Reactions of nitrosoarenes containing electron-withdrawing substituents with coordinated CO. Synthesis and structure of complexes $Pd_2(OAc)_2(p\text{-}ClC_6H_4N[p\text{-}ClC_6H_3NO])_2$ and $Pd_2(OAc)_2(o\text{-}ClC_6H_4N[o\text{-}ClC_6H_3NO])_2$

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The reaction of tetranuclear $Pd_4(\mu\text{-}COOCH_3)_4(\mu\text{-}CO)_4$ cluster (**1a**) with *p*- and *o*-chloronitrosobenzenes was found to give dinuclear nitrosoamide complexes, $Pd_2(OAc)_2(p\text{-}ClC_6H_4N[p\text{-}ClC_6H_3NO])_2$ (**4**) and $Pd_2(OAc)_2(o\text{-}ClC_6H_4N[o\text{-}ClC_6H_3NO])_2$ (**5**), respectively. The formation of complexes **4** and **5** is accompanied by evolution of CO_2, resulting from oxidation of CO coordinated in cluster **1**. Complexes **4** and **5** were characterized by elemental analysis and IR and ^1H NMR spectroscopy; their structures were studied by EXAFS. The reactions of dinuclear complex **4** with molecular hydrogen and CO were studied. The major products of reduction of **4** with hydrogen include metallic palladium, acetic acid, cyclohexanone, and molecular nitrogen. Treatment of complex **4** with CO under mild conditions (1 atm, 20 °C) affords *p*-chlorophenyl isocyanate.

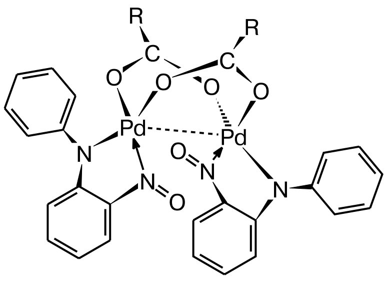
Key words: palladium, carbonyl complexes, clusters, nitrosoarenes, arylnitrenes, chloronitrosobenzene.

Palladium complexes containing nitrosoarene ligands are few and far in between.[1—8] Some of these have been prepared in our study dealing with the reactions of Pd^I carbonyl carboxylate clusters $Pd_4(\mu\text{-}COOR)_4(\mu\text{-}CO)_4$ (R = Me (**1a**), CF_3 (**1b**), Bu^t (**1c**), and Ph (**1d**)) with nitrosobenzene[9,10] and *o*-nitrosotoluene.[10,11] In this work, we studied the reactions of cluster **1a** with *p*- and *o*-chloronitrosobenzenes.

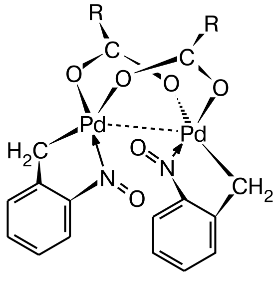
Results and Discussion

Early, we found[9—11] that the reactions of clusters **1** with nitrosobenzene and *o*-nitrosotoluene proceed through deoxygenation of the nitrosoarene molecule by the coordinated CO group to give CO_2 and an arylnitrene species, $[o\text{-}R'C_6H_4N:]$ (R´ = H and Me, respectively).

In the case of nitrosobenzene, the phenylnitrene species formed react with a second nitrosobenzene molecule, yielding finally dinuclear complex $Pd_2(\mu\text{-}COOR)_2(\eta^2\text{-}PhNC_6H_4NO)_2$ (**2a—c**), where the η^2-coordinated ligand can be considered as both a nitrosoarene derivative and an amide ligand containing a nitroso group.



2a—c



3a—d

R = Me (**a**), CF_3 (**b**), Bu^t (**c**), Ph (**d**)

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The reaction of **1** with *o*-nitrosotoluene furnishes the nitroso complexes $Pd_2(\mu\text{-}COOR)_2(\eta^2\text{-}CH_2C_6H_4NO)_2$ (**3a—d**) in which each Pd atom bears an *o*-nitrosotoluene molecule metallated at the Me group.

