aniline, accompanied by elimination of N_2 can proceed through several successive stages. First, aromatic amine is reduced (analogously to the Birch reduction[13,14]) to unsaturated cyclic amine (an unstable intermediate), which readily undergoes rearrangement into imine (imine-enamine tautomerism).



The resulting imine is subjected to hydrolysis (or acidolysis) with H_2O or carboxylic acid to give the corresponding cyclic ketone and ammonia. It seems likely that hydrolysis (or acidolysis) is favored by the decrease in the basicity of the imine through its coordination to Pd^{+2} as well as by the involvement of ammonia that formed into an amino complex of palladium.

Molecular nitrogen is generated, apparently, through intrasphere oxidation of ammonia (or amine), which is coordinated to palladium, resulting in reduction of Pd to Pd^0.

Experimental

Organic solvents were purified according to standard procedures.[16]

Palladium nitroso complexes $Pd_2(OCOR)_2(CH_2C_6H_4NO)_2$ (1) and $Pd_2(OCOR)_2(PhNC_6H_4NO)_2$ (2) (R = Me, CF_3, Bu^t, or Ph) were prepared according to procedures reported previously[7,8] from carbonyl carboxylate palladium complexes and the corresponding nitrosoaromatic compounds.

Nitrosoaromatic compounds *o*-$R'C_6H_4NO$ (R′ = H or Me) were prepared according to a general procedure[15] by oxidation of phenylhydroxylamine with sodium bichromate in aqueous H_2SO_4 (R′ = H) or by reduction of the corresponding nitro compound (R′ = Me). The resulting nitrosoarenes were isolated from the reaction mixture by azeotropic distillation with a water vapor under atmospheric or reduced pressure. The purities of the compounds were monitored by TLC on Silufol plates and based on the melting points. Taking into account that the nitroso group in nitrosoaromatic compounds is readily oxidized by atmospheric oxygen, nitrosoarenes were stored over a short period in Schlenk tubes under Ar in a refrigerator and all reactions involving these compounds were carried out under an inert atmosphere.

DTA/TGA analysis was performed on an OD-102 MOM derivatograph (Hungary) (plate platinum supports; an Ar atmosphere; the weights of the samples were 20—25 mg; the rate of heating was 10 deg min^{-1}). Gas-chromatographic analysis of gaseous reaction products was carried out on an LKhM-80 instrument (molecular sieves and Polysorb; the gas mixtures were analyzed for N_2, O_2, NO, and Ar). The liquid phases were analyzed by GLC on a 3700 chromatograph (an OV-101 column for analysis of cyclic hydrocarbons, cyclic ketones, and high-boiling aromatic amines; a REOPLEX column for analysis of low-boiling highly polar organic products). GLC-mass spectrometric analysis of organic products was carried out on an Automass instrument (Delsi Nermag, France; columns with PEG-20M phases for analysis of low-boiling highly polar organic products and SE-30 silicon for analysis of cyclic hydrocarbons, cyclic ketones, and high-boiling aromatic amines).

Thermolysis of the complexes was carried out in temperature-controlled tubes at 180 °C for 4—6 h. Complex **1** or **2** (0.25 mmol) was placed in a tube 6—7 mm in diameter and 20—25 cm in length. Then a solvent (benzene, toluene, or *m*-xylene; 2 mL) was added, the tube was evacuated, and the solvent was frozen in a Dewar vessel filled with liquid nitrogen. The tube was filled with argon (the operation was repeated three times to completely remove oxygen), sealed, heated to ~20 °C, placed in a thermostat, and heated to the reaction temperature. After completion of the reaction, the tube was cooled and opened. The liquid phase was analyzed by GLC-mass spectrometry and GLC.

Reduction of the complexes with sodium borohydride was carried out in tubes 6 mm in diameter and ~50 mm in height. The complex (~30 mg, 0.1 mmol) was placed in a pre-weighed dry tube, and $NaBH_4$ (1.0 mmol) was added. Then tetrahydrofuran (~0.25 mL) was rapidly added and the upper part of the tube was closed with a porous stopper. The reaction proceeded vigorously and was accompanied by the formation of metallic Pd and elimination of H_2. After completion of the reaction (the gas evolution ceased and the solvent turned colorless), the solution was analyzed by GLC and GLC-mass spectrometry.

