Journal of Organometallic Chemistry, 368 (1989) 357–365
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09818

Catalytic reduction of nitroaromatics with carbon monoxide and water using tricarbonyltetraphenylcyclopentadienone ruthenium(0)

Youval Shvo * and Dorotha Czarkie

School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978 (Israel)

(Received December 2nd, 1988)

Abstract

The complex (η^4-$Ph_4C_4C{=}O$)$(CO)_3Ru$ (**1**) is a catalyst precursor in the reduction reaction of nitroarenes to anilines by CO and H_2O. Azoxybenzenes and azobenzenes are by-products formed in variable quantities depending on the reaction conditions and the nature of the nitroarene used. Analysis of the reaction solution in the reaction involving nitrobenzene has revealed the presence of several complexes, including (η^4-$Ph_4C_4C{=}O$)$(CO)_2Ru(H_2NPh)$ (**5**), which was prepared independently; The behaviour of **5** under catalysis conditions was studied. Complex **1** did not catalyze hydrogenation of nitrobenzene. A multi-step catalytic reduction scheme is proposed.

Introduction

Aminoarenes, the primary source of sundry aromatic nitrogen compounds, can be produced by reduction of the corresponding nitroarenes. Commonly, dihydrogen, and hydrogen chloride serve as hydrogen sources for the reduction. Cyclohexene [1], alcohols [2], amines [3] and formic acid [4] have also been used as the hydrogen source in catalytic H-transfer reactions to nitroarenes.

Carbon monoxide and water provide a unique hydrogen source in the water-gas shift reaction (WGSR). However, the in situ hydrogenation of organic substrates with CO and H_2O does not necessarily require the generation of nascent dihydrogen. The application of the WGSR to the reduction of nitroarenes has been previously demonstrated [5]. In a recent comparative study of the reduction of $PhNO_2$ with H_2, CO/H_2 or CO/H_2O, several ruthenium(II) complexes were examined [6]. Highest turnover numbers were achieved with the last system and turnover numbers of ca. 1000 were obtained with several rhodium complexes [7]. A study of the reduction of substituted nitrobenzenes using ionic ruthenium complexes

0022-328X/89/$03.50

revealed only small effects [8]. A marked lowering of the reaction temperature and pressure was achieved under phase transfer-catalyzed reduction conditions with $PhNO_2$ in aqueous NaOH and CO [9]. $Ru_3(CO)_{12}$, in the presence of various amine ligands, was found to catalyze the reduction of $PhNO_2$ under WGSR conditions [10].

Results and discussion

We have previously described examples of the homogeneous hydrogenation of alkynes, alkenes, and carbonyl compounds under relatively mild conditions using carbonyl cyclopentadienone-ruthenium complexes [11,12]. As a continuation of our systematic investigation of the catalytic properties of this type of complex, we now report on their reactions with nitroarenes in the presence of CO and H_2O. The catalyst precursors used were tricarbonyl(η^4-tetraphenylcyclopentadienone)Ru (**1**), an air stable compound of a known structure [13], and, **2**, a *p*-chlorophenyl derivative of **1**. The reactions were carried out in a stainless steel (316) reactor (35 ml) equipped with a sampling valve and manometer. A typical reaction profile is shown in Fig. 1 (identical rates were found when an internal glass sleeve was used). No reaction was detected in absence of the precatalyst **1**. The extent of conversion of nitrobenzene and the product distribution were determined by GC analysis using the appropriate standards. The results are listed in Table 1. The stoichiometry of the reduction reaction is shown in eq. 1, and it will be seen that no pressure change occurs during the reaction. In all experiments water and CO were present in excess relative to the stoichiometric quantity of $PhNO_2$.

$$PhNO_2 + 3CO + H_2O \rightarrow PhNH_2 + 3CO_2 \qquad (1)$$

The reduction of nitrobenzene is only slightly accelerated by added base, but markedly retarded in the presence of acetic and trifluoroacetic acids. Such an effect has been observed previously, and interpreted in terms of protonation of an oxygen

