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STUDIES ON TRANSITION METAL CATALYZED REDUCTION OF AROMATIC NITRO COMPOUNDS UNDER CO/H_2O CONDITIONS

（遷移金属錯体触媒を用いる芳香族ニトロ化合物の一酸化炭素／水系還元反応に関する研究）

KOTOHIRO NOMURA

1992

PREFACE

Catalysts are widely used in various chemical reactions, and it is estimated 60 - 70 % of all chemicals in industry. Rapid growth of investigations, especially in the field of homogeneous catalysis, provides new aspects to make so-called fine-chemicals such as pharmaceuticals, specialty polymers, agricultural and electronic chemicals, by selective organic synthesis.

This thesis entitled "Studies on Transition Metal Catalyzed Reduction of Aromatic Nitro Compounds Under CO/H_2O Conditions" is a collection of studies I carried out from 1988 to 1991. The thesis presented here has been made under the guidance of Professor Noboru Sonoda at the Department of Applied Chemistry, Faculty of Engineering, Osaka University.

In particular, this thesis is divided into the following two parts:

1) Selective reduction of aromatic nitro compounds under mild conditions, room temperature and 1 atm of CO, catalyzed by rhodium-, ruthenium-carbonyl complexes
2) Ruthenium-catalyzed selective reduction of aromatic nitro compounds under CO/H_2O conditions

I hope my contribution will be appreciated and introduce new aspects to this research area.

Finally, I'd like to express my sincere acknowledgement to Prof. Noboru Sonoda for his helpful and kind discussions throughout this research.

Kotohiro Nomura

List of Publications

The contents of this thesis are composed of the following papers.

1. Selective reduction of aromatic nitro compounds using CO and water with highly active rhodium-phosphine chelate complexes

   K. Nomura, M. Ishino, and M. Hazama
   J. Mol. Catal., 65, L5 (1991).

2. Facile selective reduction of aromatic nitro compounds affording amines using $Rh_4(CO)_{12}$-9,10-diaminophenanthrene catalyst system under CO/H_2O conditions: the effect of 9,10-diaminophenanthrene

   K. Nomura, M. Ishino, and M. Hazama
   J. Mol. Catal., 66, L1 (1991).

3. Extremely efficient catalytic reduction of aromatic nitro compounds affording amines using amine-added $Rh_6(CO)_{16}$ catalyst system under CO/H_2O conditions

   K. Nomura, M. Ishino, and M. Hazama
   J. Mol. Catal., 66, L11 (1991).

4. Novel reduction of aromatic nitro compounds affording amines using CO and water catalyzed by phosphine-added $Rh(CO)_2(acac)$ complexes

   K. Nomura, M. Ishino, and M. Hazama
   J. Mol. Catal., 66, L19 (1991).

5. Efficient selective reduction of aromatic nitro compounds affording aromatic amines under CO/H_2O conditions catalyzed by amine-added rhodium-carbonyl complexes

   K. Nomura, M. Ishino, and M. Hazama
   Bull. Chem. Soc., Jpn., 64, 2624 (1991).

6. Selective catalytic reduction of aromatic nitro compounds affording amines under CO/H_2O conditions using amine-added ruthenium-carbonyl complexes

   K. Nomura
   Chem. Lett., 1679 (1991).

7. Novel selective catalytic reduction of aromatic nitro compounds affording amines using ruthenium-carbonyl complex in the presence of NEt_3 under CO/H_2O conditions

   K. Nomura
   J. Mol. Catal., 73, L1 (1992).

8. Selective reduction of aromatic nitro compounds affording aromatic amines under CO/H_2O conditions catalyzed by phosphine-added rhodium-, ruthenium-carbonyl complexes

   K. Nomura, M. Ishino, and M. Hazama
   J. Mol. Catal., in press.

List of Other Publications

1. Transition metal ketene complexes as active intermediate for catalytic carbonylation of geminal dibromoalkanes

   A. Miyashita, T. Kihara, K. Nomura, and H. Nohira
   Chem. Lett., 1607 (1986).

2. $Co_2(CH_2=C=O)(CO)_7$ as an active intermediate for cobalt-catalyzed alkoxycarbonylation of CH_2Br_2

   A. Miyashita, K. Nomura, S. Kaji, and H. Nohira
   Chem. Lett., 1983 (1989).

3. Cobalt-catalyzed aminocarbonylation of geminal dibromoalkanes. Formatin of 2-aminoamides and maloamide derivatives

   A. Miyashita, T. Kawashima, S. Kaji, K. Nomura, and H. Nohira
   Tetrahedron Lett., 32, 781 (1991).

4. n-Alkene and dihydrogen formation from n-alkanes by photocatalysis using carbonyl(halogeno)phosphine-rhodium complexes

   K. Nomura, and Y. Saito
   J. Chem. Soc., Chem. Commun., 161 (1988).

5. Photoenhanced catalytic dehydrogenation of methanol with tin(II)-coordinated iridium complexes

   K. Nomura, S. Shinoda, and Y. Saito
   J. Mol. Catal., 50, 303 (1989).

6. Photocatalytic dehydrogenation of 2-propanol with carbonyl(halogeno)phosphine-rhodium complexes

K. Nomura, S. Shinoda, and Y. Saito
J. Mol. Catal., 52, 99 (1989).

7. n-Alkene and dihydrogen formation by catalytic dehydrogenation of alkane with $RhCl(PR_3)_2$ photogenerated from $RhCl(CO)(PR_3)_2$

K. Nomura, and Y. Saito
J. Mol. Catal., 54, 57 (1989).

8. Selective head-to-tail dimer formation from acrylonitrile catalyzed by phosphine-added nickel(0) complexes

K. Nomura, and M. Ishino
J. Mol. Catal., 68, L5 (1991).

9. Phosphine-added nickel(0) complexes catalyzed selective dimerization of acrylonitrile affording methyleneglutaronitrile (2,4-dicyanobutene)

K. Nomura, and M. Ishino
J. Mol. Catal., 73, L15 (1992).

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GENERAL INTRODUCTION

1. Historical Background in Homogeneous Catalysis.
2. Fine Chemicals and Catalysis.
3. Introduction.

General Introduction

1. Historical Background in Homogeneous Catalysis

Catalysts are widely used in various chemical reactions, and it is estimated 60-70 % of all chemicals in industry. Among homogeneous catalysts, the last 40 years have seen prodigious growth. Rapid growth of investigations, especially in the field of homogeneous catalysis, provides new aspects to make so-called fine chemicals such as pharmaceuticals, specialty polymers, and agricultural and electronic chemicals.

As the general knowledge of organometallic chemistry has increased, the commercialization and application of homogeneous catalysis has begun essential dramatically. Applications of homogeneous catalysis are found in all major chemical reactions as is elucidated in Figure 1. Actually, in the early 1970's, commercialization of the five processes shown in Table 1 was started. These processes commercialized in 1970's were very successful and are unlikely to be replaced by new process.

<< Figure 1 >> << Table 1 >>

The character of industrial research seems to be changing, as previously pointed out by G.W. Parshall et al. (Pure Appl. Chem., 12, 1809 - 1818 (1985); Organometallics, 6, 687 - 692 (1988)). These three factors were considered for change:

1) maturity of the chemical industry
2) new feedstocks
3) high technology industry

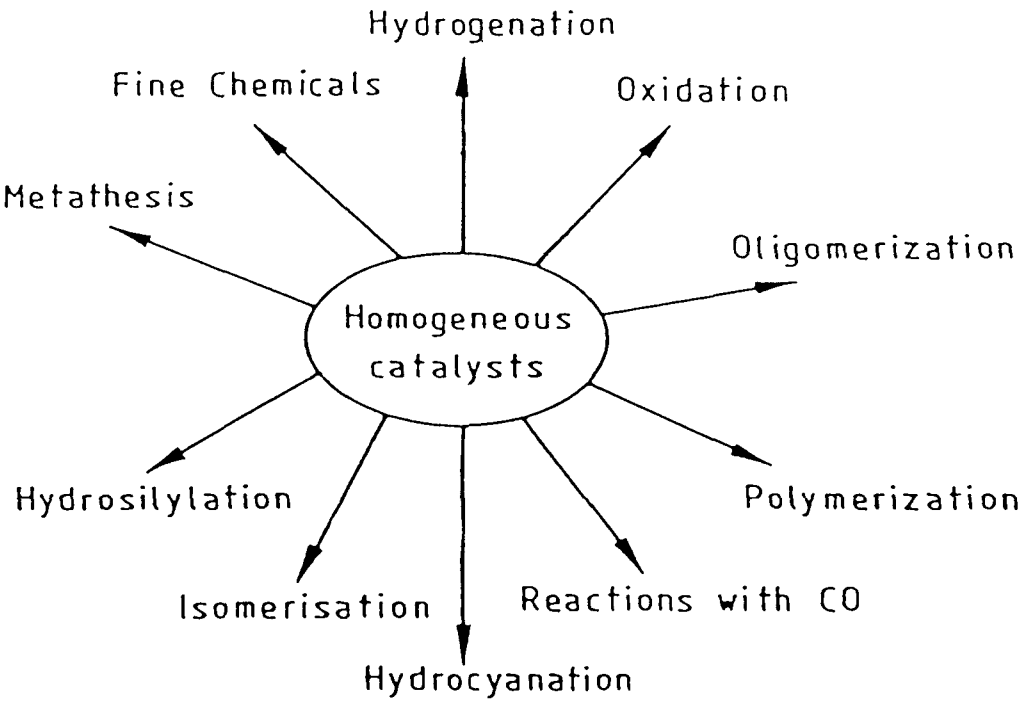

Figure 1. Reactions Catalyzed by Homogeneous Transition Metal Catalysts

Table 1. Selected Homogeneous Catalytic Processes Commercialized in the 1970's

Process	Catalyst	Company	Start up
Adiponitrile from HCN and butadiene	$Ni[P(OAr)_3]_4$	Du Pont	1971
Linear α-olefins from ethylene	$Ni(chel)_2$	Shell	1977
Rh-catalyzed hydroformylation	$RhH(CO)(PPh_3)_3$	Celanese, Union Carbide	1976
Acetic Acid from CO and methanol	$[Rh(CO)_2I_2]$	Monsanto	1970
L-Dopa by asymmetric hydrogenation	$[RhL_2(PR_3)_2]$	Monsanto	1974

In highly industrialized countries, especially, there is a great drive for fine chemicals. A drive for small volume chemicals such as pharmaceuticals, agricultural, and electronic chemicals can be seen. Small volume and high value chemicals are very well suited for the application of homogeneous catalysts.

In the 1990's, another new character of industrial research seems also to receive considerable attention, as recently pointed out by R.A. Sheldon et al. And in the next part, I'd like to focus the new aspects of catalysis.

Table 2. Fine Chemicals Manufactures: Characteristics

Fine Chemicals Manufacture : Characteristics
1. Complex, Multi-Functional Substrates/ Limited Thermal Stability
2. Liquid Phase/ Moderate Temperatures
3. Chemo-, Regio- and Stereoselectivity
4. Multi-Purpose, Batch-Wise Processing/ Different Variable/ Fixed Cost Ratio to Bulk Chemicals
5. Simplicity and Multi-Purpose Character of Operation Important

2. Fine Chemicals and Catalysis

In the 1990's, the industrial research seems to pay much more attention to environmental impact for producing chemicals, for constructing catalysis processes.

As shown in Table 3, the ratios of by-products/product for producing so-called fine chemicals, or pharmaceuticals are much larger than those for bulk chemicals and oil refining, because of long steps required or low overall yields.

As the needs for more effective and more environment-friendly processes have increased, the following characteristics have received considerable attention.

1) less inorganic effluent

2) fewer chemical steps

3) higher selectivities (chemo-, regio-, stereoselectivity)

In order to meet the above needs, the factors outlined in Figure 2 are considered to be important for new technologies.