We assumed that the introduction of electron-withdrawing substituents into the nitrosoarene molecule can change the reaction pathway and the composition of products. Therefore, we studied the reactions of cluster **1a** with *o*- and *p*-chloronitrosobenzenes in which the substituents have similar electron-withdrawing properties but somewhat different steric factors.

Reactions of cluster 1a with *p*- and *o*-chloronitrosobenzenes. The reaction of cluster **1a** with *p*-chloronitrosobenzene at 50 °C is completed over 10—15 h (reaction with nitrosobenzene requires 4—5 h at the same temperature). Some of the coordinated carbonyl groups are oxidized to CO_2, the amount of the gas evolved being at most half the amount calculated from the stoichiometry (based on cluster **1**). By fractional crystallization, a greenish-brown powder was isolated from the reaction mixture. The elemental analysis of this product was in good agreement with the composition $C_{14}H_{10}Cl_2N_2O_3Pd$. This gross composition corresponds to a compound containing one acetate group per Pd atom and one nitrosoamide ligand $p\text{-}ClC_6H_4N[p\text{-}ClC_6H_3NO]$ (similar to the ligand, which arises upon the interaction of cluster **1** with nitrosobenzene). The ^1H NMR spectrum exhibits a signal for the acetate-group protons as a broadened singlet with a maximum at δ_H 2.1 and signals for the Ph-group protons as a broad multiplet with a maximum at δ_H 7.2. The ratio of the integral intensities of the proton signals of these ligands equals ~3 : 7, which confirms the presence of one acetate group (3 H) and one nitrosoamide group (7 H). According to IR spectroscopy data, the resulting complex contains bridging acetate groups ($\nu^{as}(COO) = 1552\ cm^{-1}$, $\nu^{s}(COO) = 1420\ cm^{-1}$, $\Delta\nu(COO) = 127\ cm^{-1}$) and, hence, the complex is at least a dimer. The composition of the complex can be described as $Pd_2(OAc)_2(p\text{-}ClC_6H_4N[p\text{-}ClC_6H_3NO])_2$ (**4**), *i.e.*, *p*-chloronitrosobenzene reacts with palladium carbonyl acetate in the same way as nitrosobenzene. The yield of complex **4** was ~50% based on cluster **1**, while the rest of Pd was found as Pd black (the yield of Pd black was also ~50%).

Thus, the electron-withdrawing effect of the substituent in the *para*-position of nitroso compound has an influence on the reaction rate but does not prevent the interaction of the resulting chlorophenylnitrene species with the *p*-chloronitrosobenzene molecule.

The reaction of carbonyl acetate cluster **1a** with *o*-chloronitrosobenzene proceeds similarly to the reaction described above. The enhancement of the steric hindrance in the molecule of substituted nitrosoarene increases the reaction duration at 50 °C to 15—20 h. The amount of carbon dioxide evolved also does not exceed half the stoichiometric amount based on cluster **1**. The C,H,N-elemental analysis data for the brown substance isolated by fractional crystallization are in good agreement with the molecular formula $C_{14}H_{10}Cl_2N_2O_3Pd$. The ^1H NMR spectrum contains a broadened singlet at δ_H 2.1, corresponding to protons of the AcO groups and a poorly resolved multiplet with a maximum at δ_H 7.0, corresponding to protons of the Ph groups. The integral intensities of the signals for the AcO- and Ph-group protons are related as ~3 : 7. In the IR spectrum of the complex, the bridging AcO groups are responsible for the bands with $\nu^{as}(COO) = 1560\ cm^{-1}$ and $\nu^{s}(COO) = 1450\ cm^{-1}$ ($\Delta\nu(COO) = 110\ cm^{-1}$). The data of C,H,N-analysis and IR and ^1H NMR spectroscopy indicate that this complex also contains nitrosoamide ligands, its composition being described as $Pd_2(OAc)_2(o\text{-}ClC_6H_4N[o\text{-}ClC_6H_3NO])_2$ (**5**).