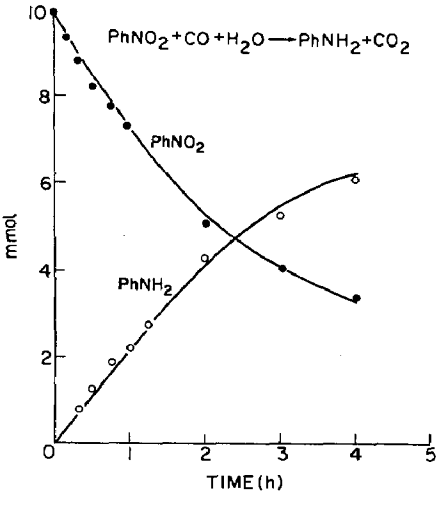

Fig. 1. Reduction profile of nitrobenzene in THF solution. Concentrations (*M*): $PhNO_2$ 1.0; H_2O 5.6; HCO_2Na 0.1; $(Ph_4C_4CO)(CO)_3Ru$ (**1**) 0.007; CO 500 psi. Temperature 105 °C.

Table 1 [a]

Reduction of nitrobenzene with $(Ph_4C_4CO)(CO)_3Ru$ (**1**) and $[(2,5\text{-}Ph)_2(3,4\text{-}p\text{-}Cl\text{-}Ph)_2C_4C{=}O](CO)_3Ru$ (**2**)

Catalyst	Additive	Time (h)	Conversion (%)	Product distribution (mol%)		
				$PhNH_2$	PhNNPh	PhNN(O)Ph
1		4	69.7	82.9	0.3	16.8
		22	100.0	92.1	0.3	7.6
1 [b]		4	85.6	48.7	1.9	49.4
		22	100.0	54.1	9.5	36.4
1 [c]		4	52.7	82.8	0.3	16.9
		22	100.0	90.7	1.1	8.2
1	Na_2CO_3	4	90.7	81.5	0.3	18.2
		22	100.0	85.9	0.6	13.5
1	$NaHCO_2$	4	79.2	97.5	0.2	2.3
		22	100.0	98.7	0.9	0.4
1	CH_3COOH	4	31.0	96.2	0.7	3.1
		22	84.3	97.1	2.9	0.0
1	CF_3COOH	4	0.0	0.0	0.0	0.0
		22	5.0	100.0	0.0	0.0
2		4	85.3	75.6	0.7	23.7
		22	100.0	88.1	0.6	11.3
2	Na_2CO_3	4	63.0	91.1	8.4	0.5
		22	100.0	94.6	4.8	0.6

[a] Standard reaction conditions: Catalyst, 0.07 mmol; Nitrobenzene, 10.0 mmol; H_2O, 56 mmol; THF (purified), to a total volume of 10.0 ml; CO, 500 psi at room temperature; T 105 ° C; additives, 1.0 mmol. [b] H_2O, 28 mmol. [c] H_2O, 84 mmol.

atom of the nitro group, thus blocking its coordination to the metal [6]. Although the selectivity toward aniline is high, two by-products are produced: azobenzene and azoxybenzene. Consistently, the concentration of azoxybenzene diminishes with time, while that of azobenzene increases in most experiments. In a separate experiment we found that azoxybenzene, under the standard reaction conditions is slowly reduced to a mixture of azobenzene (11%) and aniline (3%) during 22 h, thus accounting for most of the concentration changes of the two by-products with time (Table 1).

The formation of azoxybenzene and azobenzene is indicative of the presence in the reaction mixture of nitrosobenzene; this was not isolated but could be detected during the reaction by observation of a small peak in the GLC a (estimated at 2–3% mol). Although PhNO could have been formed via reaction 2 in the first step of the reduction process, nitrobenzene was found to be unreactive under these conditions, i.e. in the absence of water. It turns out that nitrosobenzene can undergo a thermal disproportionation reaction (eq. 3) [14].

$$PhNO_2 + CO \xrightarrow{(1)} PhNO - CO_2 \text{ (no reaction)} \tag{2}$$

$$3PhNO \rightarrow PhNO_2 + PhNN(O)Ph \tag{3}$$

$$PhNO + CO + H_2O \xrightarrow[THF]{(1)} \underset{6\%}{PhNH_2} + \underset{4\%}{PhNNPh} + \underset{90\%}{PhNN(O)Ph} \tag{4}$$

Thus, when PhNO was subjected to our standard WGSR conditions with **1** as catalyst, the predominating product (90%) was azoxybenzene (eq. 4), with 97%

Table 2 [a]