Table 3. Environmental Acceptability: The E Factor

Industry Segment	Product Tonnage	Kg By-Products/ Kg Product
Oil Refining	10^6 - 10^8	ca. 0.1
Bulk Chemicals	10^4 - 10^6	< 1 - 5
Fine Chemicals	10^2 - 10^4	5 - 50
Pharmaceuticals	10 - 10^3	25 - > 100

ENVIRONMENTALITY

1) cleaner, more effective and environment-friendly products (readily recycled and/ or biodegraded)
2) zero emission plants/ integrated waste management
3) low-salt technologies - optimal atom utilization
4) alternatives for toxic and/ or hazardous reagents ($COCl_2$, Me_2SO_4, H_2CO/HCl, heavy metals) and chlorinated solvents
5) shorter routes and alternative feedstocks (e.g. alkanes for alkenes and aromatics, carbohydrates as raw materials)
6) higher chemo-, regio- and stereoselectivities

GOAL: ZERO ENVIRONMENTAL IMPACT

Figure 2.

And in particular for catalytic processes, the following parameters have drawn considerable attention to meet the above needs:

(a) atom utilization

(b) activity (TON, TOF)

(c) selectivity

(substrate-, chemo-, regio-, enantioselectivity)

(d) stability

(e) separation and recycling of catalyst

Recently, a lot of investigations have been made, and the new commercialized catalytic processes having the above characteristics may appear in the near future. Although there are some processes which have the characteristics and are uneconomical today, they will be able to become available in the near future, and might attract attention industrially.

3. Introduction

3-1. Background of invention

The Water-Gas-Shift Reaction has drawn considerable attention from the viewpoint of the industrial utilization of carbon monoxide:

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (1)$$

It is now used commercially to produce pure hydrogen. As one of the applications related to this reaction, organic syntheses under CO/H_2 conditions, especially the reduction of aromatic nitro compounds by homogeneous catalysis, has been paid particular attention. Many studies have already been made,

$$ArNO_2 + 3CO + H_2O \longrightarrow ArNH_2 + 3CO_2 \qquad (2)$$

however, the selective reduction with high catalytic activity, as well as with high selectivity has not so far been reported.

In addition, as mentioned above, the industrial research recently seems to have paid much more attention to environmental impact for producing chemicals, for constructing catalysis processes. Especially in the process for the production of aromatic amines, the conventional practical processes still have some problems, as shown in Table 4.

<< Table 4 >>

Given the above-mentioned situation, the needs of more effective and more environment-friendly processes have increased.

In particular, the following characteristics have been paid considerable attention:

1) less inorganic effluent

2) higher selectivities

3) higher catalytic activities

4) cleaner, more effective and environment-friendly process

(no toxicity, no after-treatment of by-products)

In this paper, I'd like to present a new and cleaner, environment-friendly catalytic process for production of aromatic amines having the above characteristics, as introduced briefly in the following parts.

Table 4. Conventional Practical Processes for the Production of Aromatic Amines << Example >>

Process	Problems
1) Sulfonation and then Amination (Hg, NH_3)	(a) Toxicity of Hg, and After-Treatment of the Waste Water (b) Low Yield, Reactivity
2) Stoichiometric Reduction of $ArNO_2$ (Fe Powder, Inorganic Salts NaHS)	(a) After-Treatment of By-Products (b) Contamination of the Products
3) Catalytic Hydrogenation of $ArNO_2$ (Pd/C, Pt/C, Raney-Ni etc.)	(a) Selectivity

3-2. Introduction.

This thesis entitled,"Studies on Transition Metal Catalyzed Reduction of Aromatic Nitro Compounds Under CO/H_2O Conditions," is a collection of studies I have carried out from 1988 to 1991. In particular, this thesis is composed of the following two parts:

(1) Selective Reduction of Aromatic Nitro Compounds Under Mild Conditions, Room Temperature and 1 Atm of CO, Catalyzed by Rhodium-, Ruthenium-Carbonyl Complexes.

(2) Ruthenium Catalyzed Selective Reduction of Aromatic Nitro Compounds Under CO/H_2O Conditions

Efficient catalytic reduction with both high catalytic activities and remarkable selectivity of the nitro-group are presented in each chapter and briefly introduced as follows:

Chapter 1 describes the selective reduction of aromatic nitro compounds affording corresponding aromatic amines under mild conditions, room temperature and 1 atm of CO, catalyzed by amine-, phosphine-, chelatephosphine-added homogeneous rhodium-, ruthenium-carbonyl complexes in the presence of NaOH aq. solution. The nitro-group has been found to exhibit remarkably high selectivities as well as high catalytic activities in these catalysis.

Chapter 2 describes the study of selective reduction of

aromatic nitro compounds using CO and water catalyzed by homogeneous ruthenium-carbonyl complexes in the presence of small amounts of specified amines. Both the high selectivity of the nitro group and its significant catalytic activity have also been presented in these catalysis. The detailed results of the effects of additives, such as the mixing of other transition metals and other co-catalysts are also presented in this chapter.

In both chapters, the tentative reaction pathway on this selective reduction have also been presented and discussed.

I hope my contribution in this paper will be appreciated by the people in this research field.

TRANSITION METAL CATALYZED REDUCTION OF AROMATIC NITRO COMPOUNDS UNDER CO/H_2O CONDITIONS

Chapter 1. Selective reduction of aromatic nitro compounds under mild conditions, room temperature and 1 atm of CO, catalyzed by rhodium-, ruthenium-carbonyl complexes.

Chapter 2. Ruthenium-catalyzed selective reduction of aromatic nitro compounds under CO/H_2O conditions.

[Chapter 1]

Selective reduction of aromatic nitro compounds under mild conditions, room temperature and 1 atm of CO, catalyzed by rhodium-, ruthenium-carbonyl complexes

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1-1. Efficient selective reduction of aromatic nitro compounds affording aromatic amines under CO/H_2O conditions catalyzed by amine-added rhodium-carbonyl complexes

1-2. Selective reduction of aromatic nitro compounds affording aromatic amines under CO/H_2O conditions catalyzed by chelate-phosphine-added rhodium-, ruthenium-carbonyl complexes.

1-3. Catalytic reduction of aromatic nitro compounds using CO and water with phosphine-added rhodium-carbonyl complexes.

1-4. Chapter 1 Discussion

1-1. Efficient selective reduction of aromatic nitro compounds affording aromatic amines under CO/H_2O conditions catalyzed by amine-added rhodium-carbonyl complexes

Abstract

Remarkably high catalytic activities for the reduction of aromatic nitro compounds affording aromatic amines using CO (1 atm) and water at room temperature were exhibited by using amine-added rhodium carbonyl complexes ($Rh(CO)_2(acac)$, $Rh_4(CO)_{12}$, and $Rh_6(CO)_{16}$) in 2-methoxyethanol or diglyme (diethylene glycol dimethyl ether) containing a 5N NaOH aqueous solution. The reduction proceeded not only with high catalytic activities, but also with remarkably high nitro-group selectivities, as exhibited in the case of 1-nitroanthraquinone affording 1-aminoanthraquinone, without any other unsaturated groups, such as C=O, being reduced. The T.O.F. (turnovers/time) of 1776 mol-cat^{-1} h^{-1} (296 g-atom Rh^{-1} h^{-1}) was attained for the reduction of p-nitroanisole yielding p-anisidine using $Rh_6(CO)_{16}$-1,8-bis(dimethylamino)naphthalene catalyst.

Introduction

Water-Gas-Shift Reaction (WGSR) has drawn considerable attention from the viewpoint of industrial utilization of carbon monoxide; it is now commercially used as a pure hydrogen source.[1] Many studies have, therefore, already been made concerning this subject using both homogeneous and heterogeneous catalysts.[2]

$$H_2O + CO \longrightarrow CO_2 + H_2 \qquad (1)$$

As one of its applications related to the WGSR, organic syntheses under CO/H_2O conditions using homogeneous transition metal complex catalysts, such as hydrogenation, reduction, hydroformylation, hydromethylation, or hydrocarbonylation, are very intriguing subjects,[2] especially the selective reduction of unsaturated compounds has been paid particular attention.[3]

The reduction of aromatic nitro compounds affording aromatic amines using carbon monoxide and water with homogeneous catalysts is a also very attractive subject, and many studies have already been made.[2,3] Alper found that the reduction proceeded under

$$ArNO_2 + 3CO + H_2O \longrightarrow ArNH_2 + 3CO_2 \qquad (2)$$

atmospheric pressure of CO and room temperature by using $Ru_3(CO)_{12}$ in a benzene-2-methoxyethanol-5N NaOH aqueous solution in the presence of a phase-transfer catalyst ($PhCH_2(C_2H_5)_3N^+Cl^-$),[3a] Kaneda also reported that amine-, diamine-added $Rh_6(CO)_{16}$ showed catalytic activities for the reduction of $PhNO_2$ in 2-ethoxyethanol-H_2O solution at 80°C,[3b] and Alessio exhibited that

$Rh_6(CO)_{16}$-phenanthrolines, especially 3,4,7,8-tetramethyl-1,10-phenanthroline, in ethanol was also effective for this reduction.[3d,e] However, catalytic reduction under mild reaction conditions with high activity has not yet been reported (T.O.F. of 6 g-atom-Ru^{-1} h^{-1} was reported in ref. 3a)).

In the present papers, we wish to describe that amine-, diamine-added rhodium carbonyl complexes show remarkably high catalytic activities as well as high nitro group selectivities for the reduction of aromatic nitro compounds under extremely mild reaction conditions of room temperature and of 1 atm of CO in 2-methoxyethanol or diglyme containing a 5N NaOH aq. solution.[4]

Experimental

General Procedure

All manipulations were carried out under a nitrogen atmosphere, or in vacuo. Water and 2-methoxyethanol, diglyme (diethyleneglycol dimethyl ether) and nitrobenzene (Nakarai Tesque. Co., Ltd.) were distilled and stored in a Schlenck-type tube under a nitrogen atmosphere. Other aromatic nitro compounds were used as reagent grade (Nakarai Tesque. Co., Ltd. or Tokyo Kasei Co., Ltd.). $Rh_4(CO)_{12}$, $Rh(CO)_2(acac)$, and $Rh_6(CO)_{16}$ were also used as reagent grade (N.E. Chem. Cat. Co., Ltd.).

Reduction of Aromatic Nitro Compounds under CO/H_2O

The reaction was typically carried out as follows: a solution with $Rh_6(CO)_{16}$ (0.001 mmol) in 2-methoxyethanol (15 ml) under a nitrogen atmosphere in a Schlenck-type tube was stirred magnetically and the required amount of amine added. Then, the addition of a 5N-NaOH aq. solution (5 ml) and aromatic nitro compounds (5 mmol) into the reaction mixture was followed by the introduction of CO (1 atm). The mixture, equipped with CO gas bag, was allowed to react at room temperature (25 °C) for the prescribed time. The reaction product was then determined by GLC using an internal standard, and was identified using GLC by co-injection with an authentic sample (column OV-225, 3m) and GC-MS (QP-1000, Shimazu Co., Ltd.).[5,6]

The reduction of 1-nitroanthraquinone (Tokyo Kasei Co., Ltd.) was performed similarly. A certain excess amount of water was added into the reaction medium after the reaction; a red precipitate which was obtained by filteration was dried and redissolved in N,N-dimethylformamide and was determined by GLC (column OV-210, 1m) using an internal standard.

Results and Discussion

1. Reduction of nitrobenzene using CO and water catalyzed by amine-added $Rh(CO)_2(acac)$ complexes

The results for the reduction of $PhNO_2$ catalyzed by various amine-added $Rh(CO)_2(acac)$ complexes in a 2-methoxyethanol-5N NaOH aqueous solution under 1 atm of CO and room temperature (25 °C) for 3 h are summarized in Table 1.

