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# Efficient selective reduction of aromatic nitro compounds by ruthenium catalysis under CO/H<sub>2</sub>O conditions

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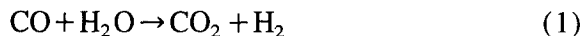
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## Abstract

Ruthenium–carbonyl complexes in the presence of small amounts of amines have exhibited both significant catalytic activities and remarkable selectivities of nitro group for reduction of aromatic nitro compounds under CO/H<sub>2</sub>O conditions. Notable increases of the catalytic activities were found upon the addition of a small amount of the specified amine, such as diisopropylamine, piperidine, dibutylamine, and triethylamine; the reaction rate increased at higher reaction temperatures, under higher CO pressures. The powerful importance of the present catalysis can be emphasized, because aromatic nitro group was reduced exclusively without the other unsaturated groups such as C=O, C=N, C=C, and C≡C being reduced: the desired aromatic amines were, therefore, catalytically obtained in high yields. The reduction was also found to proceed without by-producing hydrogen gas generated from the water–gas shift reaction (WGSR). The role of amines in this catalysis was thus suggested to be different from that in the WGSR. Comparing the results here with those reported previously, an original reaction pathway in this catalysis, such as intramolecular hydrogen transfer between metal–nitrene and hydride, can be considered; the mechanism has also been discussed and presented in this paper.

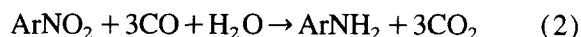
## 1. Introduction

The water–gas shift reaction (WGSR) has been one of the most important processes from the aspect of industrial utilization of carbon monoxide [1]; it has already been commercialized to produce pure hydrogen.



As one of applications related to the WGSR, organic synthesis under CO/H<sub>2</sub>O conditions using homogeneous catalysts [2], especially the reduction of aromatic nitro compounds, has

attracted considerable attention [2,3]. Many studies have already been made, however, the efficient reduction with high selectivity of nitro group, as well as with high catalytic activity, has not so far been reported [3,4]. In addition, previous patents and papers disclose that aromatic nitro compounds with optionally substituted by inert groups such as alkyl, alkoxy had limited effectiveness for this reduction using rhodium and ruthenium complexes [5].



It is been well-known that aromatic amines have been efficiently produced from the corresponding nitro compounds by (1) stoichiometric

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reduction of the corresponding aromatic nitro compounds using iron powder, or metal sulfides such as alkali metal sulfides, alkali metal hydrogen sulfides like NaHS, or (2) catalytic hydrogenation with palladium-, platinum-carbon, or Raney-nickel etc. However, some difficulties such as (1) problem of after-treatments of the by-products, or (2) loss of the selectivity of the desired amines, are still remained on the conventional processes. The exclusive catalytic reduction of aromatic nitro compounds is, therefore, one of the most attractive subjects from both synthetic and practical viewpoints, because the desired amine can be catalytically obtained as a sole product, and the above-mentioned problems can be solved.

We have already studied and discovered a new type of catalyst system that shows both high catalytic activity and selectivity for the reduction of aromatic nitro compounds under CO/H<sub>2</sub>O conditions [6]. As we reported in our previous papers [6], amine- or phosphine-added rhodium complexes in the presence of NaOH aqueous solutions exhibit the significant catalytic activities as well as high selectivities of aromatic nitro group under mild conditions of room temperature and atmospheric CO pressure [6].

In this paper, we present the new, efficient catalysts, composed of ruthenium-carbonyl complexes and small amount of specified amines, for almost exclusive reduction of aromatic nitro compounds under CO/H<sub>2</sub>O conditions [7]. An original reaction scheme by this catalysis is also presented and discussed.

## 2. Experimental

All manipulations were carried out under nitrogen atmosphere or in vacuo. Solvents such as diglyme (diethyleneglycol dimethyl ether), methanol, ethanol, 2-propanol, acetone, were used as a reagent grade (Nakarai tesque Co., Ltd.). Aromatic nitro compounds and amines were also used as a reagent grade (Nakarai tesque Co., Ltd. or Tokyo Kasei Co., Ltd.).