Reduction of X-$C_6H_4NO_2$ with **1**

Substituent (X)	Time (h)	Conversion (%)	Product distribution [b]		
			X-Aryl Amine	X-Aryl Azo	X-Aryl Azoxy
p-NH_2	4	2.7	100	–	–
	22	26.0	100	–	–
m-NH_2	4	16.2	100	–	–
	22	43.5	100	–	–
p-OCH_3	4	6.5	100	–	–
	22	26.0	100	–	–
m-OCH_3	4	7.7	100	–	–
	22	29.2	100	–	–
p-OH	4	28.0	100	–	–
	22	67.0	100	–	–
m-OH	4	18.3	100	–	–
	22	66.1	100	–	–
o-CH_3	4	9.5	100	–	–
	22	27.8	100	–	–
m-CH_3	4	47.2	96	0.5	3.5
	22	98.9	98	–	2.0
H	4	71	66	1.0	4.0
	22	100	93	3.0	4.0
p-Cl	4	64.1	61	1.5	3.5
	22	100.0	87.1	0.8	1.2
m-NO_2	4	100.0	18.9 [c]	45.3 [d]	35.8 [e]

[a] Reaction conditions: $(Ph_4C_4CO)Ru(CO)_3$ (**1**), 0.07 mmol; nitro copmound, 10 mmol; H_2O, 56 mmol; HCOONa, 1 mmol; THF volume to make up to 10 ml; CO pressure at ambient temperature, 500 psi; reaction temperature 105 ° C. [b] Product distributions were determined by GLC and are presented as area % of the relevant signals. [c] This figure refers to *m*-nitroaniline. [d] 3,3′-Dinitroazobenzene and 3-amino-3-nitroazobenzene, ca. 1/1 area % ratio. [e] 3-Amino-3′-nitro azoxybenzene.

conversion after 1 h. Similar behaviour was also noted in the absence of catalyst and also that of CO and water, although the stoichiometry of reaction 3 was not observed in either experiment. Therefore, regardless of the mechanism, PhNO can react thermally under our WGSR conditions, without the intervention of a catalyst, to give azoxybenzene.

It is very likely that free nitrosobenzene is an intermediate in the reduction of nitrobenzene to aniline (vide infra) and not a by-product of a catalytic cycle. Attempted reduction of PhNO under the standard reaction conditions (eq. 4) gave mainly azoxybenzene, with aniline as a minor product. However it should be recalled that the initial concentration of PhNO in reaction 4 is ca. one order of magnitude greater than the steady state concentration of PhNO in reaction 1. Azobenzene must be formed in a reaction between PhNO and aniline or by the reduction of azoxybenzene under the reaction conditions (vide supra).

Halving the water concentration substantially increased the formation of azoxybenzene (2nd entry; Table 1), most probably by slowing the rate of the reduction steps. Best selectivity (at good conversion) was achieved using catalyst **2** in the presence of sodium carbonate.

The reduction of a nitro group of substituted nitroarenes was also studied (Table 2). Whenever necessary a correlation of GC-MS signals for identification purposes was carried out. All experiments were performed in the presence of sodium formate (catalytic) which was found to accelerate the reduction slightly. Examination of the conversion data (Table 2) clearly reveals that electron-withdrawing groups accelerates the reduction of the nitro group (2.7 vs. 100% conversion of *p*-nitroaniline and *m*-dinitrobenzene respectively in 4 h). The difference in reduction rates between the *p*- and *m*-substituted nitrobenzenes is small, except in the case of the nitrotoluenes, for which they differ by a factor of ca. 5. It was expected that electron-poor substrates would be reduced faster than electron-rich substrates, but with $RuHCl(CO)(PPh_3)_3$, under similar conditions, the opposite trend was observed; it was argued that a mono- rather than a di-hydride complex is the active catalytic species [6].

The selectivity for the substituted anilines is excellent with the series of nitrobenzenes substituted with electron-donating groups, and falls sharply upon passing to electron-withdrawing groups, and is especially poor with *m*-dinitrobenzene.

In order to gain some insight into the mechanism of reaction 1, we carried out additional experiments, which led to the following observations:

(a) Complex **1** did not induce catalytic H-transfer from ethanol or formic acid to nitrobenzene.

(b) No carbamates could be detected when the water in reaction 1 was replaced by ethanol.

(c) Surprisingly, complex **1** did not induce the reduction of nitrobenzene with dihydrogen (500 psi) in THF at 105 °C in the presence or absence of water.

(d) A solution of nitrosobenzene in THF when subjected to hydrogen pressure (500 psi) at 105 °C was, after 0.5 h, quantitatively converted into a mixture of aniline (20%) and azoxybenzene (80%).