<< Table 1 >>

The reduction proceeded at remarkable rates with the use of a NaOH aqueous solution; a corresponding amount of aniline was obtained as the reaction product (Table 1).[5,6]

It should be noted that the rate markedly increased upon the addition of a small amount of amines; especially, 9,10-diaminophenanthrene and o-phenylenediamine were effective for this reaction. As revealed from this table, the catalytic activities shown here (ex. 57 g-atom-Rh^{-1} h^{-1} for $Rh(CO)_2(acac)$/ 9,10-diaminophenanthrene cat.) are much higher than those previously reported (ex. 6 g-atom-Ru^{-1} h^{-1} from ref. 3a, it is the highest value so far reported).

Table-2 shows a time-course plot for this reaction using a $Rh(CO)_2(acac)$-9,10-diaminophenanthrene catalyst.

<< Table 2 >>

It was revealed that the reaction proceeded at a significant rate during the initial stage (72 turnovers for 1h), but that the

Table 1. The reduction of nitrobenzene catalyzed by amine-added $Rh(CO)_2(acac)$ complexes - The effect of amine additives -

amine	molar ratio[1)]	turnovers*
none[2)]	---	< 1
none	---	37
$H_2N(CH_2)_2NH_2$	1.5	52
$Me_2N(CH_2)_2NMe_2$	1.5	68
o-phenylenediamine	1.5	155
2,3-diaminonaphthalene	1.5	99
9,10-diaminophenanthrene	1.5	122
9,10-diaminophenanthrene	1.5	172[3)]
1,8-diaminonaphthalene	1.5	68
pyridine	3.0	61
NEt_3	3.0	66

Reaction conditions: 2-methoxyethanol/5N-NaOH aq. = 15/5 (ml), $Rh(CO)_2(acac)$ 0.02 mmol, $PhNO_2$ 5 mmol, 25 °C, CO 1 atm, 3 h.

1) molar ratio of amine/Rh;

2) H_2O (5 ml) was used instead of 5N-NaOH aq. solution.

3) $Rh(CO)_2(acac)$ 0.01mmol.

*: turnovers = amount of aromatic amine produced (mmol)/ amount of catalyst (mmol)

Table 2. Time-course for reduction of nitrobenzene catalyzed by $Rh(CO)_2(acac)$-9,10-diaminophenanthrene catalyst under CO/H_2O conditions.

time/h	aniline formed/mmol	turnovers
1	1.44	72
3	2.44	122
6	3.62	181
10	4.34	217

Reaction conditons: $Rh(CO)_2(acac)$/9,10 diamino--phenanthrene (0.02/ 0.03 mmol), 2-methoxyethanol/ 5N NaOH aq. = 15/5 (ml), $PhNO_2$ 5 mmol, CO 1 atm, 25 °C.

rate decreased gradually, because of, perhaps, changes in the NaOH base concentrations (Na_2CO_3 was accompanied, accumlated from NaOH and CO_2 in the reaction mixture), as mentioned below.

The results for the reduction of nitrobenzene under various NaOH concentration conditions are shown in Table 3. The 5N-NaOH aqueous solution used was thought to play an important role in this reaction to proceed at a significant rate. 2-methoxyethanol was also favorable as a solvent.

<< Table 3 >>

2. Selective catalytic reduction of aromatic nitro compounds using amine-added $Rh_4(CO)_{12}$ complexes

2-1. Reduction of aromatic nitro compounds using 9,10-diaminophenanthrene-added $Rh_4(CO)_{12}$ complex

As shown in Table 4, the reaction rate for the reduction of nitrobenzene using a $Rh_4(CO)_{12}$ complex also remarkably increased upon the addition of 9,10-diaminophenanthrene (from 108 to 225 turnovers with a diamine/Rh molar ratio varying from 0 to 2.25, respectively). Turnovers of 610 mol-cat^{-1} (153 g-atom Rh^{-1}), for 3 h were obtained at low $Rh_4(CO)_{12}$ concentration.

<< Table 4 >>

Table 5 summarizes the results for the reduction of various substituted nitrobenzenes using the $Rh_4(CO)_{12}$-9,10-diamino-phenanthrene catalyst for 90 min.

Table 3. 9,10-Diaminophenanthrene-added $Rh(CO)_2(acac)$ catalyzed reduction of nitrobenzene under CO/H_2O conditions

solvent (ml)	NaOH aq. base conditions (ml)	turnovers
2-methoxyethanol(15)	1.5N NaOH aq. (5)	64
2-methoxyethanol(15)	3N NaOH aq. (5)	94
2-methoxyethanol(15)	5N NaOH aq. (2.5)	78
2-methoxyethanol(15)	5N NaOH aq. (5)	122
2-methoxyethanol(8)	5N NaOH aq. (5)	79
2-propanol(15)	5N NaOH aq. (5)	69

Reaction conditions: $Rh(CO)_2(acac)$/9,10-diaminophenanthrene = 0.02/0.03 (mmol), $PhNO_2$ 5 mmol, CO 1 atm, 25 °C, 3h.

Table 4. Reduction of nitrobenzene catalyzed by 9,10-diaminophenanthrene-added $Rh_4(CO)_{12}$ complex under CO/H_2O conditions.

molar ratio*	turnovers/mol-cat^{-1}
0	108
1.09	200
2.25	225
1.50	610#

Reaction conditions: $Rh_4(CO)_{12}$ 0.02 mmol, 2-methoxyethanol/5N NaOH aq. = 15/5 (ml), $PhNO_2$ 5 mmol, CO 1 atm, r.t. (25 °C), 3 h.
*molar ratio of 9,10-diaminophenanthrene/Rh;
#$Rh_4(CO)_{12}$ 0.005 mmol.

<< Table 5 >>

It should be noted that these reductions proceeded not only with significant rates but also with high selectivities of nitro-group. The order, p-NH_2 (>250) > o-NH_2 (233) > p-Cl (218) > o-Cl (190) > p-Me (178), P-OMe (175) > H (158), was obtained for this reaction, which is somewhat different from that previously obtained using the $Rh_4(CO)_{12}$-dppe (dppe: $Ph_2P(CH_2)_2PPh_2$) catalyst system (p-NH_2 (>250) > o-Cl (210) > o-NH_2 (190) > p-Cl (158) > p-OMe (140), p-Me (128) > H (110 turnovers, mol-cat^{-1} for 90 min)) under the same reaction conditions,[4a] although the high nitro-group selectivities were almost the same as those obtained using Rh-dppe catalyst system.[7] Further, the reduction of aromatic nitro compounds came to completing upon further stirring; p-nitrobenzonitrile was converted to afford p-aminobenzonitrile almost exclusively without the C≡N bond being reduced (Table 6).

<< Table 6 >>

2-2. Reduction of 1-nitroanthraquinone affording 1-aminoanthraquinone catalyzed by amine-added $Rh_4(CO)_{12}$ complexes under CO/H_2O conditions

Importantly, it was also found that 1-nitroanthraquinone was completely reduced to produce 1-aminoantharquinone (10 h, >99.9 % yield, >250 turnovers) using the above-mentioned $Rh_4(CO)_{12}$-diamine catalyst without any other unsaturated groups, such as

Table 5. Selective reduction of aromatic nitro compounds using CO and water with $Rh_4(CO)_{12}$-9,10-diaminophenanthrene catalyst.

Reactant	Product	turnovers/mol-cat^{-1}
nitrobenzene	aniline	158
o-chloronitrobenzene	o-chloroaniline	190
o-nitroaniline	o-phenylenediamine	233
p-nitroaniline	p-phenylenediamine	>250$^{\$}$
p-nitroanisole	p-anisidine	175
p-nitrotoluene	p-toluidine	178
p-chloronitrobenzene	p-chloroaniline	218

Reaction conditions: $Rh_4(CO)_{12}$/9,10-diaminophenanthrene = 0.02/0.12 (mmol), 2-methoxyethanol/5N NaOH aq. = 15/5 (ml), aromatic nitro compounds 5 mmol, CO 1 atm, r.t. (25 °C), 1.5 h.
$: >99 % yield

Table 6. Reduction of aromatic nitro compounds under CO/H_2O conditions.

reactant	product	yield/%
nitrobenzene	aniline	>99
o-chloronitrobenzene	o-chloroaniline	>99
p-nitrobenzonitrile	p-aminobenzonitrile	>99
1-nitroanthraquinone	1-aminoanthraquinone	>99

Reaction conditions: $Rh_4(CO)_{12}$/9,10-diaminophenanthrene = 0.02/0.12 (mmol), 2-methoxyethanol/5N NaOH aq. = 15/5 (ml), aromatic nitro compounds 5 mmol, CO 1 atm, r.t. (25 °C), 10 h.

C=O, being reduced (Table 6). Aminoanthraquinone has been one of the most important key materials used as dyes and their intermediates; although it has been commercially produced by either a stoichiometric or catalytic reduction of nitro-anthraquinone or by sulfonating before amination, there are still some problems. We believe that the above-mentioned fact is very important from both industrial and synthetic viewpoints; it may be commercially used in the future as a process for the production of amines by a selective catalytic reduciton of aromatic nitro compounds after much further development of this subject.

The results for the reduction of 1-nitroantharquinone with various amine-added $Rh_4(CO)_{12}$ are summarized in Table 7.

<< Table 7 >>

The reduction rate increased upon the addition of only a small amount of amines, especially NEt_3 and 4,4-(dimethylamino)-pyridine.[7] The important fact was also found that the effective amines were different between the reduction of $PhNO_2$ using amine-added $Rh(CO)_2(acac)$ and that of 1-nitroanthraquinone using amine-added $Rh_4(CO)_{12}$.

3. Catalytic reduction of nitrobenzene under CO/H_2O or H_2 conditions catalyzed by 9,10-diaminophenanthrene-added $Rh(CO)_2(acac)$ complex

Particular attention should be paid to Table-8 regarding the different reaction rates obtained for the reduction of

Table 7. Reduction of 1-nitroanthraquinone affording 1-aminoanthraquinone under CO/H_2O conditions catalyzed by amine-added $Rh_4(CO)_{12}$ complexes.

amine	molar ratio*	turnovers/mol-cat^{-1}
none	---	373
9,10-diamino--phenanthrene	1.5	419
NEt_3	3.0	554
4-(dimethyamino)--pyridine	3.0	529
1-aminoanthraquinone	3.0	469

Reaction conditions: diglyme (diethylene glycol dimethyl ether)/ 5N NaOH aq. = 30/10 (ml), 1-nitroanthraquinone 10.7 mmol, $Rh_4(CO)_{12}$ 0.01 mmol, CO 1 atm, r.t. (25 °C), 3 h.

*molar ratio of amine/Rh.

nitrobenzene under CO/H_2O and under H_2 conditions. Hydrogen gas was not formed after the reaction mixture under these CO/H_2O conditions;[8] clearly indicating that the reduction under CO/H_2O using this catalyst system did not proceed by the reaction of aromatic nitro compounds and the hydrogen gas that was formed by the Water-Gas-Shift Reaction. This suggests that a different reaction mechanism can be considered for this reduction under CO/H_2O.[9]

<< Table 8 >>

4. Efficient catalytic reduction of aromatic nitro compounds affording amines using amine-added $Rh_6(CO)_{16}$ catalyst systems under CO/H_2O conditions

The results show the effects of various amine additives on the reductions of p-nitroanisole and p-nitrotoluene with $Rh_6(CO)_{16}$ in a 2-methoxyethanol/5N-NaOH aqueous solution under 1 atm of CO at room temperature (25 °C) for 1 h (summarized in Table 9).