The catalytic reductions were typically carried out as follows: in an autoclave (110 or 50 cm<sup>3</sup>) made of stainless steel and equipped with a stirrer driven by magnetic force, were charged by Ru<sub>3</sub>(CO)<sub>12</sub> (0.003 mmol), prescribed amount of the amine, solvent (10 ml), water (4 ml) and nitrobenzene (ca. 10 mmol). The reaction mixture was stirred under CO (20 atm) at 150°C for 100 min. Reaction product was then determined by GLC using an internal standard and was identified using GLC by co-injection with the authentic sample (column OV-225, 3 m) and GC-MS (QP-1000, Shimadzu Co., Ltd.). The only product from nitrobenzene was aniline [8].

The reductions of other aromatic nitro compounds were also performed by the same manner. An excess amount of water was added into the reaction mixture in the reduction of 1-nitroanthraquinone; the resultant red precipitates after filtration were redissolved in *N,N*-dimethylformamide, determined by GLC. Identification was made by comparison of the retention time of the chromatogram (GLC: column OV-210 (1 m), or OV-225 (3 m)), elemental analysis, and GC-MS. After these reduction procedures, the desired aromatic amines were obtained exclusively with 100% selectivity of nitro group.

## 3. Results and discussion

### 3.1. Reduction of nitrobenzene using CO and water catalyzed by ruthenium-carbonyl complexes in the presence of amines

#### 3.1.1. Effect of amine additives, solvents

The reduction of nitrobenzene proceeded at significant rate in the presence of Ru<sub>3</sub>(CO)<sub>12</sub> complex under CO (20 atm)/H<sub>2</sub>O conditions (150°C). The rates did not decrease during the course of the reaction, affording the desired product, aniline, in high yield [9]. The results for the reduction in the presence of various amine additives are summarized in Table 1.

It should be noted that the rates were found to increase upon the addition of small amount of

Table 1  
Effect of amine additives on the reduction of nitrobenzene under CO/H<sub>2</sub>O conditions catalyzed by Ru<sub>3</sub>(CO)<sub>12</sub> in the presence of amines

Amine	Molar ratio <sup>a</sup>	Temp./°C	Turnovers <sup>b</sup> /mol-cat <sup>-1</sup>
pyrrolidine	5	150	1573
piperidine	3	150	1524
HN(i-Pr) <sub>2</sub>	50	150	1683
HN(i-Pr) <sub>2</sub>	70	150	2016
HNEt <sub>2</sub>	25	150	1510
HNBu <sub>2</sub>	35	150	1883
HN(c-C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub>	50	150	1694
NEt <sub>3</sub> <sup>c</sup>	100	150	1778

Reaction conditions: Ru<sub>3</sub>(CO)<sub>12</sub> 0.003 mmol, EtOH/H<sub>2</sub>O = 10/4 ml, PhNO<sub>2</sub> ca. 10 mmol, CO 20 atm, 100 min.

<sup>a</sup> Molar ratio of amine/Ru.

<sup>b</sup> Turnovers (mol-cat<sup>-1</sup>) = amine produced (mmol)/complex (mmol).

<sup>c</sup> Ru<sub>3</sub>(CO)<sub>12</sub> 0.005 mmol, EtOH/H<sub>2</sub>O = 5/2 ml, 2 h.

amines (HNR<sub>2</sub>) [10]; especially, diisopropylamine, dibutylamine, and piperidine were preferred. Triethylamine was also found to be preferred for this reaction. It was also revealed that the effective molar ratios of each amine into ruthenium were different.

Table 2 shows the results in various solvents for the reduction catalyzed by Ru<sub>3</sub>(CO)<sub>12</sub> complex in the presence of HN<sup>i</sup>Pr<sub>2</sub>, or NEt<sub>3</sub>.