We recall that **1** is a catalyst precursor in H-transfer reactions from alcohols to ketones (eq. 5a), as well as in the hydrogenation of ketone with dihydrogen and with $CO + H_2O$ (eq. 5b and 5c). In all of these reactions we have previously identified the catalytic reactive species **3**, $(\eta^5\text{-}Ph_4C_4COH)(CO)_2RuH$ [11], stable only in solution under inert atmosphere.

$$R_2C{=}O \xrightarrow[\text{(c) } CO + H_2O\ [12]]{\substack{\text{(a) Alcohols [15]} \\ \text{(b) Dihydrogen [11]}}} R_2CHOH \tag{5}$$

In view of observations a and c, we must conclude:

1. That **3** is not a catalytically reactive species in the slow step of nitroarene reduction with **1** (eq. 1).
2. No dihydrogen is involved in the slow step of reaction 1.

The infrared spectrum of the CO region of reaction 1 exhibited bands at 2018 and 1957 cm^{-1}. These frequencies practically coincide with those exhibited by the reaction mixtures represented by eq. 5a–5c (2014, 1954 cm^{-1}), and have been assigned to the hydridic species **3** [11,12,15]. If we assign the spectrum of reaction 1 to complex **3**, then it is not clear why $PhNO_2$ could not be hydrogenated with **1**, since these are the conditions under which **3** is formed. Careful TLC monitoring of the reaction solution (eq. 1) during the first 4 h revealed the presence of **3** as a spot of **4** [16*], which is known to be the sole decomposition product from **3** on TLC [17*]. However, another intense spot assigned to $(Ph_4C_4CO)(CO)_2Ru(H_2NPh)$ (**5**), was clearly visible. Complex **5**, a member of a family of previously investigated amine complexes [19], was now obtained, as shown in equation 6, after 25 min at room temperature using **4a** [20] in THF solution. Its infrared spectrum (CO region)

$$\underset{(\mathbf{4a})}{[(Ph_4C_4CO)(CO)_2Ru]_2} + PhNH_2 \rightarrow \underset{(\mathbf{5})}{(Ph_4C_4CO)(CO)_2RuNH_2Ph} \qquad (6)$$

showed two bands at 2018 and 1958 cm^{-1}, and a single TLC spot identical with that of the reaction solution (eq. 1).

The chemistry of **5** under catalysis conditions was studied by subjecting a THF solution of **5** containing water and an excess of aniline to CO (500 psi) at 105 °C with TLC and infrared spectral monitoring. After 10 min a weak band at 2080 cm^{-1} (complex **1**) grew up in the original spectrum, and TLC showed the presence of the aniline complex **5**, the hydride complex **3** and the tricarbonyl **1**. After 30 minutes, **1** had almost disappeared, leaving only **5** and **3**, as determined by TLC and IR (2017, 1956 cm^{-1}). Obviously it is very difficult to differentiate spectroscopically between **3** and **5**, especially when they are present as a mixture; however, their qualitative identification by IR and TLC is unambiguous. The above results allow us to formulate some of the reactions that take place under catalysis conditions (eqs. 7–9).

$$\underset{(\mathbf{5})}{(Ph_4C_4CO)(CO)_2RuNH_2Ph} + CO \rightarrow \underset{(\mathbf{1})}{(Ph_4C_4CO)(CO)_3Ru} + PhNH_2 \qquad (7)$$

$$(Ph_4C_4CO)(CO)_3Ru + H_2O \rightarrow \underset{(\mathbf{3})}{(Ph_4C_4COH)(CO)_2RuH} + CO_2 \qquad (8)$$

$$\underset{(\mathbf{3})}{(Ph_4C_4COH)(CO)_2RuH} + CO + H_2O \rightarrow \text{No Reaction} \qquad (9)$$

$$PhNO_2 + \mathbf{3} \rightarrow \text{No reaction} \qquad (10)$$

Reaction 7 is a simple ligand exchange process whereby a better π acid replaces an inferior one. Its occurrence enables reaction 8, which generates the hydride complex **3**, to take place. In a separate experiment it was shown that **3** does not liberate dihydrogen in the presence of $CO + H_2O$, and in fact does not serve as a carrier for hydrogen evolution in the WGSR, substantiating eq. 9. Thus, free hydrogen is not involved in the reduction of nitro-aromatics under our conditions. The only way **3** can react is by transferring its hydrogen atoms to an acceptor. But, since $PhNO_2$ could not be reduced with hydrogen, i.e. under the reaction conditions under which **3** is known to be formed, obviously it can not serve as an acceptor for **3** (eq. 10), although its presence (together with **5**) in reaction 1 has been demonstrated.