<< Table 9 >>

It should be noted that the rate remarkably increased upon the addition of a very small amount of amines, especially N,N-dimethylbenzylamine, N,N,N',N'-tetramethyl-1,4-diaminobutane, and tributylamine for the reduction of p-nitrotoluene and 1,8-bis(dimethylamino)naphthalene, 2-pyridinol, and tributylamine for the reduction of p-nitroanisole. It should also be noted that the

Table 8. Catalytic reduction of nitrobenzene under CO/H_2O or under H_2 conditions

catalyst	conditions	temp./°C	time/h	turnovers*
$Rh(CO)_2(acac)$/ 9,10-diaminophenanthrene	CO/H_2O	r.t.	3	122
	H_2	r.t.	3	16
5%-Pd/C	H_2	r.t.	24	trace
	H_2	50	3	134

Reaction conditions: a) under CO/H_2O; $Rh(CO)_2(acac)$/diamine = 0.02/0.03 (mmol), 2-methoxyethanol/5N NaOH aq. = 15/5 (ml), nitrobenzene 5 mmol, CO 1 atm. b) under H_2; the same reaction conditions except that 5N NaOH aq. was not added.

*g-atom catalyst metal^{-1}

Table 9. Efficient catalytic reduction of aromatic nitro compounds affording corresponding amines using amine-added $Rh_6(CO)_{16}$ complexes under CO/H_2O conditions.

amine	molar ratio[1)]	reactant	turnovers mol-cat^{-1}(g-atom Rh^{-1})
$Me_2N(CH_2)_4NMe_2$	1	p-nitrotoluene	1050 (175)
o-phenylenediamine	1	p-nitrotoluene	738 (123)
$PhCH_2NMe_2$	3	p-nitrotoluene	1218 (203)
N^nBu_3	3	p-nitrotoluene	1008 (168)
1,8-bis(dimethyl--amino)naphthalene	1.5	p-nitroanisole	1776 (296)
2-pyridinol	3	p-nitroanisole	1764 (294)
$PhCH_2NMe_2$	3	p-nitroanisole	1350 (225)
N^nBu_3	3	p-nitroanisole	1416 (236)
none	-	nitrobenzene	486 (81#)

Reaction conditions: $Rh_6(CO)_{16}$ 0.001 mmol, 2-methoxyethanol/5N NaOH aq. = 15/5 (ml), nitro compounds 5 mmol, CO 1 atm, r.t. (25 °C), 1 h.

1): amount of amine or diamine (mmol)/ amount of catalyst metal (mmol). #: $Rh_6(CO)_{16}$ 0.001 mmol, 5 h.

effective amines are different between these two compounds. The catalytic activity (T.O.F.) of 1776 mol-cat^{-1} h^{-1} (296 g-atom Rh^{-1} h^{-1}) was attained for the reduction of p-nitroanisole, even under these extremely mild reaction conditions. The catalytic activities shown in Table-9 are, as far as we know, much higher than those previously reported.[3)]

The factors affecting these reduction rates and mechanistic studies are now under investigation.

Summary

In conclusion, this paper can be summarized as follows:

(i) Remarkably high catalytic activities for the reduction of aromatic nitro compounds to yield aromatic amines were exhibited by using amine-added rhodium carbonyl complexes under extremely mild reaction conditions: room temperature and atmospheric pressure of carbon monoxide in the presencce of a sodium hydroxide aqueous solution.

(ii) The reduction proceeded not only with high catalytic activities, but also with remarkably high nitro-group selectivities, as exhibited in the case of 1-nitroanthraquinone affording 1-aminoanthraquinone and so on.

(iii) Taking into account the above results, a different reaction mechanism will be considered for the selective reduction of aromatic nitro compounds using amine-added rhodium carbonyl complexes under CO/H_2O conditions.

References and Notes

1) For example (Review),

a) R. M. Laine, E. J. Crawford, J. Mol. Catal., 44, 357 (1988).

b) P. C. Ford, A. Rokicki, Adv. Organomet. Chem., 28, 139 (1988).

2) For example (Review),

a) P. Escaffre, A. Thorez, P. Kalck, J. Mol. Catal., 33, 87 (1985).

b) Y. Sugi, Shokubai(Catalyst), 25, 464 (1983).

3) For example,

a) H. Alper, S. Amaratunga, Tetrahedron Lett., 21, 2603 (1980).

b) K. Kaneda, M. Hiraki, T. Imanaka, S. Teranishi, J. Mol. Catal., 12, 385 (1981).

c) R. C. Ryan, G. M. Wilemon, M. P. Dalsanto, C. U. Pittman, Jr., ibid., 5, 319 (1979).

d) E. Alessio, G. Zassinovich, G. Mestroni, ibid., 18, 113 (1983).

e) E. Alessio, F. Vinzi, G. Mestroni, ibid., 22, 327 (1984).

f) K. Januszkiewicz, H. Alper, ibid., 19, 139 (1983).

g) K. E. Hashem, J. F. Petrignani, H. Alper, ibid., 26, 285 (1984).

h) M. Miura, M. Shinohara, M. Nomura, ibid., 45, 151 (1988).

4) We recently have discovered new catalyst systems for selective reduction of aromatic nitro compounds under the mild reaction conditions of room temperature (25 °C) and CO atmosphere:

a) K. Nomura, M. Ishino, and M. Hazama, J. Mol. Catal., 65, L5 (1991).

b) idem. ibid., 66, L1 (1991).

c) idem. ibid., 66, L11 (1991).

d) idem. ibid., 66, L19 (1991).

e) idem. Bull. Chem. Soc., Jpn., 64, 2624 (1991).

f) idem. J. Mol. Catal., in press.

5) During and after the reaction, sodium carbonate was accompanied which was generated from the reaction of sodium hydroxide and CO_2.

6) The reaction products were only corresponding amines and no other products were observed on this reaction, except that trace amount of other deoxygenated products (azobenzene, azoxybenzene) were sometimes observed on GLC scale in the reduction of nitrobenzene.

7) The rate also increased at higher reaction temperature, or higher CO pressure; K. Nomura, unpublished results.

8) The important fact was also found that a trace amount of dihydrogen (ca. 0.026 mmol) from the reaction mixture was detected after the reduction of $PhNO_2$ (ca. 5 mmol) using $Rh_4(CO)_{12}$ (0.02 mmol) in 2-methoxyethanol(15 ml)-5N NaOH aq. solution (5 ml) under CO (1 atm) at 25 °C for 4 h. This result, that the reduction proceeded without by-producing hydrogen gas which was formed by the Water-Gas-Shift-Reaction, is very important from the industrial viewpoints, and also indicates the above-mentioned assumption.

9) We believe that an original reaction pathway, such as via

metal-nitrene intermediate, might be considered for this selective reduction under CO/H_2O conditions; mechanistic studies are now being carried out.

For example, R. A. Sheldon,"Chemicals from Synthesis Gas," D. Reidel Publishing Co., Ltd., pp. 181 (1981); T. Ikariya, Shokubai (Catalyst), 5, 271 (1989).

1-2. Selective reduction of aromatic nitro compounds affording aromatic amines under CO/H_2O conditions catalyzed by chelatephosphine-added rhodium-, ruthenium-carbonyl complexes

Abstract

High catalytic activities for the selective reduction of aromatic nitro compounds yielding corresponding amines under the mild reaction conditions of room temperature and 1 atm of CO were found to be exhibited by chelatephosphine (dppe, dppm etc.; dppe: 1,2-bis(diphenylphosphino)ethane, dppm: bis(diphenylphosphino)methane)-added rhodium and ruthenium carbonyl complexes containing a 5N NaOH aqueous solution. The reduction proceeded not only with high catalytic activities, but also with remarkably high selectivities of nitro group, as exhibited in the case of 1-nitroanthraquinone affording 1-aminoanthraquinone without other unsaturated groups such as carbonyl group being reduced.

Introduction

"The activation of small molecules" is one of the most important subjects in current chemistry, especially in the field of catalysis.[1] From the aspects of industrial utilization of carbon monoxide, the Water-Gas-Shift Reaction (WGSR) has attracted considerable attention and is commercially used to produce pure hydrogen.[2] Therefore, a lot of studies of this reaction have been made using homogeneous and heterogeneous catalysts.[2]

$$H_2O + CO \longrightarrow CO_2 + H_2 \qquad (1)$$

As one of the applications related to the WGSR, organic syntheses under CO/H_2O conditions using homogeneous transition metal complex catalysts,[3] especially the selective reduction of unsaturated compounds have attracted particular attention.[3,4]

The reduction of aromatic nitro compounds affording aromatic amines using carbon monoxide and water with homogeneous catalysts is, therefore, a very attractive subject, and many studies have already been reported.[3,4] Alper et al. found that the reduction

$$ArNO_2 + 3CO + H_2O \longrightarrow ArNH_2 + 3CO_2 \qquad (2)$$

proceeded under atmospheric pressure of CO and room temperature using $Ru_3(CO)_{12}$ in benzene-2-methoxyethanol-5N NaOH aqueous solution in the presence of a phase-transfer catalyst ($PhCH_2(C_2H_5)_3N^+Cl^-$).[4a] Kaneda et al. also exhibited that amine-, diamine-added $Rh_6(CO)_{16}$ in 2-ethoxyethanol-H_2O solution showed catalytic activities for the reduction of nitrobenzene,[4b] and

Alessio et al. reported that $Rh_6(CO)_{16}$-phenanthrolines, especially 3,4,7,8-tetramethyl-1,10-phenanthroline, in ethanol was effective for this reaction.[4d,e] However, catalytic reduction under mild reaction conditions with high activities has not so far been reported (T.O.F. of 6 g-atom-Ru^{-1} h^{-1} was reported in ref. 4a)).

In the present paper, we would like to describe that the reduction of aromatic nitro compounds proceeded at significant rates, as well as with high nitro group selectivities, under the mild conditions of room temperature and atmospheric pressure of CO, using rhodium and ruthenium carbonyl complexes in the presence of various chelatephosphines.[5]

Experimental

General Procedure

All manipulations were carried out under nitrogen atmosphere, or in vacuo. Water and 2-methoxyethanol (Nakarai Tesque. Co., Ltd.) and nitrobenzene (Nakarai Tesque. Co., Ltd.) were distilled and stored in a Schlenck-type tube under nitrogen atmosphere. Other aromatic nitro compounds were reagent grade (Nakarai Tesque. Co., Ltd. or Tokyo Kasei Co., Ltd). $Rh_4(CO)_{12}$, $Rh(CO)_2(acac)$, and $Ru_3(CO)_{12}$ were also reagent grade (N.E. Chem. Cat. Co., Ltd.).

Reduction of aromatic nitro compounds under CO/H_2O

Reactions were typically carried out in a Schlenck-type tube containing $Rh_4(CO)_{12}$ (0.02 mmol), chelatephosphine (0.02 mmol), into which 2-methoxyethanol (15 ml) was added under nitrogen wiht vigorou stirring. Then, a 5N-NaOH aq. solution (5 ml) and $PhNO_2$ (5 mmol) were added followed by the introduction of CO (1 atm). The mixture, equipped with CO gas bag, was allowed to react at room temperature (25 °C) for the prescribed time. The reaction products were then determined quantitatively by GLC using an internal standard, and identified by co-injection method in GLC with an authentic sample (column OV-225, 3m) and by GC-MS (QP-1000, Shimazu Co., Ltd.).[6,7,)]

The reduction of 1-nitroanthraquinone (Tokyo Kasei Co.) was performed similarly. An excess amount of water was added to the reaction medium after the reaction; a red precipitate was

obtained by filteration, and was dried, redissolved in N,N-dimethyl formamide was analyzed by GLC (column OV-210, 1m) using an internal standard. Identification was made by comparison of the retention time of chromatogram, elemental analysis, and GC-MS.

Results and Discussion

1. Reduction of nitrobenzene using $Rh_4(CO)_{12}$ complex under CO/H_2O conditions:

-Effect of solvents and base concentrations-

Table 1 summarizes the results obtained for the reduction of nitrobenzene catalyzed by $Rh_4(CO)_{12}$ in various solvents under CO/H_2O conditions (3 h).

