

NITROBENZENE REDUCTION CATALYZED BY SOLUBLE CARBONYLRHODIUM COMPLEXES OF METHYL AND DIMETHYL PYRIDINE LIGANDS

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ABSTRACT

The catalytic reduction of nitrobenzene by rhodium(I) complexes of the type *cis*-[Rh(CO)₂(amine)₂](PF₆) (amine = 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, or 2,6-dimethylpyridine) in methanol under an atmosphere of carbon monoxide is described. A single organic product, aniline, is seen in the post-reaction mixture. The amount of product formed depends upon the nature of the amine coordinated to the rhodium center.

Key Words: Catalysis, nitrobenzene reduction, rhodium complexes; carbon monoxide.

INTRODUCTION

Interests in the catalytic reduction of nitrobenzene to aniline under an atmosphere of CO/H₂O (Eq. [1]), promoted by transition metal complexes, has been shown in several recent investigations due to the great potential of this reaction for industrial applications.¹⁻³



The nature of the metal-containing active species formed by the catalysts during the reduction of such aromatic nitro compounds by CO and H₂O was partially dealt with in a review by Nomura⁴.

The ability of soluble cationic carbonylrhodium(I) complexes of pyridine and related ligands to be applied as catalysts for the carbonylation of methanol has been demonstrated⁵, as has their ability to function as catalysts for the oligomerization of CO/ethylene⁶ and the hydroformylation-acetalization of 1-hexene⁷. The utility of these types of complexes in the preceding reactions have been realized due, in part, to their easy preparation, good stability, high or moderate catalytic activities and the fine balance that is had between the electronic and steric effects induced by the methyl group on the pyridinic ring.

Work in our laboratories have long been concerned with the use of soluble *cis*-[Rh(CO)₂(amine)₂](PF₆) complexes (amine = 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, or 2,6-dimethylpyridine) or the analogous complexes immobilized on poly(4-vinylpyridine) as catalysts for the reduction of nitrobenzene⁸⁻¹⁰ and nitrofurans¹¹ under CO/H₂O. However, little is known about the carbonylation of nitrobenzene by these Rh/pyridine systems in an alcoholic solvent under a CO atmosphere.

We report in the present study the influence of the nature of the coordinated methyl- or dimethylamine on the catalytic reduction of nitrobenzene to aniline by these rhodium(I) complexes.

EXPERIMENTAL

Materials: methyl pyridines and 2,6-dimethyl pyridine were obtained from Aldrich and distilled over KOH. Methanol (Aldrich) was distilled prior to use. Nitrobenzene (Aldrich) was distilled from H₂SO₄ (1M) and redistilled from CaCl₂ before use. All gas mixtures (He/H₂ (91.4%/8.6%, v/v), CO/CH₄ (95.8%/4.2%, v/v) and CO/CH₄/CO₂/H₂ (84.8%/5.1%/5.3%/4.8%, v/v)) were purchased from BOC Gases and used as received. Metal complexes of the type *cis*-[Rh(CO)₂(amine)₂](PF₆) (amine = 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, or 2,6-dimethylpyridine) were synthesized and characterized as reported by Denise and Pannetier¹² and their identity and purity confirmed by their IR spectra in chloroform (two strong bands in the ν_(CO) region at 2095 and 2020 cm⁻¹).

Instrumentation: Gas sample analyses from catalysis runs were performed as previously detailed¹³ on a Hewlett-Packard 5890 Series II programmable (ChemStation) gas chromatograph equipped with a thermal conductivity detector. The column employed was Carbosieve-B (80-100 mesh) obtained from Hewlett-Packard. The instrument was programmed with a temperature ramp from 60 to 175 °C at a He/H₂ carrier-gas flow rate of 50 mL/min. Analyses of the liquid phases were done on a Buck Scientific 910 programmable gas chromatograph equipped with an apiezon column and a flame ionization detector. The instrument was ramped from 60 to 160 °C at a He carrier-gas flow rate of 30 mL/min. A Hewlett-Packard 6890 Series programmable gas chromatograph fitted with a HP-1 (crosslinked methylsiloxane) (10 m x 0.25 mm x 0.5 μm) column was used to confirm the identity of the organic reaction products at the end of each run. The organic product was also separated by column chromatography and analyzed by ¹³C and ¹H-NMR in a Jeol Eclipse 270 NMR spectrometer (δ_c = 146.6, 129.3, 118.4 and 115.1 ppm and δ_H = 7.1, 6.7, 6.6 and 3.6 ppm).