Importantly, various kinds of solvents were effective in these catalyses, especially, ethanol, methanol, and diglyme (diethyleneglycol dimethyl ether): it will be highly possible to choose the desired solvent for the recycling process in these catalysis.

### 3.1.2. Effect of reaction temperatures and CO pressures

Considerable attention should be paid to Table 3 regarding the rates markedly increased under higher CO pressures at higher reaction temperatures.

The turnover numbers (100 min) increased at higher reaction temperature (150 → 180°C): turnovers of > 10500 could be attained (yield > 99%) at 180°C, CO 50 atm. Much more active catalysis will be accomplished under these con-

ditions. We believe, this catalysis may be effectively used for production of aromatic amines after more development on this subject.

Table 2  
Ru<sub>3</sub>(CO)<sub>12</sub> catalyzed reduction of nitrobenzene under CO/H<sub>2</sub>O conditions in the presence of NEt<sub>3</sub>. Effect of Various Solvents

Amine	Solvent	Temp./°C	CO/atm	Turnovers /mol-cat <sup>-1</sup>
HN(i-Pr) <sub>2</sub>	ethanol	150	20	2016
HN(i-Pr) <sub>2</sub>	methanol	150	20	1707
HN(i-Pr) <sub>2</sub>	isoamyl alcohol	150	20	1665
HN(i-Pr) <sub>2</sub>	diglyme	150	20	1994
HN(i-Pr) <sub>2</sub>	acetone	150	20	1919
NEt <sub>3</sub>	methanol <sup>a</sup>	150	20	1986
NEt <sub>3</sub>	isoamyl alcohol	150	20	1872
NEt <sub>3</sub>	ethanol	150	20	1778
NEt <sub>3</sub>	acetone	150	20	1771
NEt <sub>3</sub>	isopropyl alcohol	150	20	1614
NEt <sub>3</sub>	diglyme	150	20	1582

Reaction conditions: (a) Ru<sub>3</sub>(CO)<sub>12</sub>/HN(i-Pr)<sub>2</sub> = 0.003/0.63 mmol, solvent/H<sub>2</sub>O = 10/4 ml, PhNO<sub>2</sub> ca. 10 mmol, 100 min. (b) Ru<sub>3</sub>(CO)<sub>12</sub>/NEt<sub>3</sub> = 0.005/1.5 mmol, solvent/H<sub>2</sub>O = 5/2 ml, PhNO<sub>2</sub> ca. 10 mmol, 2 h.

<sup>a</sup> > 99% yield.

Table 3  
Effect of reaction temperature and CO pressure on the reduction of nitrobenzene by Ru<sub>3</sub>(CO)<sub>12</sub>-amine catalysis under CO/H<sub>2</sub>O conditions

Amine	Solvent	Temp./°C	CO/atm	Turnovers/ mol-cat <sup>-1</sup>
NEt <sub>3</sub>	diglyme	150	20	1582
NEt <sub>3</sub>	diglyme <sup>c</sup>	180	20	2058
NEt <sub>3</sub>	diglyme <sup>a</sup>	180	50	10500
piperidine <sup>b</sup>	ethanol	150	20	1524
piperidine	ethanol <sup>c</sup>	180	20	3422
HN(i-Pr) <sub>2</sub>	ethanol	150	20	1683
HN(i-Pr) <sub>2</sub>	ethanol <sup>c</sup>	180	20	3421
HNEt <sub>2</sub> <sup>d</sup>	ethanol	150	20	1510
HNEt <sub>2</sub> <sup>d</sup>	ethanol <sup>c</sup>	180	20	3448

Reaction conditions: (a) Ru<sub>3</sub>(CO)<sub>12</sub>/HN(i-Pr)<sub>2</sub> = 0.003/0.45 mmol, solvent/H<sub>2</sub>O = 10/4 ml, PhNO<sub>2</sub> ca. 10 mmol, 100 min. (b) Ru<sub>3</sub>(CO)<sub>12</sub>/NEt<sub>3</sub> = 0.005/1.5 mmol, solvent/H<sub>2</sub>O = 5/2 ml, PhNO<sub>2</sub> ca. 10 mmol, 2 h.