<< Table 1 >>

The reaction proceeded at a significant rate even under the mild reaction conditions of room temperature and 1 atm of CO; 2-methoxyethanol was more favorable than the other solvents used here for this reaction.

It was also found that the reduction rate decreased (32 turnovers) under atmospheric pressure of hydrogen, in place of CO, in 2-methoxyethanol using $Rh_4(CO)_{12}$ catalyst,[8] suggesting that the reduction under CO/H_2O using this catalyst did not proceed by the reaction of aromatic nitro compounds and the hydrogen gas generated from the Water-Gas-Shift Reaction, and therefore a different reaction pathway will be considered for this reduction under CO/H_2O.

The results for this reduction using various NaOH concentrations are summarized in Table 2.

<< Table 2 >>

Table 1. Reduction of nitrobenzene catalyzed by $Rh_4(CO)_{12}$ under CO/H_2O conditions

- Catalytic activities in various solvents -

catalyst	solvent	aniline formed /mmol	turnovers /mol-cat^{-1}
$Rh_4(CO)_{12}$	2-methoxyethanol	1.86	93
	THF	1.33	67
	1,4-dioxane	1.29	64
	benzene	1.35	67
	2-propanol	1.56	78

Reaction conditions: solvent/5N-NaOH aq. = 15/5 (ml), $Rh_4(CO)_{12}$ 0.02mmol, $PhNO_2$ ca. 5mmol, CO 1 atm, room temperature (25 °C), 3 h.

Table 2. $Rh_4(CO)_{12}$-catalyzed reduction of nitrobenzene using CO and water in various NaOH base concentrations.

catalyst	NaOH aq.	aniline formed /mmol	turnovers $mol\text{-}cat^{-1}$
$Rh_4(CO)_{12}$	H_2O	trace	< 1
	3N-NaOH	1.25	62
	5N-NaOH	1.86	93

Reaction conditions: 2-methoxyethanol/NaOH aq. = 15/5 (ml), $Rh_4(CO)_{12}$ 0.02 mmol, $PhNO_2$ ca. 5mmol, room temperature, CO 1 atm, 3 h.

As previously pointed out by Alper et al., for the reduction of $ArNO_2$ using $Ru_3(CO)_{12}$ complex in benzene-2-methoxyethanol-5N NaOH aqueous solution in the presence of a phase-transfer catalyst,[4a] the NaOH aqueous solution added was also very important for this reaction to proceed at a remarkable rate, even in the absence of the phase-transfer catalyst.[4a]

2. Reduction of nitrobenzene using chelatephosphine-added Rh and Ru carbonyl complexes under CO/H_2O:
-Effect of chelatephosphine additives-

The results obtained for the reduction of nitrobenzene using $Rh_4(CO)_{12}$ complex, in the presence of organophosphines, are summarized in Table 3.

<< Table 3 >>

It should be noted that the rate markedly increased with the addition of chelatephosphine such as dppm ($Ph_2PCH_2PPh_2$), dppe ($Ph_2P(CH_2)_2PPh_2$), and dppp ($Ph_2P(CH_2)_5PPh_2$), although the rate decreased with the addition of PPh_3. A similar effect was also observed in the reduction of $PhNO_2$ using $Ru_3(CO)_{12}$ and $Rh(CO)_2(acac)$ complexes. The catalytic activities shown in this table were higher than those previously reported.[4]

It was also revealed from Table 4, that the amount of phosphine chelate added to rhodium, or ruthenium complexes is very important in order for this reaction to proceed at a significant rate. Quite different reaction rates were obtained for the reduction of $PhNO_2$ using $Rh_4(CO)_{12}$-dppm catalyst on

Table 3. Reduction of nitrobenzene using CO and water with chelatephosphine-added rhodium, ruthenium complexes.

complex	phosphine#	molar ratio*	turnovers/mol-cat^{-1}
$Rh_4(CO)_{12}$	----	----	93
$Rh_4(CO)_{12}$	dppm	0.25	199
$Rh_4(CO)_{12}$	dppe	0.25	168
$Rh_4(CO)_{12}$	dppp	0.25	187
$Rh_4(CO)_{12}$	PPh_3	0.25	50
$Rh(CO)_2(acac)$	----	----	37
$Rh(CO)_2(acac)$	dppm	0.40	42
$Rh(CO)_2(acac)$	dppe	0.50	43
$Rh(CO)_2(acac)$	dppe	1.00	51
$Rh(CO)_2(acac)$	dppp	1.00	51
$Rh(CO)_2(acac)$	dpph	1.00	45
$Ru_3(CO)_{12}$	----	----	51
$Ru_3(CO)_{12}$	dppe	0.50	95
$Ru_3(CO)_{12}$	PPh_3	0.33	43

Reaction conditions: 2-methoxyethanol/5N-NaOH aq. = 15/5 (ml), $PhNO_2$ ca. 5 mmol, CO 1 atm, r.t., 3 h, catalyst 0.02 mmol.

#dppm: $Ph_2PCH_2PPh_2$; dppe: $Ph_2P(CH_2)_2PPh_2$;

dppp: $Ph_2P(CH_2)_5PPh_2$; dpph: $Ph_2P(CH_2)_6PPh_2$.

*: molar ratio = chelatephosphine (mmol)/ amount of catalyst metal (mmol).

changing the dppm/Rh molar ratio (93, 128, 199, 59 and 40 mol-cat^{-1} to a molar ratio of 0, 0.09, 0.25, 0.50 and 1.00, respectively). This effect was also observed in the reduction of $PhNO_2$ using $Ru_3(CO)_{12}$-dppe catalyst.

<< Table 4 >>

3. Reduction of various aromatic nitro compounds using the $Rh_4(CO)_{12}$-dppe catalyst system under CO/H_2O conditions.

Table 5 summarizes the results obtained for the reduction of various aromatic nitro compounds using $Rh_4(CO)_{12}$-dppe catalyst for 1.5 h under room temperature (25 °C) and atmospheric CO pressure.

<< Table 5 >>

Considerable attention should be paid to the fact that the reduction proceeded not only with high catalytic activities, but also with significant nitro-group selectivities. Chloro-substituted nitrobenzenes were reduced to yield the corresponding chloroanilines: the reduction was completed in the case of p-nitroaniline. It was also revealed that the rates for substituted nitrobenzenes increased in the order of p-NH_2 > o-Cl > o-NH_2 > p-Cl > p-Me, p-OMe > H.

We believe it also important that 1-nitroanthraquinone was converted to 1-aminoanthraquinone with high selectivity without reduction of any other unsaturated groups such as carbonyl group.[9] Aminoanthraquinone is a key material in dyes and their

Table 4. Reduction of nitrobenzene using CO and water catalyzed by $Rh_4(CO)_{12}$-, $Ru_3(CO)_{12}$-chelatephosphine complexes.

complex	chelatephosphine	molar ratio*	turnovers/mol-cat^{-1}
$Rh_4(CO)_{12}$	dppm	---	93
	dppm	0.09	128
	dppm	0.25	199
	dppm	0.50	50
	dppm	1.00	40
$Ru_3(CO)_{12}$	dppe	---	51
	dppe	0.25	67
	dppe	0.33	82
	dppe	0.50	95
	dppe	1.00	49

Reaction conditions: 2-methoxyethanol/5N-NaOH aq. = 15/5 (ml), $PhNO_2$ ca. 5 mmol, CO 1 atm, r.t., 3 h, catalyst 0.02 mmol.
*see Table 3.

Table 5. Selective reduction of aromatic nitro compounds using CO and water with $Rh_4(CO)_{12}$-dppe catalyst.

Reactant	Product	turnovers/mol-cat^{-1}
nitrobenzene	aniline	110
o-chloronitrobenzene	o-chloroaniline	210#
o-nitroaniline	o-phenylenediamine	190
p-nitroaniline	p-phenylenediamine	>250$
p-nitroanisole	p-anisidine	140
p-nitrotoluene	p-toluidine	128
p-chloronitrobenzene	p-chloroaniline	158
1-nitroanthraquinone	1-aminoanthraquinone	128

Reaction conditions: $Rh_4(CO)_{12}$/dppe = 0.02/0.02 (mmol), 2-methoxyethanol/5N NaOH aq. = 15/5 (ml), nitro compounds 5 mmol, CO 1 atm, r.t. (25 °C), 1.5 h.
#:84%yield; $: >99%yield.

intermediates. Therefore, this fact is, we believe, very important from both the industrial as well as the synthetic point of view; this reaction may be able to be used in the near future as a process for the production of aromatic amines by selective reduction of aromatic nitro compounds after more development.

Summary

In conclusion, this paper can be summarized as follows:

(i) Remarkably high catalytic activities for the reduction of aromatic nitro compounds to yield aromatic amines were exhibited by using rhodium and ruthenium phosphine chelate complexes under the extremely mild reaction conditions of room temperature and atmospheric pressure of carbon monoxide, in a sodium hydroxide aqueous solution.

(ii) The reduction proceeded not only with high catalytic activities, but also with high nitro-group selectivities, as for example in the reduction of 1-nitroanthraquinone affording 1-aminoanthraquinone.

(iii) An original reaction pathway may be considered for the reduction of aromatic nitro compounds using chelatephosphine-added rhodium and ruthenium carbonyl complexes under CO/H_2O conditions.[10)]

References and Notes

1) For example, R. H. Crabtree,"The Organometallic Chemistry of the Transition Metals," Willey & Sons, Inc., pp.280-302 (1988).

2) For example (Review), R. M. Laine, E. J. Crawford, J. Mol. Catal., 44, 357 (1988); P. C. Ford, A. Rokicki, Adv. Organomet. Chem., 28, 139 (1988).

3) For example (Review), P. Escaffre, A. Thorez, P. Kalck, J. Mol. Catal., 33, 87 (1985); Y. Sugi, Shokubai(Catalyst), 25, 464 (1983).

4) For example,

a) H. Alper, S. Amaratunga, Tetrahedron Lett., 21, 2603 (1980).

b) K. Kaneda, M. Hiraki, T. Imanaka, S. Teranishi, J. Mol. Catal., 12, 385 (1981).

c) R. C. Ryan, G. M. Wilemon, M. P. Dalsanto, C. U. Pittman, Jr., ibid., 5, 319 (1979).

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e) E. Alessio, F. Vinzi, G. Mestroni, ibid., 18, 113 (1983).

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g) K. E. Hashem, J. F. Petrignani, H. Alper, ibid., 26, 285 (1984).

h) M. Miura, M. Shinohara, M. Nomura, ibid., 45, 151 (1988).

5) a) K. Nomura, M. Ishino, and M. Hazama, J. Mol. Catal., 65, L5 (1991).

b) idem. ibid., 66, L1 (1991).

c) idem. ibid., 66, L11 (1991).

d) idem. ibid., 66, L19 (1991).

e) idem. Bull. Chem. Soc., Jpn., 64, 2624 (1991).

f) idem. J. Mol. Catal., in press.

6) During and after the reaction, sodium carbonate was accompanied which was generated from the reaction of sodium hydroxide and CO_2.

7) The reaction products were only corresponding amines and no other products were observed on this reaction, except that trace amount of other deoxygenated products (azobenzene, azoxybenzene) were sometimes observed on GLC scale in the reduction of nitrobenzene.

8) Reaction conditions; $Rh_4(CO)_{12}$ (0.02 mmol), 2-methoxyethanol (15 ml), $PhNO_2$ (ca. 5 mmol), at room temperature for 3 h.

9) The reaction was completed by further stirring; K. Nomura, unpublished results.

10) For example, R. A. Sheldon,"Chemicals from Synthesis Gas," D. Reidel Publishing Co., Ltd., pp. 181 (1981); T. Ikariya, Shokubai (Catalyst), 5, 271 (1989).