Catalytic tests: Catalytic runs were carried out in a 30 mL mechanically stirred stainless steel Parr autoclave charged with 1 x 10⁻⁴ mol of the *cis*-[Rh(CO)₂(amine)₂](PF₆) complexes, 10 mL of methanol, 0.26 mL (2 x 10⁻³ mol) of nitrobenzene pressurized with CO/CH₄ (30 atm). The autoclave was placed in a temperature-controlled heating device at 150 ± 1 °C and mechanically stirred for 6 h. These pressures and temperatures were chosen by taking an average from previously reported systems.¹⁴ At the end of the set reaction time gas and liquid samples were taken and analyzed by GC. Identity of the products was confirmed by GC-MS. A response factor method for the GC analyses of the aniline was employed.¹⁵ The GC-MS spectrum of the aniline (molecular ion peak at m/e = 93 and base peak at m/e = 66) product is comparable to the obtained from a pure sample of aniline. Methane was used as an internal standard to allow calculation of absolute quantities of CO consumed and CO₂ produced in 6 h with calibration curves being prepared periodically for CO, CH₄ and CO₂.

RESULTS AND DISCUSSION

The *cis*-[Rh(CO)₂(amine)₂](PF₆) complexes were examined as catalytic precursors for the reduction of nitrobenzene to aniline under CO. The results are summarized in Table I. Control experiments showed no reduction of nitrobenzene to aniline under CO when a mixture of methanol and nitrobenzene were exposed to similar experimental conditions as those in our catalytic tests in the absence of one of our carbonylrhodium catalysts. Even though the reagents and solvents used were pre-dried some residual water always remained. In addition, in situ generation of water occurred via methanol dimerization, Eq. [2], under the catalytic conditions (150 °C). The GC analyses of the gas phase of the catalytic runs allowed for the identification of CO₂ as a sole gaseous product in accordance with Eq. [1]. The relative amounts of aniline and CO₂ produced matched stoichiometrically as required by Eq. [1] (CO₂/aniline ca. 3.1).



Table I. Reduction of nitrobenzene by *cis*-[Rh(CO)₂(amine)₂](PF₆) complexes under CO/H₂O^a.

Amine (pKa) ^b	Yield of CO ₂ (mol x 10 ⁻³) ^c	Yield of aniline (mol x 10 ⁻³) ^c	Nitrobenzene conversion (%) ^c	TF(aniline) ^d
3-methylpyridine (5.52)	5.9	1.9	100	315
2-methylpyridine (5.97)	1.1	0.4	16	64
4-methylpyridine (6.00)	5.8	2.0	100	385
2,6-dimethylpyridine (6.75)	2.8	0.9	49	124

^a[Rh] = 1 x 10⁻⁴ mol, 0.26 mL (2 x 10⁻³ mol) of nitrobenzene, 4-nitrobenzene/Rh molar ratio = 25, 10 mL of methanol, P(CO) = 30 atm at 150 °C by 6 h.