<sup>a</sup> Ru<sub>3</sub>(CO)<sub>12</sub> 0.002 mmol, solvent/water = 10/4 ml, PhNO<sub>2</sub> ca. 21 mmol, 5 h, > 99% yield.

<sup>b</sup> Conditions (a), piperidine/Ru = 3.

<sup>c</sup> > 98% yield.

<sup>d</sup> Conditions (a), HNEt<sub>2</sub>/Ru = 25.

Table 4  
Reduction of various aromatic nitro compounds using CO and water by ruthenium–amine catalysis

ArNH <sub>2</sub>	Amine	Product	Yield/%
<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	HN( <i>i</i> -Pr) <sub>2</sub>	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	> 99
<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	NEt <sub>3</sub>	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	> 99
<i>o</i> -BrC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	HN( <i>i</i> -Pr) <sub>2</sub>	<i>o</i> -BrC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	> 99
<i>o</i> -BrC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	NEt <sub>3</sub>	<i>o</i> -BrC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	> 99
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	HN( <i>i</i> -Pr) <sub>2</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	> 99
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	NEt <sub>3</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	> 99
<i>p</i> -NCC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	HN( <i>i</i> -Pr) <sub>2</sub>	<i>p</i> -NCC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	> 99
<i>p</i> -NCC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	NEt <sub>3</sub>	<i>p</i> -NCC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	> 99
<i>p</i> -PhCOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	HN( <i>i</i> -Pr) <sub>2</sub>	<i>p</i> -PhCOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	> 99
<i>p</i> -PhCOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	NEt <sub>3</sub>	<i>p</i> -PhCOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	> 99
1-nitroanthraquinone	HN( <i>i</i> -Pr) <sub>2</sub>	1-aminoanthraquinone	> 99
1-nitroanthraquinone	NEt <sub>3</sub>	1-aminoanthraquinone	> 99

Reaction conditions: Ru<sub>3</sub>(CO)<sub>12</sub>/amine = 0.01/1.5 mmol, diglyme/H<sub>2</sub>O = 15/5 ml, CO 20 atm, 150°C, 2 h, ArNO<sub>2</sub> 5 mmol.

Table 5  
Reaction of various substrates under CO/H<sub>2</sub>O conditions

Substrate	Amine	Product	Yield/%
PhNO <sub>2</sub>	HN( <i>i</i> -Pr) <sub>2</sub>	PhNH <sub>2</sub>	> 99
PhNO <sub>2</sub>	NEt <sub>3</sub>	PhNH <sub>2</sub>	> 99
PhCOCH <sub>3</sub>	HN( <i>i</i> -Pr) <sub>2</sub>		no reaction <sup>a</sup>
PhCOCH <sub>3</sub>	NEt <sub>3</sub>		no reaction <sup>a</sup>
PhC≡CH	HN( <i>i</i> -Pr) <sub>2</sub>		no reaction <sup>a</sup>
PhC≡CH	NEt <sub>3</sub>	PhCH=CH <sub>2</sub>	1.3%
PhCH=CH <sub>2</sub>	NEt <sub>3</sub>	PhCH <sub>2</sub> CH <sub>3</sub>	0.3%
PhCHO	NEt <sub>3</sub>	PhCH <sub>2</sub> OH	0.08%
PhC≡N	HN( <i>i</i> -Pr) <sub>2</sub>		no reaction <sup>a</sup>

Reaction conditions: Ru<sub>3</sub>(CO)<sub>12</sub>/amine = 0.01/1.5 mmol, diglyme/H<sub>2</sub>O = 15/5 ml, CO 20 atm, 150°C, 2 h, substrate 5 mmol.