The structures of complexes **4** and **5** were studied by EXAFS. In the simulation, the EXAFS spectra of complexes **4** and **5** were compared with the spectra of complex **2**, whose structure has been established by X-ray diffraction. In all cases, good agreement to within the accuracy of the method was attained. In the calculation, O and N were taken as the ligands nearest to Pd and all bond lengths for each ligand were taken to be equal. The spectra of the complexes show a set of distances corresponding to the Pd—O and Pd—N bonds in the range of 1.9—2.2 Å. This does not provide a reliable description of the coordination environment and, in particular, gives rise to underestimated effective coordination numbers.

The EXAFS data for complexes **2a**, **4**, and **5** and the X-ray diffraction data for **2a** are listed in Table 1. Comparative analysis of the data demonstrates that all complexes are in fact dimers with relatively short distances between the metal atoms linked by the bridging AcO groups. The underestimation of the Pd...Pd distance (2.74 Å) in the EXAFS spectrum of complex **2a** with respect to the distance derived from the X-ray diffraction data (2.84 Å) can be attributed to the large Debye factor caused by the pronounced nonrigidity of the complex

Table 1. Comparative analysis of the EXAFS data for complexes **2a**, **4**, and **5** and X-ray diffraction data for complex **2a**

Complex	Bond	EXAFS (X-ray diffraction) data		
		Bond length/Å	CN*	Debye factor
2a	Pd—N	2.05 (2.02, 1.98)	1.1 (2)	0.008
	Pd—O	1.99 (2.06)	1.1 (2)	0.001
	Pd—Pd	2.74 (2.84)	0.7 (1)	0.025
4	Pd—N	2.11	1.2	0.006
	Pd—O	2.00	1.3	0.004
	Pd—Pd	2.78	0.6	0.017
5	Pd—N	2.12	0.8	0.001
	Pd—O	2.01	1.4	0.001
	Pd—Pd	2.77	0.9	0.027

* The number of bonds of this type.

molecule and by the great amplitude of thermal vibrations of the metal atom. Apparently, the same situation holds for complexes **4** and **5**. Each metal atom is chelated by a nitrogen-containing arylnitrosoarene ligand, which is linked to the Pd atom through the N atoms of the amide and nitroso groups.

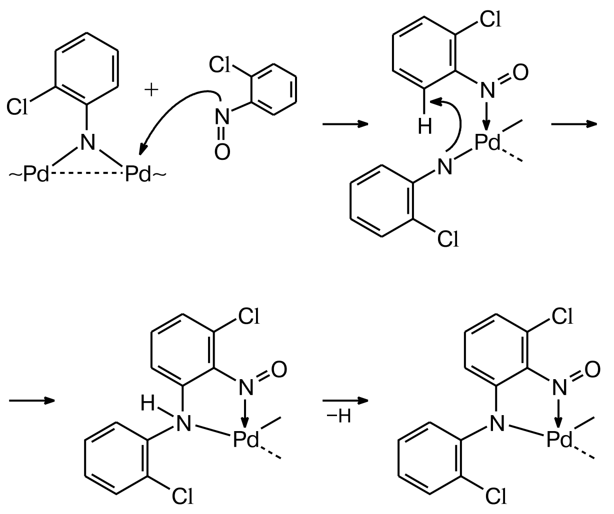
Thus, the reactions of carbonyl carboxylate clusters **1** with *o*- and *p*-chloronitrosobenzenes appear to proceed similarly to the reaction with nitrosobenzene. The first stage is elimination of the O atom from the chloronitrosobenzene molecule coordinated by the CO group giving rise to a chlorophenylnitrene species (Scheme 1).

Scheme 1

$$\sim\mathrm{Pd[CO]}\sim + \mathrm{Cl{-}C_6H_4{-}NO} \longrightarrow \mathrm{CO_2} + \sim\mathrm{Pd[Cl{-}C_6H_4{-}N{:}]}\sim$$

The subsequent transformations of the chlorophenylnitrene species include, as those of the phenylnitrene species, insertion into the C—H bond of the benzene ring of the second chloronitrosobenzene molecule yielding the nitrosoamide ligand $\mathrm{ClC_6H_4N[ClC_6H_3NO]}$. Apparently, in the reaction of cluster **1a** with *o*-chloronitrosobenzene, which has no C—H bond in position 2, the chloronitrene species is inserted in position 6 of the Ph ring (Scheme 2).