1-3. Catalytic reduction of aromatic nitro compounds using CO and water with phosphine-added rhodium-carbonyl complexes.

Abstract

PR_3 added $Rh(CO)_2(acac)$ complexes (PR_3: $PEtPh_2$, PEt_2Ph, PEt_3 etc., acac: acetylacetonato) in diglyme containing a 5N NaOH aqueous solution were found to show significant catalytic activities for the selective reduction of aromatic nitro compounds affording corresponding amines under room temperature (25°C) and atmospheric pressure of carbon monoxide. Both electronic and steric factors of phosphine ligands are important in order for this reaction to proceed at such remarkable rates.

Introduction

Water-Gas-Shift Reaction (WGSR) has been one of the most important processes from the viewpoints of industrial utilization of carbon monoxide and of a pure hydrogen source.[1] As one of its applications related to the WGSR, the reduction of unsaturated compounds, especially reduction of aromatic nitro compounds using CO and water has been paid particular attention.[2]

$$H_2O + CO \longrightarrow CO_2 + H_2 \qquad (1)$$

$$ArNO_2 + 3CO + H_2O \longrightarrow ArNH_2 + 3CO_2 \qquad (2)$$

Many studies have already been reported for the reduction of aromatic nitro compounds (eq. 2), however, the catalytic reduction under mild conditions with high activity has not so far been reported.[3]

In this papers, we report that $Rh(CO)_2(acac)$-PR_3 complexes (PR_3: t-phosphine) were found to show significant catalytic activities, as well as high nitro-group selectivities, for the reduction of aromatic nitro compounds affording corresponding amines even under the extremely mild conditions of room temperature (25°C) and atmospheric pressure of carbon monoxide.[4,5]

Experimental

General proceduere

All manipulations were carried out under nitrogen atmosphere, or in vaccuo. Diglyme (diethylene glycol dimethyl ether), nitrobenzene (Nakarai tesque Co., Ltd.) and water were deaerated, distilled under nitrogen atmosphere and stored in a Schlenck-type tube. Other aromatic nitro compounds were also used as a reagent grade (Nakarai tesque Co., Ltd.).

The typical reaction procedure is performed as follows: a solution with $Rh(CO)_2(acac)$ (N. E. Chem. Cat. Co., Ltd.) in diglyme under nitrogen atmosphere was stirred and added with prescribed amount of phosphine. Then, the addition of 5N sodium hydroxide aqueous solution and nitrobenzene into the reaction mixture was followed by the introduction of carbon monoxide (1 atm). The mixture equipped with CO gas bag was allowed to react at a specified temperature (25 °C or 50°C). The reaction product was then determined by GLC using an internal standard, and was identified by co-injection method in GLC with an authentic sample (column OV-225, 3 m) and GC-MS (QP-1000 Shimazu Co., Ltd.). The reaction product was only corresponding amine, aniline from nitrobenzene, and no other products were observed.

Results and Discussion

1. Phosphine-added $Rh(CO)_2(acac)$ complexes catalyzed reduction of nitrobenzene under CO/H_2O conditions:
- Effect of phosphine -

The results for the reduction of nitrobenzene using various phosphine added $Rh(CO)_2(acac)$ complex catalysts are summarized in Table 1.

<< Table 1 >>

The rate increased remarkably upon the addition of organophosphines, especially PEt_2Ph and PEt_3. Triethylphosphine, PEt_3, was found to be the most effective; the reaction rate increased in the order: none < PPh_3 < $PEtPh_2$ << PEt_2Ph < PEt_3, as shown in this table. It was also revealed that the electronic nature of the phosphine ligand has an important effect on the rate of this reduction. And it appears that the electrophilic nature of phosphine-ligand-coordinated complexes is important for this reaction to activate water, as previously pointed out by Yoshida et al., for the Water-Gas-Shift Reaction using phosphine-coordinated rhodium-carbonyl complexes.[6] However, the rates with electrodonative and bulky phosphine ligands such as $P(i\text{-}Pr)_3$, $P(t\text{-}Bu)_3$, PCy_3 were low, suggesting that both electronic and steric factors are important for this reduction to proceed at a significant rate. Phosphite ligand additives were also effective on this reduction.

Table 1. Reduction of nitrobenzene using phosphine added $Rh(CO)_2(acac)$ complexes under CO/H_2O conditions.

phosphine	δOPR_3/ppm*	cone angle**	turnovers/mol-cat^{-1}
none	---	---	5
PPh_3	-27	145	7
$PEtPh_2$	-33	140	14
PEt_2Ph	-42	136	116
PEt_3	-48	132	241
PCy_3	-50	170	35
$P(i\text{-}Pr)_3$	-55	160	27
$P(OEt)_3$	+1	109	21
$P(OPh)_3$	+18	128	39
$P(t\text{-}Bu)_3$	-41	182	15

Reaction conditions: diglyme (7.5 ml), 5N-NaOH aq. (2.5 ml), nitrobenzene (5 mmol), CO 1 atm, 25°C, 2 h. *see ref. 9. **see ref. 10.

2. Effect of molar ratio

It should be noted that the different reaction rates in Table 2 were obtained for the reduction of $PhNO_2$ under the above-mentioned CO/H_2O conditions by changing the phosphine/Rh molar ratio of the $Rh(CO)_2(acac)$-PEt_3 catalyst.

<< Table 2 >>

A PEt_3/Rh molar ratio of 1 was found to be preferred value for this reduction; the rate decreased upon further addition. This is thought to be due to suppression of coordination of the aromatic nitro group to rhodium metal by further added phosphines.

3. Effect of temperature and the reduction of the other aromatic nitro compounds

It should also be noted that the reduction rates reamrkably increased when the reaction temperature was raised (from 25°C to 50 °C) witout changing the selectivity of the products, as shown in Table 3.

<< Table 3 >>

These results indicate that much greater catalytic activities may be achievable by using this catalyst system at higher reaction temperatures and under higher CO pressures.

We also found that the reduction proceeded with high selectivities of nitro-group. For example, 1-nitroanthraquinone was reduced to yield 1-aminoanthraquinone almost exclusively.

Table 2. Reduction of nitrobenzene under CO/H_2O conditions using $Rh(CO)_2(acac)$-phosphine complexes.

- Effect of molar ratio -

phosphine	P/Rh*	temp./°C	turnovers/mol-cat^{-1}
PEt_3	1	25	241
PEt_3	2	25	154
PEt_3	5	25	140
PEt_3	10	25	102

Reaction conditions: see Table 1.

*molar ratio of phosphine/$Rh(CO)_2(acac)$.

Table 3. Phosphine-added rhodium carbonyl complexes catalyzed reduction of nitrobenzene

- Effect of temperature -

phosphine	P/Rh*	temp./°C	turnovers/mol-cat^{-1} a)
$PEtPh_2$	1	25	14
$PEtPh_2$	1	50 b	52
PEt_2Ph	1	25	116
PEt_2Ph	1	50 b	609
PEt_3	1	25	241
PEt_3	1	50 b,c	861

Reaction conditions: see Table 1, except

b: diglyme (15 ml), 5N-NaOH (5 ml).

*molar ratio of phosphine/$Rh(CO)_2(acac)$.

a) turnovers = amount of $PhNH_2$ (mmol) /Rh (mmol)

c) $Rh(CO)_2(acac)/PEt_3$ = 0.001/0.001 (mmol).

p-Chloronitrobenzene was also converted to give p-chloroaniline as the sole product (> 99 % for 12 h) without hydrolysis by-products (p-nitrophenol, p-aminophenol).[7] We believe that it is also important from both the synthetic and industrial viewpoints.

An original reaction pathway for the reduction of aromatic nitro compounds using the catalysis described, such as via a metal-nitrene intermediate,[8] may be considered and further studies are now under way.

References and Notes.

1) For example (Review),

a) R. M. Laine, E. J. Crawford, J. Mol. Catal., 44, 357 (1988).

b) P.C. Ford, and A. Rokucki, Adv. Organomet. Chem., 28, 139 (1988).

2) For example (Review),

a) P. Escaffre, A. Thorez, P. Kalck, J. Mol. Catal., 45, 151 (1988).

b) Y. Sugi, Shokubai(Catalyst), 25, 464 (1983).

3) a) H. Alper, S. Amaratunga, Tetrahedron Lett., 21, 2603 (1980).

b) K. Kaneda, M. Hiraki, T. Imanaka, and S. Teranishi, J. Mol. Catal., 12, 385 (1981).

c) E. Alessio, G. Zassinovich, and G. Mestroni, J. Mol. Catal., 18, 113 (1983).

d) E. Alessio, F. Vinzi, G. Mestroni, J. Mol. Catal., 22, 327 (1984).

e) K. Januszkiewicz, and H. Alper, J. Mol. Catal., 19, 139 (1983).

f) K.E. Hashem, J.F. Petrignani, and H. Alper, J. Mol. Catal., 26, 285 (1984).

g) M. Miura, M. Shinohara, and M. Nomura, J. Mol. Catal., 45, 151 (1988).

h) R.C. Ryan, G.M. Wilemon, M.P.Dalsanto, and C.U. Pittman, Jr., J. Mol. Catal., 5, 319 (1979).

4) Under these reaction conditions, some reports had already

been made using $Ru_3(CO)_{12}$-$PhCH_2(C_2H_5)_3N^+Cl^-$ in benzene-2-methoxyethanol containing a 5N NaOH aqueous solution,[3a] or using $Co_2(CO)_8$[3d] catalysts. However, T.O.F. (turnovers/time) of 6 g-atom Ru h^- was the highest value so far reported.[3a]

5) We recently discovered new catalyst systems for this reaction:
a) K. Nomura, M. Ishino, and M. Hazama, J. Mol. Catal., 65, L5 (1991).
b) idem. ibid., 66, L1 (1991).
c) idem. ibid., 66, L11 (1991).
d) idem. ibid., 66, L19 (1991).
e) idem. Bull. Chem. Soc., Jpn., 64, 2624 (1991).
f) idem. J. Mol. Catal., in press.

6) T. Yoshida, D. L. Thorn, T. Okano, J. A. Ibers, S. Ostuka, J. Am. Chem. Soc., 102, 4212 (1980).

7) Reaction conditions: $Rh(CO)_2(acac)/PEt_3$ = 0.02/0.02 mmol, diglyme/5N NaOH aq. = 15/5 ml, p-chloronitrobenzene (5 mmol), CO 1 atm, for 12 h: unpublished results.

8) For example, R.A. Sheldon,"Chemicals from Synthesis Gas," Reidel, Dortrecht, pp. 181 (1981); T. Ikariya, Shokubai (Catalyst), 5, 271 (1989).

9) T. T. Derensenyi, Inorg. Chem., 20, 665 (1981).

10) C. A. Tolman, Chem. Rev., 77, 313 (1977).