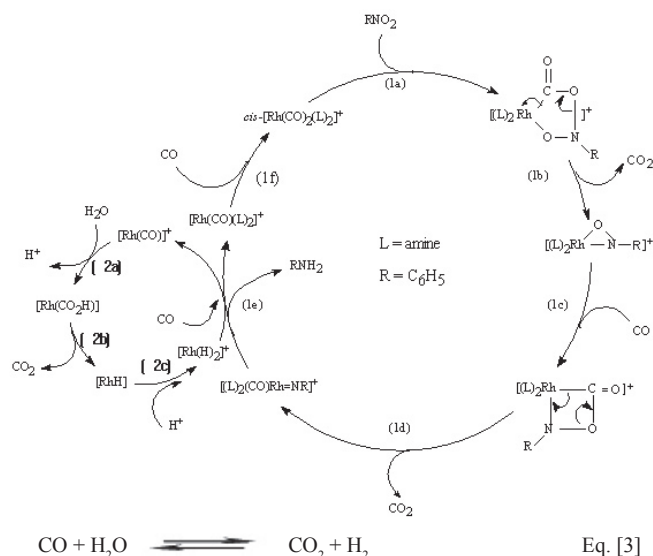
^bFrom Ref. [12].

^cAfter 6 h.

^dTF(aniline) = [(mol of aniline)/(mol of Rh) x (rt)] x 24 h, where (rt) = reaction time in hours. Experimental uncertainty < 10%.

The results show that the turnover frequency per day values (TF(aniline)/24 h) depend on the nature of the coordinated amine and decrease in the following order: 4-methylpyridine > 3-methylpyridine > 2,6-dimethylpyridine > 2-methylpyridine. Accordingly, the catalytic nitrobenzene reduction by these Rh(amine)₂ complexes appears influenced by the basic nature of the amine, with the Rh(4-methylpyridine)₂ system the most active. The observed reverse order in the case of the Rh(2-methylpyridine)₂ system is likely due to the steric factor which overwhelms the electronics of the ligands. It is interesting to see on the Rh(2,6-dimethylpyridine)₂ system that the steric factor does not completely overwhelm the electronic factor although the 2,6-dimethylpyridine amine sterically crowds the metal center more than any other amine used in this work. Surprisingly, these results are different from the previous results reported on the catalytic reduction of nitrobenzene to aniline by the Rh(amine)₂ system under CO in aqueous amine solution⁸. The activity of the Rh(2-methylpyridine)₂ complex was maximized (TF(aniline) 42 (24 h)⁻¹) under the following conditions: [Rh] = 10 mM, [substrate]/[Rh] = 2500, 8 mL of amine, 2 mL of H₂O, P(CO) = 0.9 atm at T = 100 °C for 3 h. As we can see, both Rh/aqueous amine and Rh/methanol catalytic system differ with the nature of the reaction medium and with the reaction conditions, with both having a strong influence on the reaction rate. It is likely that the nature of the catalytic species varies across the systems. *In situ* FT-IR and ¹H and ¹³C characterization studies of these Rh(amine)₂/methanol system under CO are in progress and should give some insight on the nature of the catalytic intermediates. Similar studies of the Rh(amine)₂/aqueous amine system have revealed the presence of Rh-H species as well as the formation of aminocarbonyl-Rh species with different nuclearities^{17,18}.

The promoting effect of water in this reduction process has been related to the formation of an active rhodium-hydride (Rh-H) species (steps 2b and 2c, Scheme I), important steps in the catalytic cycle, via a reaction closely related to the water gas shift reaction (WGS, Eq. [3])¹⁹. Accordingly, it should be possible that these (Rh-H and Rh-H₂) species reacts with a rhodium-nitrene intermediate^{20,21} (step 1e) to give aniline. Catalytic schemes for the reduction of nitrobenzene to aniline have been proposed in which nitrobenzene cycloaddition (step 1a) to a metal carbonyl complex is an important first step¹. A detailed discussion of similar mechanistic schemes proposed for the reduction of nitro compounds under CO/H₂O catalyzed by rhodium^{2,11} and copper³ complexes have been reported.

**Scheme 1.** Proposed mechanism.

The reductive carbonylation of nitrobenzene to N-phenylmethylcarbamates in the presence of methanol under an atmosphere of CO catalyzed by rhodium complexes has been reported (Eq. [4]).^{14,22,23} With these Rh(amine)₂ systems, however, such direct conversion of nitrobenzene to the carbamate was not observed, with aniline being the only observed product.