Scheme 2



Apart from the organopalladium products, the reaction of cluster **1** with *o*-chloronitrosobenzene yields a broad set of N-containing organic products, which were detected by GC/MS analysis. The analysis confirms the intermediate formation of the chlorophenylnitrene species during the reaction. Bis(2-chlorophenyl)diazene arises apparently upon dimerization of two chlorophenylnitrene species. *N*,*N*′-Bis(2-chlorophenyl)diazene *N*-oxide is the product of reaction of *o*-chlorophenylnitrene with *o*-chloronitrosobenzene. The insertion of *o*-chlorophenylnitrene species into the solvent (toluene) molecule affords 2-chlorophenyltolylamines. *o*-Chloroaniline may result from the reduction of *o*-chlorophenylnitrene. Finally, *o*-chlorophenyl isocyanate is produced in the reaction of *o*-chlorophenylnitrene with the coordinated carbonyl group.

Thus, the reaction of carbonyl carboxylate clusters **1** with *o*- and *p*-chloronitrosobenzenes proceeds similarly to the reaction with unsubstituted nitrosobenzene and gives finally dinuclear complexes with the chelating arylnitrosoarene ligand. The presence of electron-withdrawing atoms in the nitrosoarene molecule results only in a substantial retardation of the reaction, without influencing the composition or the structure of Pd-containing products.

Chemical properties of the complexes obtained. The chemical behavior of the synthesized compounds was studied in relation to complex **4**. The major products formed in the reaction of **4** with hydrogen include palladium metal, acetic acid, cyclohexanone, and molecular nitrogen (identified by GC); the two last-mentioned substances could be formed only from the chelating amide ligand. Judging by the final products, complex **4** reacts with H_2 similarly to complexes **2** and **3**.[12] The first step affords aromatic amine (Scheme 3).

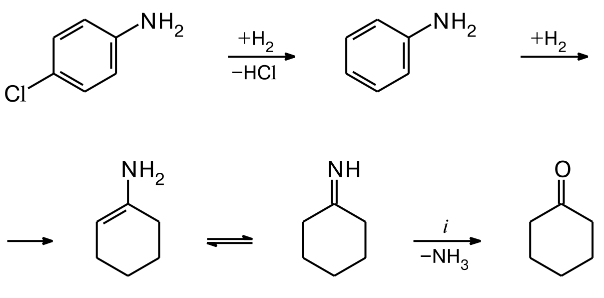
Scheme 3

$$\underset{\mathbf{4}}{\mathrm{Pd_2(OAc)_2(}p\mathrm{\text{-}ClC_6H_4N[}p\mathrm{\text{-}ClC_6H_3NO])_2}} + \mathrm{H_2} \longrightarrow$$

$$\longrightarrow \mathrm{Pd^0} + \mathrm{AcOH} + p\text{-}\mathrm{ClC_6H_4NH_2} + \ldots$$

Although we were unable to detect the intermediate products of transformation of the aromatic amine into cyclohexanone, we may consider that the process is similar to the transformation of complexes **2** and **3**. The reduction of aromatic amine yields an unstable unsaturated cyclic amine, which can rearrange into imine (imino—enamine tautomerism). On treatment with water

Scheme 4



i. H_2O or AcOH.

or carboxylic acid, the imine is converted into cyclic ketone and ammonia (Scheme 4).

Apparently, this hydrolysis (or acidolysis) is facilitated by a decrease in the basicity of the imine due to its coordination to the Pd^{II} atom and by binding of the ammonia evolved into the palladium amino complex. Molecular nitrogen is formed, most likely, in the inner-sphere oxidation of the Pd-coordinated ammonia (or amines).

Treatment of complex **4** with CO under mild conditions (1 atm, 20 °C, ~20 h) gives rise to *p*-chlorophenyl isocyanate (Scheme 5).