<sup>a</sup> Trace amount of product (< 0.05%) might be detected on GLC.

Table 6  
Product distributions of the reduction of various aromatic nitro compounds using Ru<sub>3</sub>(CO)<sub>12</sub>–amine catalysts under CO/H<sub>2</sub>O conditions

Catalyst (mmol)	Reactant (mmol)	Product (mmol)	Products (gas phase/mmol)
Ru <sub>3</sub> (CO) <sub>12</sub> /NEt <sub>3</sub> <sup>a</sup> (0.005/1.5)	1-nitroanthraquinone (10.2)	1-aminoanthraquinone (> 98%)	H <sub>2</sub> (0.02): CO <sub>2</sub> (30.2)
Ru <sub>3</sub> (CO) <sub>12</sub> /HN( <i>i</i> -Pr) <sub>2</sub> <sup>b</sup> (0.01/1.5)	<i>o</i> -chloronitrobenzene (5.0)	<i>o</i> -chloroaniline (> 99%)	H <sub>2</sub> (< 0.4): CO <sub>2</sub> (14.7)
Ru <sub>3</sub> (CO) <sub>12</sub> /pyrrolidine <sup>c</sup> (0.01/0.045)	1-nitroanthraquinone (10.2)	1-aminoanthraquinone (> 98%)	H <sub>2</sub> (0.08): CO <sub>2</sub> (34.2)
Ru <sub>3</sub> (CO) <sub>12</sub> /HN( <i>i</i> -Pr) <sub>2</sub> <sup>d</sup> (0.01/1.5)	benzonitrile (5.0)	No Reaction	H <sub>2</sub> (< 0.4) and CO

Reaction conditions: CO 20 atm, 150°C.

For <sup>a</sup> and <sup>b</sup> see Eq. 3.

For <sup>c</sup> and <sup>d</sup> see Table 5.

### 3.2. Reduction of various aromatic nitro compounds using Ru<sub>3</sub>(CO)<sub>12</sub>–amine catalysis under CO/H<sub>2</sub>O conditions

Table 4 summarizes the results for various aromatic nitro compounds by Ru<sub>3</sub>(CO)<sub>12</sub>–amine (HN(*i*-Pr)<sub>2</sub> or NEt<sub>3</sub>) catalyses.

It should be noted that the reductions proceeded with marked selectivity of aromatic nitro group (almost 100%), resulting in obtaining the desired aromatic amines in high yield. Selectivities of nitro group did not change irrespective of the kind of amines (HN(*i*-Pr)<sub>2</sub>, NEt<sub>3</sub>, and piperidine). Halogen substituted nitrobenzenes were found to be reduced to produce the corresponding anilines without accompanying a decomposition of the halogen group. In addition, importantly, *p*-cyanonitrobenzene, *p*-nitrobenzophenone and 1-nitroanthraquinone were also found to be converted to afford corresponding *p*-aminobenzonitrile, *p*-aminobenzophenone and 1-aminoanthraquinone, respectively, without C=O, C≡N being reduced. As far as we know, previous patents and papers disclose that aromatic nitro compounds optionally substituted by inert group such as alkyl, alkoxy were limited to be effective for this type of reduction by rhodium or ruthenium catalysis. Therefore, we believe, these results are very important from both synthetic and industrial viewpoints.