1-4. Chapter 1 Discussion (Tentative reaction pathway)

As described above in Chapter 1-1, 1-2, 1-3, significant catalytic activities as well as remarkably high selectivities of nitro-group under the extremely mild CO/H_2O conditions have been found for the reduction of aromatic nitro compounds affording corresponding amines in the presence of catalysts composed of amine-, diamine-, phosphine-, chelatephosphine-added rhodium-, or ruthenium-carbonyl complexes dissolved in 2-methoxyethanol, or diglyme containing a 5N NaOH aqueous solution.

$$ArNO_2 + 3CO + H_2O \xrightarrow{\text{cat.}} ArNH_2 + 3CO_2$$

cat.: a) amine-, diamine-added Rh-, Ru-carbonyl complexes

b) $Rh(CO)_2(acac)$-phosphine complexes

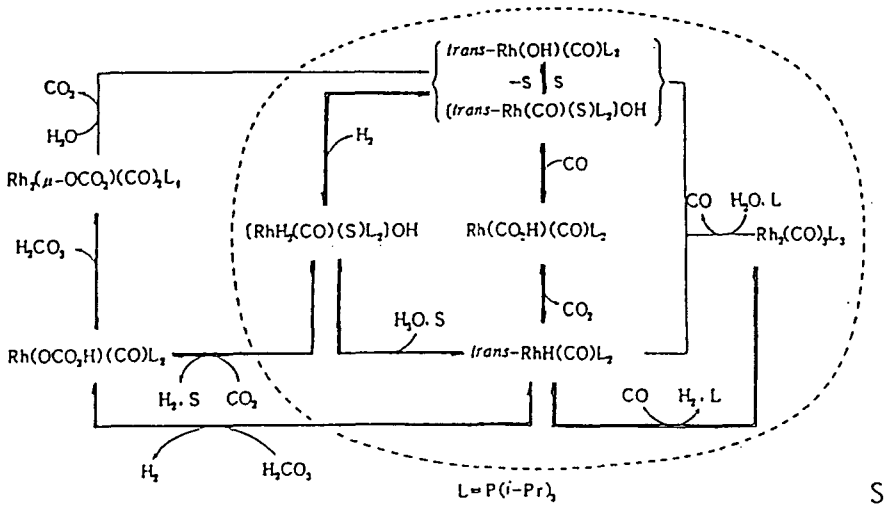
c) chelatephosphine-added Rh-, Ru-carbonyl complexes

d) $Rh_6(CO)_{16}$-amine, diamine complexes

In this part, we would like to present the tentative reaction pathway for this selective reduction of aromatic nitro compounds in these catalysis on the basis of previous reports and our experimental results.

It was already reported that tri-isopropylphosphine coordinated rhodium-carbonyl complex shows the remarkable WGSR activity. Triisopropylphosphine, $P(i\text{-}Pr)_3$, plays an important

role to proceed at significant rate, because the electron-donating nature of the phosphine ligand facilitate to activate water, and the reaction was proceeded by the mechanism postulated in Scheme I.[1]



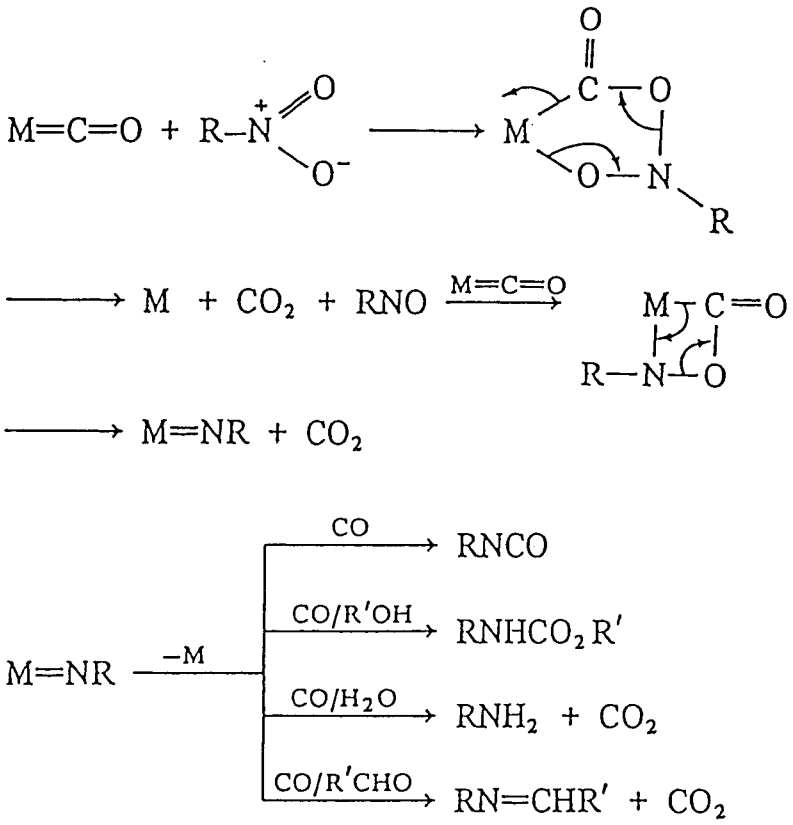
Scheme I

It was also revealed that electronic nature of phosphine ligand is also important for the reduction of aromatic nitro compounds under CO/H_2O conditions, as described in chapter 1-3.

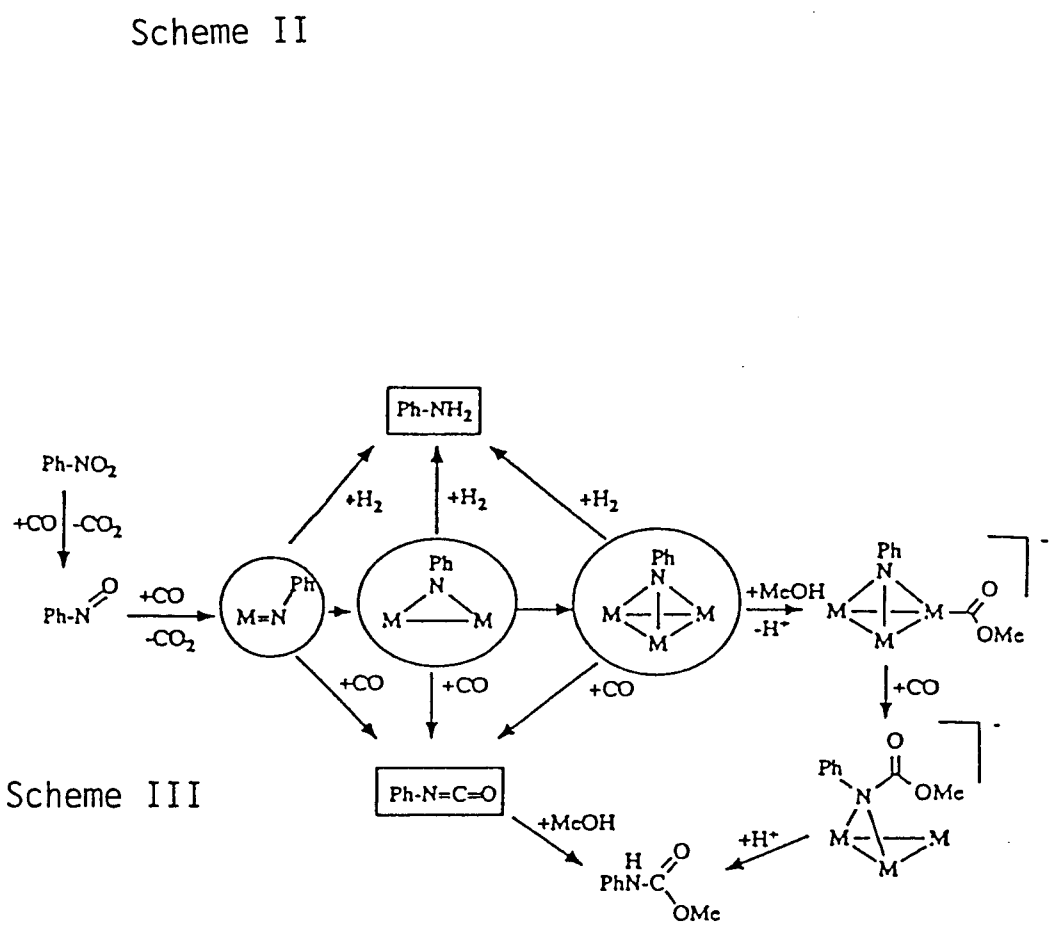
Taking into account the above results, rhodium-hydride species which was generated by the decarboxylation of Rh-COOH ligand plays an important key role in these catalysis. Electronic nature of phosphine ligand is thought to facilitate to generate the catalytically-active species, rhodium-hydride species.

The mechanism of reduction of aromatic nitro compounds by metal carbonyls has not been clearly resolved but it has been postulated that this reaction involves successive oxygen transfer reactions between the nitro compound and coordinated carbonyl

ligand to afford alkylimido-metal species. And this can be conveniently envisaged as formally involving cycloaddition of $ArNO_2$ and ArNO to a metal-carbonyl double bond and subsequent extrusion of carbon dioxide shown in Scheme II.[2] And it has also often been postulated that amines were obtained by hydrogenation of metal-nitrene species shown in Scheme III.[3]



Scheme II

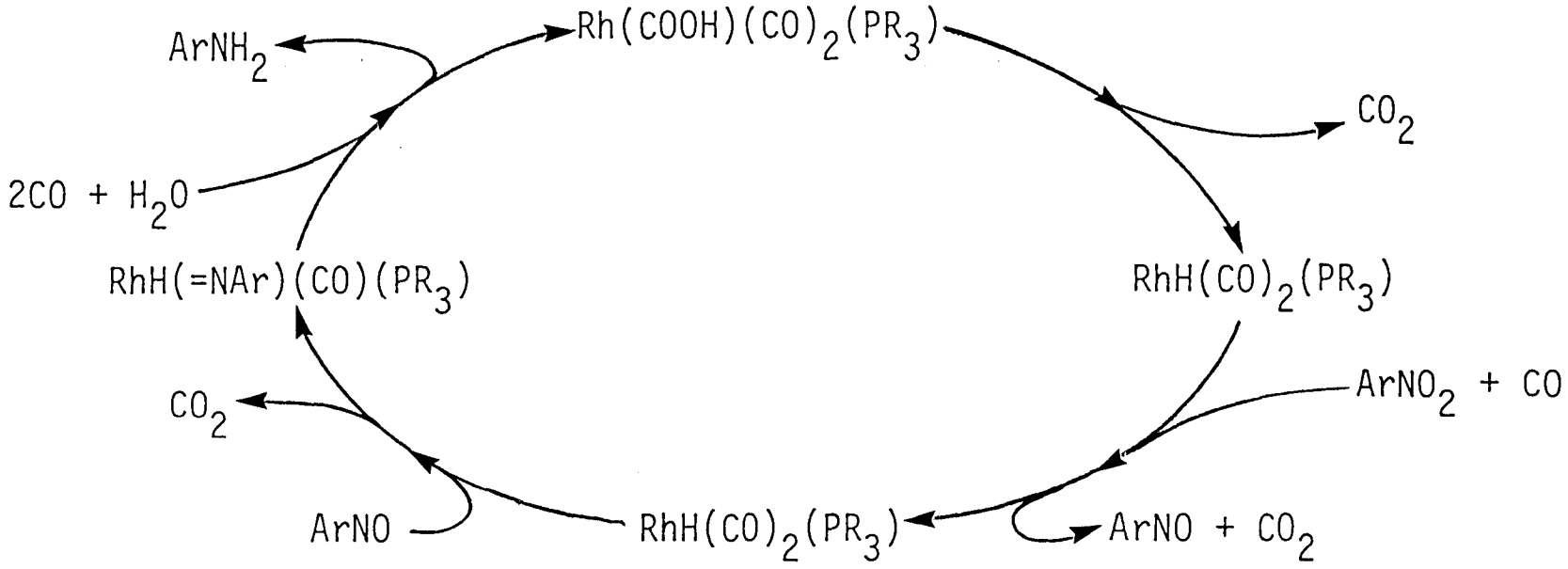


Scheme III

We reported that the reduction proceeded with high selectivities of nitro-group and without by-producing hydrogen gas which was formed by the Water-Gas-Shift Reaction. These results clearly indicate that the selective reduction under CO/H_2O conditions presented in this paper does not proceed by the hydrognation of metal-nitrene, or hydrogenation of nitro group. Therefore, another reaction pathway can be considered.