Scheme 5

$$\underset{\mathbf{4}}{Pd_2(OAc)_2(p\text{-}ClC_6H_4N[p\text{-}ClC_6H_3NO])_2} + CO \longrightarrow$$

$$\longrightarrow Pd^0 + AcOH + p\text{-}ClC_6H_4NCO$$

The results of this study indicate that the presence of electron-withdrawing substituents in the arylnitrosoarene ligand of complexes **4** and **5** does not affect much the behavior of these complexes in reducing media, and the compounds resulting from reductive decomposition are similar to those obtained upon the reduction of complex **2**.[12,13]

Experimental

Elemental microanalysis of the reaction products for carbon, nitrogen, and hydrogen was carried out using a C,H,N-analyzer (Carlo Erba, Italy). The IR spectra of complexes in the region of 400—4000 cm^{-1} were measured on a Specord M-80 spectrometer (as a suspension in mineral oil). The ^1H NMR spectra of complexes in CD_2Cl_2 solutions were recorded on a Varian-200 instrument (200 MHz).

The reaction products were analyzed by GC for CO, CO_2, O_2, H_2, Ar, N_2, and NO_x on an LKhM-80 instrument (molecular sieves and Polysorb). The liquid phase was analyzed by GLC on a 3700 chromatograph (OV-101 column for the analysis of cyclic hydrocarbons, cyclic ketones, and high-boiling aromatic amines; a REOPLEX column for the analysis of volatile polar organic products) and by CC/MS on an Automass instrument (Delsi Nermag, France) (columns with the silicon SE-30 phases for the analysis of cyclic hydrocarbons, cyclic ketones, and high-boiling aromatic amines, and with PEG-20M for the analysis of volatile polar organic products).

The palladium *K*-edge EXAFS absorption spectra were recorded on an EXAFS station of a VEPP-3 storage ring (Siberian Center of Synchrotron Radiation, Novosibirsk) with an electron beam energy of 2 GeV and an average current during measurement of 60 mA. A double single-block Si(111) monochromator crystal was used for monochromatization. No harmonic suppression was applied, because only the third harmonics (72 keV), whose intensity is negligibly low, is reflected from the monochromator crystal. The spectra were recorded at ~20 °C in the transmission mode using for detection ionization chambers filled with xenon (complete absorption) and an Ar—He mixture (1 : 1) (monitoring chamber) up to a pressure of 1 atm. The energy resolution was ~4 eV. Samples of the complexes were prepared by mixing the powder with Apieson and squashing the paste between two flat surfaces. The absorption jump in the palladium K-edge was 0.8—1.0.

The oscillating part of the absorption spectrum was cut out by a standard procedure[14] using the VIPER program package.[15] The pre-edge part of the absorption spectrum was interpolated to the EXAFS region by Victoreen polynomials. The smooth part of the absorption coefficient was simulated by three interpolating cubic splines. The inflection point at the edge of the absorption jump was taken as the initial point E_0 ($k = 0$). The spectrum was simulated by the $k^2\chi(k)$ function in the range of wave numbers of 3.5—15.0 $Å^{-1}$. The simulation was carried out using the EXCURV92 program.[16]

Organic solvents were purified by standard procedures.[17]

Nitrosoaromatic compounds, *p*- and *o*-ClC_6H_4NO, were prepared by the general procedure[18,19] by reduction of *p*- and *o*-chloronitrobenzene with zinc dust to *p*- and *o*-chlorophenylhydroxylamine followed by oxidation of phenylhydroxylamine with sodium dichromate in aqueous H_2SO_4 to the corresponding chloronitroso compound. The resulting chloronitrosoarenes were isolated from the reaction mixture by azeotropic distillation with steam under atmospheric pressure. The purity of compounds was checked by TLC on Silufol and on the basis of the melting point. Due to the possibility of oxidation of the nitroso group in nitrosoaromatic compounds with air oxygen, chloronitrosoarenes were stored for short periods in a Schlenk vessel under argon in refrigerators and all reactions with these compounds were carried out under argon.