Noteworthy is that the other substrates such as acetophenone, phenylacetylene, and benzonitrile,

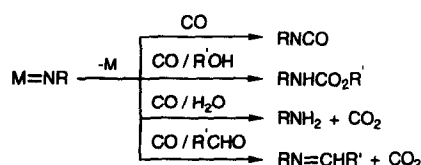
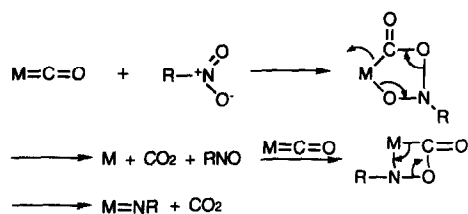
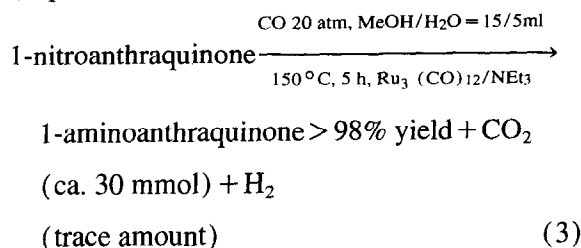
styrene, and benzaldehyde were not reduced in these catalyses ( $\text{Ru}_3(\text{CO})_{12}\text{-NEt}_3$  or  $\text{HN}(\text{i-Pr})_2$ ), as exemplified in Table 5.

The powerful importance of these catalyses can be emphasized, because the desired aromatic amines can be obtained in high yield by using these catalyses. It also suggests that an original reduction pathway will exist for this exclusive nitro group reduction.

### 3.3. Product distribution for ruthenium catalyzed selective reduction of aromatic nitro compounds affording aromatic amines under $\text{CO}/\text{H}_2\text{O}$ conditions

It should be noted that a stoichiometric amount of  $\text{CO}_2$  was formed at the end of the reduction: thus hydrogen gas did not accompany in these catalyses (Table 6).

In addition, no production of carbon dioxide, and hydrogen gas in trace amount, were detected for the reaction of benzonitrile under the same conditions. These facts are, we believe, very important especially from the practical viewpoints (Eq. 3).



Scheme 1.

It has already been reported that a certain excess amount of hydrogen gas, generated by the water-gas shift reaction, was observed for the reduction of nitrobenzene in the presence of catalyst composed of ruthenium-carbonyl complexes and an excess amount of trimethylamine aqueous solution, because of its exceptionally high WGS activity [3,4].

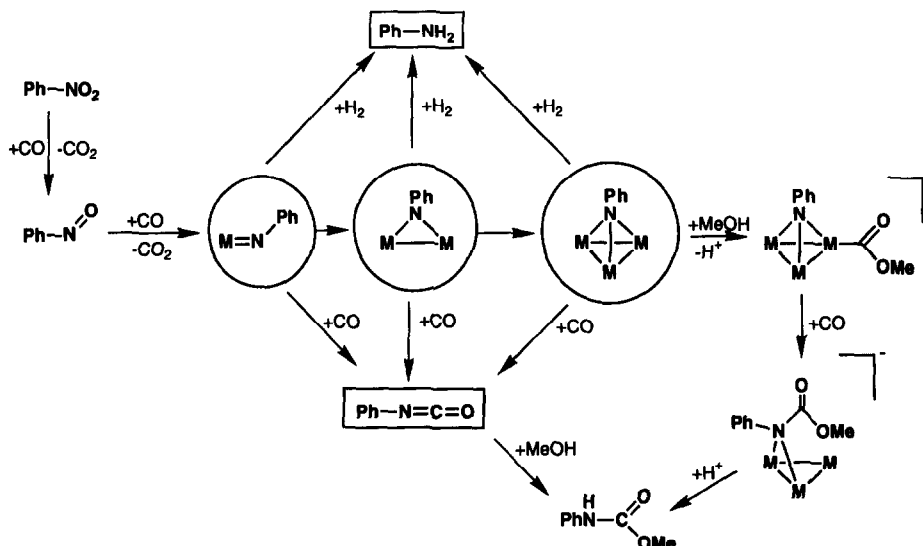
Contrariwise, carbon monoxide was effectively consumed without accompanying the dihydrogen in the above mentioned catalyses, strongly suggesting that this type of catalytic reduction does not proceed by the hydrogenation of aromatic nitro compounds with hydrogen gas generated from the WGS.