The apparent dilemma can be resolved by considering a multi-step reduction process in which **3** is not involved in the first reduction step of the nitro compound. A reasonable interpretation of the results is presented in Scheme 1.

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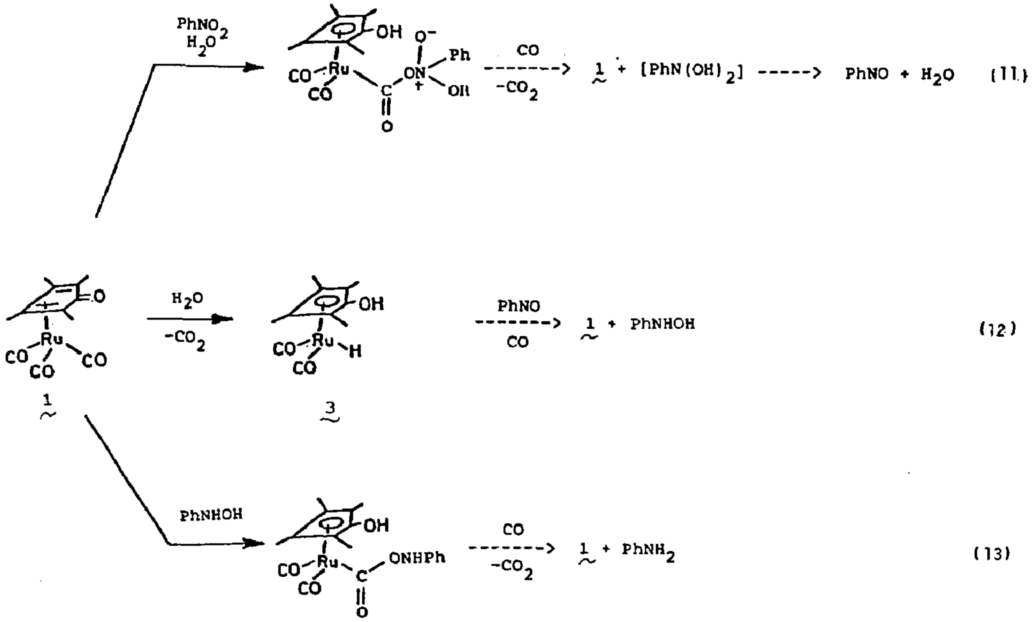
* Reference number with asterisk indicates a note in the list of references.



Scheme 1. (Ring phenyls are omitted)

In Scheme 1 we suggest a possible mechanistic route for the reduction of nitroaryls to anilines with CO + H_2O and **1** as a catalyst precursor. The observation of PhNO during the catalytic reaction 1 and the formation of azoxybenzene led us to the conclusion that the reduction is a multi-step process during which the organic intermediates are released to the reaction solution. Our observations indicate that the initial interaction of **1** which leads to products requires both the nitro compound and water (vide supra), as shown in eq. 11. Furthermore, although hydride **3** exists in the reaction solution, it is not involved in the first step, since nitrobenzene is not reduced by hydrogen in the presence of **1**. Therefore, attack of the oxygen of the nitro group on a carbon monoxide ligand is the probable first step, as proposed by Landesberg [2] and Alper [21] for similar systems. The resulting intermediate complex loses CO_2, thereby transferring an oxygen atom from nitrogen to carbon, generating PhNO and regenerating **1** with CO.

Complex **1** is known to react with water (eq. 12), and in particular under base catalysis, to give the hydride complex **3**, which was actually observed in the catalytic reaction mixture. We suggest that **3** delivers its H atoms to PhNO, in a manner similar to ketones [12], giving phenylhydroxylamine and thereby regenerating **1** with CO. It should be pointed out that **3** is stable in the presence of CO and water under the experimental conditions. Its participation in the catalytic cycle requires a hydrogen acceptor, namely nitrosobenzene. A metal-stabilized nitrene intermediate [5] which is subsequently reduced to aniline, can be ruled out, since no diphenyl urea, a product from a reaction of phenyl nitrene with CO, was detected in our experiments.