Palladium carbonyl acetate $Pd_4(\mu\text{-}COOMe)_4(\mu\text{-}CO)_4$ (1a) was prepared by procedures reported previously.[20—22]

Syntheses of complexes 4 and 5 were carried out at 50 °C in a two-necked jacketed flask equipped with a magnetic stirrer, connected to a thermostat and to a gas burette for measuring the volume of the evolved gas and to a system for evacuation and filling with an inert gas (argon). The flask was charged with cluster **1** (1 mmol, 4 mg-at Pd). Then toluene (16 mL) was added, the system was evacuated and filled with argon, and the reaction mixture was stirred. A solution of chloronitroso compound (4 mmol) in 24 mL of toluene was added in an argon flow to the resulting suspension, the system was again purged with argon, and the mixture was stirred and heated to 50 °C. The reaction was monitored by volumetry based on CO_2 evolution. After completion of the reaction (10—20 h), the solution was filtered to remove the Pd black, toluene was completely evaporated at a reduced pressure, and the complex thus obtained was dissolved in CH_2Cl_2. The complex was isolated in two steps: precipitation with pentane from a partially concentrated solution in CH_2Cl_2, and, after repeated drying of the filtrate, dissolution of the residue in CH_2Cl_2, and concentration, precipitation with heptane (in the presence of a small amount of Et_2O in CH_2Cl_2). After collection on a filter, the product was dried *in vacuo* and stored under argon.

Bis(acetato)bis[2-(5-chloro-2-nitrosophenyl)-(4-chlorophenyl)amine]dipalladium, $Pd_2(OAc)_2(p\text{-}ClC_6H_4N[p\text{-}ClC_6H_3NO])_2$ (4). The reaction of cluster **1a** with *p*-chloronitrosobenzene was over within 10—15 h. A finely crystalline greenish-brown precipitate was isolated from the reaction mixture. Found (%): C, 38.73; N, 5.71. $C_{28}H_{20}Cl_4N_4O_6Pd_2$. Calculated (%): C, 38.94;

N, 6.49. IR, ν/cm^{-1}: 1632; 1552; 1420; 1088. ^{1}H NMR, δ: 2.10, 7.20 (both br.m). The ratio of the integral intensities of the signals of AcO- and Ph-group protons was ~3 : 7. The yield of compound **4** was 45—50% (based on Pd), decomp. point (in argon) 185 °C.

Bis(acetato)bis[2-(3-chloro-2-nitrosophenyl)-(2-chlorophenyl)amide]dipalladium, $Pd_2(OAc)_2(o\text{-}ClC_6H_4N[o\text{-}ClC_6H_3NO])_2$ (5). The reaction of cluster **1a** with *o*-chloronitrosobenzene was over within 15—20 h. A finely crystalline greenish-brown precipitate was isolated from the reaction mixture. Found (%): C, 37.24; N, 5.57. $C_{28}H_{20}Cl_4N_4O_6Pd_2$. Calculated (%): C, 38.94; N, 6.49. IR, ν/cm^{-1}: 1700; 1560; 1450; 1240. ^{1}H NMR, δ: 2.10, 7.00 (both br.m). The ratio of the integral intensities of the signals of AcO- and Ph-group protons was ~3 : 7. The yield of compound **5** was 50—60% (based on Pd).

GC/MS analysis of the reaction mixture revealed a mixture of organic products.

Bis(2-chlorophenyl)diazene. MS (EI, 70 eV), m/z (I_{rel} (%)): 252—250 $[M]^+$ (18—29), 152 $[M - C_5H_3Cl]^+$ (11), 141—139 $[M - C_6H_4Cl]^+$ (18—54), 113—111 $[M - C_6H_4Cl - N_2]^+$ (32—100), 85 $[M - C_6H_4Cl - N_2 - C_2H_2]^+$ (7), 75 $[M - C_6H_4Cl - N_2 - HCl]^+$ (71), 50 $[M - C_6H_4Cl - N_2 - C_2H_2 - Cl]^+$ (18).

***N,N´*-Bis(2-chlorophenyl)diazene *N*-oxide.** MS (EI, 70 eV), m/z (I_{rel} (%)): 268—266 $[M]^+$ (1—4), 252—250 $[M - O]^+$ (4—7), 233—231 $[M - Cl]^+$ (32—93), 168 $[M - C_5H_3Cl]^+$ (28), 152 $[M - C_5H_3Cl - O]^+$ (4), 141—139 $[M - C_6H_4Cl - O]^+$ (4—11), 127—125 $[M - C_5H_3Cl - O - NCH]^+$ (7—18), 113—111 $[M - C_6H_4Cl - O - N_2]^+$ (36—100), 101—99 $[M - C_5H_3Cl - O - CH - NCH - NC]^+$ (4—14), 90 $[M - C_5H_3Cl - O - NCH - Cl]^+$ (36), 75 $[M - C_5H_3Cl - O - CH - N_2 - HCl]^+$ (82).