### 3.4. Tentative reaction pathway for the exclusive reduction of aromatic nitro group under $\text{CO}/\text{H}_2\text{O}$ conditions

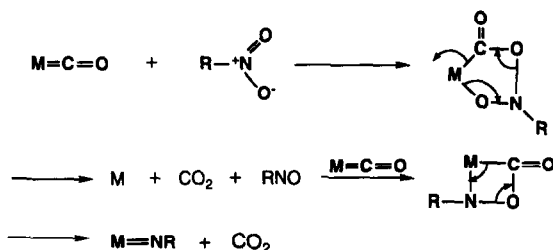
It has been postulated that the reaction of aromatic nitro compounds involves successive oxygen transfer reactions between the nitro compounds and coordinated metal-carbonyl ligand [11]. In addition, this can be conveniently envisaged as formally involving cycloaddition of  $\text{ArNO}_2$  and  $\text{ArNO}$  to a metal-carbonyl double bond and subsequent extrusion of carbon dioxide, as shown in Scheme 1.

It has also often been suggested for carbonylation or reduction of nitrobenzene by ruthenium catalysis that metal imido ligands bound to one, two or three metal atoms that was generated by the stepwise deoxygenation of nitrobenzene, nitrosobenzene would be hydrogenated to give aniline whereas carbonylated to give phenyl isocyanate, as shown in Scheme 2 [12–15]. Therefore, the reduction of nitrobenzene was believed to proceed by the hydrogenation of metal-nitrene species, because ruthenium-cluster nitrene complex was hydrogenated to afford aniline [14], and the reduction accompanied an excess amount of hydrogen gas that was generated from the water-gas shift reaction [3b,4].

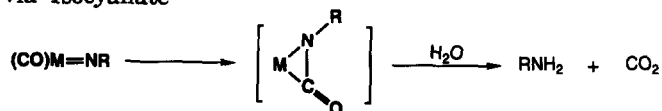
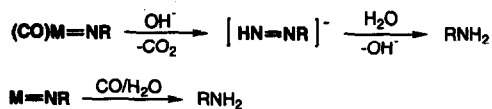
However, we believe, another reaction pathway



Scheme 2.



## 1) via Isocyanate

2) Intramolecular hydrogen transfer reaction

Scheme 3.

can be considered for the present catalysis, because (1) hydrogen gas from the WGS was not detected at the end of the reduction, and (2) the reduction proceeds with exclusive selectivity of aromatic nitro group. The role of amine for the reduction can be demonstrated to be different from

that in the water-gas shift reaction, as previously pointed out by Kaneda et al. [16].

Taking into account the results described above, two possible reaction pathways via (i) decarboxylation of isocyanates with water, or (ii) intramolecular hydrogen transfer between metal-

nitrene and hydride, can be considered, as shown in Scheme 3.

The products from nitrobenzene in the absence of water were nitrosobenzene, azobenzene, and aniline in these catalysis. Therefore, we believe that the present catalysis can be concluded to proceed by the exclusive intramolecular hydrogen transfer reaction. Further studies are now under way.