Reaction of $Pd_2(CF_3COO)_2(CH_2C_6H_4NO)_2$ (2, R = CF_3) with an ethanolic solution of KOH was carried out according to the following procedure: the complex (0.1 mmol, 35 mg) was placed in a round-bottom flask and an ethanolic solution of KOH (10 mL, 2.5 mol L^{-1}) was added. The system was evacuated and purged with argon. The reaction mixture was stirred at 20 °C until the solution turned colorless (~5 min). Then the solution was filtered off from metallic Pd through a porous filter, which was preliminarily dried to a constant weight. The filtrate (a pale-yellow solution) was studied by GLC and GLC-mass spectrometry. The filter containing metallic Pd was brought to a constant weight at ≤100 °C (to prevent the formation of palladium oxide) and weighed. Metallic Pd was obtained in a yield of ~10 mg (0.1 mg-at. of Pd).

Studies of the reactions of complexes 1 and 2 with H_2 were carried out in a two-neck flask equipped with a magnetic stirred and a sampler for gas and liquid phases at 20 °C under the gas pressure of 1 atm. Complex **1** or **2** (0.25 mmol) was placed in a flask, a solvent (benzene or toluene; 2 mL) was added, the system was evacuated, H_2 was fed to the mixture, and the stirrer was turned on. The gaseous and liquid reaction products were analyzed in the course of the experiments during several weeks by GLC and GLC-mass spectrometry.

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References

1. *The Chemistry of Metal Cluster Complexes*, Eds. D. F. Shriver, H. D. Kaesz, and R. D. Adams, VCH, 1990.
2. R. G Arnold, J. A. Nelson, and J. J. Verbanc, *Chem. Rev.*, 1957, **57**, 47.
4. C. V. Wilson, *Org. Chem. Bull.*, 1963, **35**, 2.
5. G. Besenyei, L. Parkanyi, I. Foch, L. I. Simandi, and A. Kalman, *J. Chem. Soc.*, *Chem. Commun.*, 1997, 1143.
6. T. A. Stromnova, S. T. Orlova, I. P. Stolyarov, S. B. Katser, and I. I. Moiseev, *Dokl. Akad. Nauk SSSR,* 1997, **352**, 68 [*Dokl. Chem.*, 1997, **352**, 7 (Engl. Transl.)].
7. T. A. Stromnova, S. T. Orlova, D. N. Kazyul′kin, I. P. Stolyarov, and I. L. Eremenko, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 147 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 150].
8. S. T. Orlova, D. N. Kazyul′kin, D. V. Pashchenko, I. P. Stolyarov, and T. A. Stromnova, *Zh. Neorg. Khim.*, 2000, **45**, 472 [*Russ. J. Inorg. Chem.*, 2000, **45**, 406 (Engl. Transl.)].
9. T. A. Stromnova, N. Yu. Tikhonova, L. K. Shubochkin, and I. I. Moiseev, *Koord. Khim.,* 1993, **19**, 460 [*Russ. J. Coord. Chem.,* 1993, **19** (Engl. Transl.)].
10. I. I. Moiseev, T. A. Stromnova, and M. N. Vargaftik, *J. Molec. Catal.*, 1994, **86**, 71.
11. T. A. Stromnova and I. I. Moiseev, *Koord. Khim.,* 1998, **24**, 1 [*Russ. J. Coord. Chem.,* 1998, **24**, 227 (Engl. Transl.)].
12. I. I. Moiseev, T. A. Stromnova, and M. N. Vargaftik, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 807 [*Russ. Chem. Bull.*, 1998, **47**, 777 (Engl. Transl.)].
13. A. Birch and H. Smith, *Quart. Revs.*, 1958, **12**, 17.
14. A. Birch and D. Nasipuri, *Tetrahedron*, 1959, **6**, 148.
15. *Organic Syntheses*, Ed. C. F. H. Allen, New York, V. **20**, 1948.
16. A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, *Organic Solvents*, Interscience Publishers, Inc., New York, 1955.

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