The reaction of **1** with phenylhydroxylamine (eq. 13) is analogous to that with water (eq. 12). The phenylhydroxylamine ester loses CO_2 thereby generating aniline and regenerating **1** with CO.

The decomposition of the three intermediates (eqs. 11–13) most probably goes through the coordinatively unsaturated 16e$^-$ species $(Ph_4C_4CO)(CO)_2Ru$, which may either coordinate a CO ligand leading to **1**, or aniline leading to **5**; the latter was detected in the reaction solution (vide supra). It has been demonstrated that **5** also gives **1** under CO pressure (eq. 7). Thus, aniline serves merely as a transient ligand in the catalytic cycle.

It has been found (Table 2) that electron-poor nitroaryls are clearly more reactive than electron rich ones. Since the rate of the first step of reaction 11 must depend on the nucleophilicity of the nitro group oxygen atom, it is ruled out as being rate determining.

Experimental

Monitoring of the reduction reactions of the nitroaryls was carried out with Varian Vista Gas Chromatography instrument, model CDS 401 equipped with FID. GLC traces were calibrated with standardized solutions of nitrobenzene, aniline, and azoxybenzene. Infrared spectra were obtained with Perkin–Elmer 281 and 177 Grating Infrared spectrometers. Complexes **1** and **2** were prepared according to previous description [15]. TLC analyses were carried out with silica plastic strips, with methylene chloride/n-hexane mixtures as eluents.

General procedure

All the experimental variables for the reactions which are reported in Tables 1 and 2 are described in the footnotes of the respective tables. Products' distribution values are expressed in mol%. THF was distilled from sodium metal prior to each use. The reactions were carried out in a glass-sleeved SS-316 reactor 935 ml) equipped with a pressure gauge and a liquid sampling valve. The reactor was immersed in a thermo-regulated oil bath and the reaction solution was magnetically stirred. No reaction took place upon omission of the catalyst.

*Reaction of **4a** [20] with aniline*

A solution of **4a** (37.8 mg; 0.07 mmol) and aniline (470 mg; 5 mmol) in THF (10 ml) was kept under nitrogen at room temperature. After 10 min the IR spectrum of the solution was recorded (ν_{max} 2018, 1958 cm^{-1}); TLC showed a single spot, which was assigned to **5**, and was identical with that from the reaction solution (1st entry, Table 1).

Water (0.5 ml) was added to the above reaction solution. The solution was placed in a reactor, which was then pressurized with CO (500 psi) and kept at 105° C. After 10 min a new IR band at ν_{max} 2080 cm^{-1} was observed; after 30 min ν_{max} 2080, 2017, 1956 cm^{-1}. The TLC showed spots of **1**, **4** and **5**.

Hydrogenation of nitrobenzene

A solution of nitrobenzene (1.23 g; 10 mmol), **4** (0.038 g; 0.07 mmol) and water (1.0 ml; 56 mmol) in THF (10 ml) was placed in a reactor which was then pressurized with hydrogen (500 psi) and kept at 105°C. A similar experiment was carried out but with **1** in place of **4**. In both reactions no aniline was detected after 5 h. After 1 h IR ν_{max} 2018, 1955 cm^{-1}.

Reaction of PhNO with $CO + H_2O$

A solution of nitrosobenzene (1.23 g; 10 mmol), water (1 ml; 56 mmol) and **1** (40 mg; 0.07 mmol) in THF (10 ml) was pressurized with CO (500 psi) and kept at 105 °C. After 1 h there was formed a mixture of aniline (6%), azobenzene (4%), azoxybenzene (90%) at 98% conversion of nitrosobenzene. Similar results were obtained when **1**, CO, and water were omitted.

Reaction of $PhNO_2$ *with CO*

The reaction described in the 1st entry of Table 1 was carried out, omitting the water. GLC analysis indicated that no reaction took place.

Reaction of 3 with CO

A solution of **4** (38 mg; 0.07 mmol) in THF (10 ml) was pressurized with hydrogen (500 psi) in a reactor and kept at 105 °C. After 1 h a colorless solution of **3** was obtained, IR ν_{max}: 2018, 1953 cm^{-1}. The reactor was cooled, depressurized, and flushed twice with nitrogen; water (1 ml) was added and the reactor was pressurized with CO (500 psi) and heated at 105 °C. The infrared spectrum of this reaction solution did not change during 1.5 h.

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