The absence of carbamate from the products of the reaction under CO pressure used in this work (30 atm) can be explained based not only on the fact that carbamates are usually formed under much higher CO pressures (> 60 atm)^{22,23} but also on the known ability of these Rh(amine)₂ system to be selective in their catalytic reduction of nitrobenzene to aniline in aqueous amine solutions⁸, as previously mentioned. The Rh(amine)₂/methanol system favors the formation of aniline rather than the corresponding carbamate in the presence of trace amounts of water. In this case the role of the methanol is principally as a solvent for these rhodium complexes rather than to form a reactive compound (Eq. [4]). Accordingly, these results illustrate again the high selectivity of these Rh(amine)₂ system for the catalytic reduction of nitrobenzene to aniline under CO/H₂O.

It is worth mentioning that other kinds of amine ligands have been used in the reduction of nitrobenzene to aniline by rhodium complexes. Namely, Kaneda et al.²⁴ reported the use of following aliphatic amines in the presence of Rh₆(CO)₁₆ under CO (0.9 atm) at 80 °C for 2.5, 4 or 10 h: NH₂(CH₂)₃NH₂, NH₂(CH₂)₄NH₂, NH₂(CH₂)₅NH₂, NH₂(CH₂)₆NH₂, NH₂(CH₂)₇NH₂, NH₂(CH₂)₈NH₂, NH₂(CH₂)₉NH₂, NH₂(CH₂)₁₀NH₂, NH₂(CH₂)₁₁NH₂, NH₂(CH₂)₁₂NH₂, NH₂(CH₂)₁₃NH₂, NH₂(CH₂)₁₄NH₂, NH₂(CH₂)₁₅NH₂, NH₂(CH₂)₁₆NH₂, NH₂(CH₂)₁₇NH₂, NH₂(CH₂)₁₈NH₂, NH₂(CH₂)₁₉NH₂, NH₂(CH₂)₂₀NH₂. They found that increasing the length of the hydrocarbon chain in NH₂(CH₂)_nNH₂ increases the conversion to aniline (from 34 to 50%) and among the alkyldiamines, methyl substituents on the nitrogen promote the conversion (from 45 to 100%). Alessio et al.²⁵ reported the use of pyridine, 2,2'-bipyridine (bipy), 4,4'-Me₂bipy, phenantrolinone (phen), 4,7-Me₂phen, 3,4,7,8-Me₄phen and 3,4,5,6,7,8-Me₆phen as ligands in the same type of reactions, observing a progressive increase of conversion to aniline (from 0, 0.8, 3.0, 7.5, 25, 53 to 73%, respectively) in the presence of Rh₆(CO)₁₆ under CO (30 atm) at 165 °C. Unfortunately, TF(aniline) values were not reported in these two works negating any comparison with our catalytic system.

Ford, et. al.² also reported an efficient catalytic system based on RhCl₃/amine (amine = diethylamine, trimethylamine, triethylamine, tetramethylenediamine, 2-methylamine, or tetramethylethylenediamine) for the reduction of nitrobenzene to aniline. The TF(aniline)/24 h values followed the order tetr amethylethylenediamine (131) > 2-methylamine (78) > triethylamine (31) > tetramethylenediamine (20) > diethylamine (17) > trimethylamine (13) under the following reaction conditions: [Rh] = 5 mmol, 10 mL of amine/water 8/2 (v/v), P(CO) = 0.9 atm at 100 °C for 3h. The reaction conditions used in the RhCl₃/amine catalytic system are milder than those employed in our Rh(amine)₂

catalytic system. The results show the RhCl₃/amine catalytic systems are more active than ours based on Rh(amine)₂. However, in comparison with our system the former used a large amount of water which could affect a different mechanism of action and strongly influence the observed difference.

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