## Acknowledgements

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- [4] (a) The reduction using homogeneous ruthenium catalysts in the absence of NaOH aqueous solution, such as in the presence of trimethylamine aqueous solution [3b], phenanthrolines [3h,j,a], or others [3f], have also been known. However, some difficulties, such as selectivity, or catalytic activities, are encountered in the conventional process for the production of aromatic amines [5]. (b) It was already known that  $\text{Ru}_3(\text{CO})_{12}$  complex in the presence of an excess amount of trimethylamine aqueous solution exhibited the catalytic activity for nitrobenzene reduction [3b]. However, a certain excess amount of hydrogen gas (52% in the gas phase (300 ml autoclave) at the end of the reaction) was accompanied, because of the exceptionally high activity for the WGS: W.A.R. Slegeir, R.S. Sapienza and B. Easterling, *ACS Symp. Ser.*, 152 (1981) 325.
- [5] For example, patents: (a) G. Mestroni, G. Zassinovich and E. Alessio, *Eur. Pat.* 97592 (1983); (b) A.F.M. Iqbal, *US Pat.* 3944615 (1976).
- [6] We have recently discovered new catalyst systems which show both high catalytic activities and selectivities of nitro group for the reduction of aromatic nitro compounds under the mild conditions of room temperature and atmospheric pressure of CO: (a) K. Nomura, M. Ishino and M. Hazama, *J. Mol. Catal.*, 65 (1991) L5; (b) *idem. ibid.*, 66 (1991) L1; (c) *idem. ibid.*, 66 (1991) L11; (d) *idem. ibid.*, 66 (1991) L19; (e) *idem. Bull. Chem. Soc., Jpn.*, 64 (1991) 2624; (f) *idem. J. Mol. Catal.*, 78 (1993) 273.
- [7] (a) K. Nomura, *Chem. Lett.*, 1679 (1991); (b) K. Nomura, *J. Mol. Catal.*, 73 (1992) L1.
- [8] In some cases, trace amount of azobenzene, or azoxybenzene may be detected during the course of the reduction of  $\text{PhNO}_2$ . However, these compounds will be easily reduced to afford aniline by further stirring.
- [9] The rates were not retarded by accumulating the product, aniline, in these catalysis.
- [10] Turnovers of  $329 \text{ mol-cat}^{-1}$  was obtained for the reduction of nitrobenzene (10 mmol) using  $\text{Ru}_3(\text{CO})_{12}$  (0.01 mmol) in 2-methoxyethanol (15 ml),  $\text{H}_2\text{O}$  (5 ml), under CO (20 atm) at  $150^\circ\text{C}$  for 2 h.
- [11] (a) R.A. Sheldon, *Chemicals from Synthesis Gas*, Vol. 5, Reidel, Dordrecht, 1989, p. 271; (b) T. Ikariya, *Shokubai (Catalyst)*, 5 (1989) 271.
- [12] S. Cenini, M. Pizzotti and C. Crotti, in R. Ugo (Ed.), *Aspects of Homogeneous Catalysis*, Vol. 6, Reidel, Dordrecht, 1988, p. 97.
- [13] S.-H. Han, J.-S. Song, P.D. Macklin, S.T. Nguyen, G.L. Geoffroy and A. Reingold, *Organometallics*, 8 (1989) 2127.
- [14] Isolation of a ruthenium–nitrene complex: S. Bhauduri, K.S. Gopalkrishnan, W. Clegg, P.G. Jones, G.M. Sheldrick and D. Stalke, *J. Chem. Soc., Dalton Trans.*, (1984) 1765. In this paper, aniline was obtained by hydrogenation of metal–nitrene complex, and therefore, it was proposed that the reduction of nitrobenzene under  $\text{CO}/\text{H}_2\text{O}$  by  $\text{Ru}_3(\text{CO})_{12}$  proceeds by hydrogenation of metal–nitrene.
- [15] E. Alessio et al. also presented another possibility [3j] that the reduction of nitrobenzene using  $\text{Ru}_3(\text{CO})_{12}$  with 3,4,7,8-tetramethyl-1,10-phenanthroline proceeded by the simple hydrogenation of aromatic nitro compounds with hydrogen which was generated from the water–gas shift reaction. We believe that we can easily exclude this mechanism for this catalysis, because the reduction proceeds without accompanying hydrogen gas which was generated from the

water–gas shift reaction, and with high selectivity of aromatic nitro group.

- [16] K. Kaneda et al. [3e] previously suggested that the role of amines in nitrobenzene reduction under CO/H<sub>2</sub>O conditions is different from that in the water–gas shift reaction. This also

suggests the reduction does not proceed by hydrogenation of metal–nitrene with hydrogen from the WGSR.