2-Chlorophenyltolylamines. 2-Chlorophenyl-*o*-tolylamine, MS (EI, 70 eV), m/z (I_{rel} (%)): 219—217 $[M]^+$ (32—93), 182 $[M - Cl]^+$ (100), 180 $[M - H_2Cl]^+$ (93), 167 $[M - Cl - Me]^+$ (68), 106 $[M - Cl - C_6H_4]^+$ (7), 90 $[M - Cl - Me - C_6H_4 - H]^+$ (18). 2-Chlorophenyl-*p*-tolylamine, MS (EI, 70 eV), m/z (I_{rel} (%)): 219—217 $[M]^+$ (25—75), 182 $[M - Cl]^+$ (79), 180 $[M - H_2Cl]^+$ (29), 167 $[M - Cl - Me]^+$ (100), 90 $[M - Cl - Me - C_6H_4 - H]^+$ (11).

***o*-Chloroaniline.** MS (EI, 70 eV), m/z (I_{rel} (%)): 129—127 $[M]^+$ (35—100), 92 $[M - Cl]^+$ (21), 91 $[M - HCl]^+$ (7), 65 $[M - Cl - NCH]^+$ (35), 39 $[M - Cl - NCH - C_2H_2]^+$ (11).

***o*-Chlorophenyl isocyanate** MS (EI, 70 eV), m/z (I_{rel} (%)): 155—153 $[M]^+$ (33—100), 127—125 $[M - CO]^+$ (15—43), 98 $[M - CO - NCH]^+$ (6), 90 $[M - CO - Cl]^+$ (47), 63 $[M - CO - Cl - NCH]^+$ (25), 49 $[M - CO - Cl - NCH - CH_2]^+$ (4).

Reduction of nitrosoarene complex 4 with hydrogen or carbon monoxide was carried out at 20 °C and a gas pressure of 1 atm in a two-necked flask equipped with a stirrer and a sampler for gases and liquids. The flask was charged with the complex (0.25 mmol), 2 mL of a solvent (benzene or toluene) was added, and the system was evacuated. Then H_2 or CO was fed and the mixture was stirred. The gaseous and liquid reaction products were analyzed by GLC and GC/MS in the course of experiments, which lasted for several weeks for the reaction with H_2 and for 2—3 days for the reaction with CO.

In the reaction of complex **4** with H_2, cyclohexanone was detected in the reaction mixture. MS (EI, 70 eV), m/z (I_{rel} (%)): 98 $[M]^+$ (25), 83 $[M - Me]^+$ (8), 80 $[M - H_2O]^+$ (4), 70 $[M - CO]^+$ (17), 69 $[M - CHO]^+$ or $[M - Me - CH_2]^+$ (25), 56 $[M - CH_2CO]^+$ (13), 55 $[M - Me - 2\,CH_2]^+$ (79), 42 $[M - CH_2CO - CH_2]^+$ (100), 41 $[M - Me - 3\,CH_2]^+$ (50), 39 $[M - Me - 2\,CH_2 - O]^+$ (50).

In the carbonylation of complex **4**, AcOH and *p*-chlorophenyl isocyanate were the major products.

AcOH, MS (EI, 70 eV), m/z (I_{rel} (%)): 60 $[M]^+$ (46), 45 $[M - Me]^+$ (88), 44 $[M - O]^+$ (8), 43 $[M - OH]^+$ (100), 42 $[M - OH - H]^+$ (17).

p-ClC_6H_4NCO, MS (EI, 70 eV), m/z (I_{rel} (%)): 155—153 $[M]^+$ (33—100), 127—125 $[M - CO]^+$ (8—29), 98 $[M - CO - NCH]^+$ (2), 90 $[M - CO - Cl]^+$ (17), 85 $[M - CO - CH_2CN]^+$ (4), 63 $[M - CO - Cl - NCH]^+$ (33), 50 $[M - CO - CH_2CN - Cl]^+$ (17).

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