On the basis of the above results, the reduction of aromatic nitro compounds described in this paper may be assumed to proceed by the combination of the elementary steps shown in Scheme IV of (a) initial formation of rhodium-hydride carbonyl species which was generated by the decarboxylation of Rh-COOH complex, (b) oxygen transfer reactions between aromatic nitro group and Rh-carbonyl ligand to afford rhodium-nitrene species, (c) intramolecular hydrogen transfer reaction between metal-nitrene and hydride, and then production of aromatic amines and regenerate Rh-COOH, and rhodium-hydride carbonyl species.

The reaction pathways on the reduction using chelatephosphine-, or amine-added rhodium-carbonyl complexes will be thought to be able to be explained by the scheme via intramolecular hydrogen transfer reaction. An original reaction pathway for the selective reduction of aromatic nitro group can be demonstrated in these catalysis.



Scheme IV Tentative Reaction Pathway for Reduction of Aromatic Nitro Compounds under CO/H_2O Conditions

References

[1] T. Yoshida, T. Okano, S. Otsuka, J. Am. Chem. Soc., 102, 5966 (1980); T. Yoshida, D.L. Thorn, T. Okano, S. Otsuka, and J.A. Ibers, ibid., 102, 6451 (1980); Y. Sugi, Shokubai(Catalysts), 25, 464 (1983).

[2] R.A. Sheldon,"Chemicals from Synthesis Gas," D. Reidel Publishing Co., Dortrecht, pp. 181 (1981).

[3] S-.H. Han, J-.S Song, P.D. Macklin, S.T. Nguyen, G.L. Geoffroy, and A. Rheingold, Organometallics, 8, 2127 (1989); S. Cenini, M. Pizzotti, C. Crotti, in R. Ugo (Ed.), "Aspect of Homogeneous Catalysis", Vol. 6, D. Reidel, Dortrecht, 97 (1988).

[Chapter 2]

Ruthenium-catalyzed selective reduction of aromatic nitro compounds under CO/H_2O conditions

<< Contents >>

2-1. Novel selective catalytic reduction of aromatic nitro compounds affording aromatic amines using ruthenium-carbonyl complex in the presence of NEt_3 under CO/H_2O conditions.

2-2. Selective catalytic reduction of aromatic nitro compounds affording amines under CO/H_2O conditions using amine-added ruthenium-carbonyl complexes.

2-3. Selective reduction of nitroanthraquinone affording aminoanthraquinone using CO and water by homogeneous rhodium or ruthenium catalysis.

2-4. Chapter 2 Discussion

Chapter 2. Ruthenium-Catalyzed Selective Reduction of Aromatic Nitro Compounds Under CO/H_2O Conditions

2-1. Novel selective catalytic reduction of aromatic nitro compounds affording amines using ruthenium-carbonyl complex in the presence of NEt_3 under CO/H_2O conditions

Abstract

$Ru_3(CO)_{12}$ complex in the presence of NEt_3 has been found to exhibit the remarkably high selectivities of nitro group as well as high catalytic activities for the reduction of aromatic nitro compounds affording amines using CO and water. Aromatic nitro group was reduced almost exclusively without the other unsaturated groups such as C=O, C≡N, C=C, and C≡C being reduced under these reaction conditions; the almost exclusive reduction of aromatic nitro group proceeded without by-producing hydrogen gas which was formed by the Water-Gas-Shift Reaction.

Introduction

Water-Gas-Shift Reaction (WGSR) has been one of the most important processes from the aspect of industrial utilization of

$$H_2O + CO \longrightarrow CO_2 + H_2 \qquad (1)$$

carbon monoxide.[1] As one of the applications related to the WGSR, organic synthesis under CO/H_2O conditions using homogeneous catalysts,[2] especially the reduction of aromatic nitro compounds has attracted considerable attention.[2,3] A lot of studies have already been made, however, the efficient reduction with high selectivity of nitro-group, as well as high catalytic activity, has not so far been reported.[4] In addition, as for selectivity, previous patent described that aromatic nitro compounds with optional substitutions by inert groups such as alkyl, alkoxyl etc. had limited effectiveness for this reduction using rhodium and ruthenium complexes.[5]

$$ArNO_2 + 3CO + H_2O \longrightarrow ArNH_2 + 3CO_2 \qquad (2)$$

In this paper, we wish to describe that $Ru_3(CO)_{12}$ complex in the presence of NEt_3 exhibits not only high catalytic activity, but also remarkably high selectivity of nitro-group for this reduction.[6]

Experimental

Catalytic reductions were typically carried out as follows: in an autoclave (110 or 50 cc) made of stainless steel and equipped with a magnetic stirrer derivable were charged $Ru_3(CO)_{12}$ (0.005 mmol,), NEt_3 (1.5 mmol), solvent (5 ml), water (2 ml) and nitrobenzene (ca. 10 mmol). The reaction mixture was stirred under CO (20 atm) at 150°C for 2 h. 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, 3m) and GC-MS (QP-1000, Shimazu Co., Ltd.). The only reaction product was aniline from nitrobenzene and corresponding amines from aromatic nitro compounds.

Results and Discussion

1. The reduction of nitrobenzene using NEt_3-added $Ru_3(CO)_{12}$ complex under CO/H_2O conditions

The results for the reduction of $PhNO_2$ using NEt_3-added $Ru_3(CO)_{12}$ complex in various solvents under CO/H_2O conditions are summarized in Table 1.

<< Table 1 >>

It was found that the reaction proceeded at a significant rate using this catalyst system, the rate increased with the addition of NEt_3.[7] The reduction was also found to be almost completed under these reaction conditions,[8] resulting in obtaining the desired amine in high yield. It was also revealed from this table that many kind of solvents can be used in this reaction.

It should be noted from Table 2 that the rates markedly increased at higher reaction temperatures under higher CO pressures. The turnover numbers were found to be enhanced at low catalyst concentration region, especially in ethanol or others.[9] Turnovers of 10500 was obtained under the above described conditions in this catalysis. Much larger turnover numbers (catalytic activities) will be attained under these conditions: this catalytic process may be used to produce amines after much more development on this subject.

<< Table 2 >>

Table 1. $Ru_3(CO)_{12}$-NEt_3 catalyzed reduction of $PhNO_2$ using CO and water

solvents	$PhNH_2$ /mmol	turnovers /mol-cat^{-1}
methanol	9.93	1986[1)]
isoamyl-alcohol	9.36	1872[2)]
ethanol	8.89	1778
acetone	8.86	1772
isopropyl-alcohol	8.07	1614
diglyme	7.71	1582

1) > 99.3 % yield, 2) 93.6 % yield.

Table 2. Reduction of nitrobenzene catalyzed by NEt_3-added $Ru_3(CO)_{12}$ complex using CO and H_2O

solvents	cat. /mmol	aniline /mmol	turnovers /mol-cat^{-1}
ethanol	0.005	8.89	1778
ethanol	0.003	7.25	2415
diglyme	0.005	7.61	1582
diglyme	0.002	3.29	1650
diglyme	0.005	10.29	2058[1)]
diglyme	0.002	21.00	10500[2)]

Reaction conditions: $Ru_3(CO)_{12}$, CO 20 atm, 150°C, 2 h, solvent/H_2O = 5/2 ml.

1) at 180 °C, > 99.7% yield.

2) $Ru_3(CO)_{12}$ 0.002 mmol, diglyme/H_2O = 10/4 ml, $PhNO_2$ 21.0 mmol, CO 60 atm, 180 °C, 5 h.

2. The reduction of aromatic nitro compounds under CO/H_2O conditions catalyzed by $Ru_3(CO)_{12}$-NEt_3 catalyst

The results for the reduction of various aromatic nitro compounds catalyzed by $Ru_3(CO)_{12}$ complex in the presence of NEt_3 are shown in Table 3.

<< Table 3>>

Particular attention should be paid to the fact that remarkably high selectivities of nitro-group, as well as high catalytic activities were found to be exhibited for this reduction under these conditions. Halogen-substituted nitrobenzenes were reduced to give corresponding chloro- or bromoanilines without Cl or Br being reacted; p-cyanonitrobenzene, p-nitrobenzophenone and 1-nitroanthraquinone were also reduced to yield p-aminobenzonitrile, p-aminobenzophenone and 1-aminoanthraquinone, respectively, without the other unsaturated groups such as carbonyl, nitrile being reduced. We believe that these results are very important from both the industrial and the synthetic point of view.

3. Selective reduction of aromatic nitro compounds using CO and water catalyzed by $Ru_3(CO)_{12}$ complex in the presence of NEt_3

It should also be noted that the other unsaturated substrates such as acetophenone, styrene etc. were not reacted under the above described conditions (Table 4).[10)]

<< Table 4 >>

Table 3. NEt_3-added $Ru_3(CO)_{12}$ catalyzed reduction of aromatic nitro compounds under CO/H_2O conditions

reactant	product	yield/%
o-chloronitrobenzene	o-chloroaniline	>99.9
o-bromonitrobenzene	o-bromoaniline	>99.9
p-chloronitrobenzene	p-chloroaniline	>99.9
p-cyanonitrobenzene	p-aminobenzonitrile	>99.9
p-nitrobenzophenone	p-aminobenzophenone	>99.9
1-nitroanthraquinone	1-aminoanthraquinone	>99.9

Reaction conditions: $Ru_3(CO)_{12}$ 0.01 mmol, NEt_3 1.5 mmol, diglyme/H_2O = 15/5 ml, CO 20atm, 150°C, 2h, $ArNO_2$ 5 mmol.

Table 4. NEt_3-added $Ru_3(CO)_{12}$ catalyzed reaction of various substrates under CO/H_2O conditions

substrate	product	yield/%
$PhNO_2$	$PhNH_2$	>99.5
$PhCOCH_3$	reaction did not proceed	
PhCHO	$PhCH_2OH$	0.08
$PhCH=CH_2$	$PhCH_2CH_3$	0.3
$PhC\equiv CH$	$PhCH=CH_2$	1.3

Reaction conditions: see Table-3.

The aromatic nitro group was found to be reduced almost exclusively without other unsaturated groups, such as C=O, C≡N, C=C, C≡C, being reduced in these catalysis. We believe that this result is potentially-important from both the synthetic and the industrial viewpoints.

Note that only a trace amount of hydrogen gas was detected, whereas a stoichiometric amount of CO_2 was obtained in the reduction of 1-nitroanthraquinone (eq.(3)),[11] indicating that this type of reduction was not proceeded by the reaction of aromatic nitro compounds with hydrogen gas that was formed by the WGSR.

Compared these results with the reduction using $Ru_3(CO)_{12}$ catalyst in the presence of NMe_3,[3b] we see that they are quite different, threfore, another reaction pathway can be considered. In addition, the above-mentioned fact, that the reduction proceeded without by-producing hydrogen gas, is potentially-important from an industrial point of view, because carbon monoxide is effectively consumed for production of the desired amines.

1-nitroanthraquinone
10.2 mmol

CO 20 atm
150°C, 5 h

⟶ 1-aminoanthraquinone
>98% yield, ca. 98% conv. of 1-NAQ

\+ CO_2 (ca. 30 mmol)

\+ H_2 (trace amount)

<< Reaction conditions >>

$Ru_3(CO)_{12}$ 0.005 mmol, NEt_3 1.5 mmol,

$MeOH/H_2O$ = 15/5 ml.

(3)

Taking into account the above-described results, an original reaction pathway for the reduction of aromatic nitro compounds under CO/H_2O conditions will be considered,[12] and more detailed studies are now under investigation.[13]

Summary

In conclusion, this paper can be summarized as follows.

1) Ruthenium-carbonyl complex in the presence of NEt_3 exhibits a significant catalytic activity for the redction of aromatic nitro compounds under CO/H_2O conditions.

2) The turnover numbers are remarkably increased at higher reaction temperatures under higher CO pressures; much larger turnover numbers will be attained in these catalysis under the above conditions.

3) The reduction proceeded not only at marked rates, but also with almost exclusive selectivity of nitro-group, resulting in obtaining the desired amines in high yield.

4) The reduction did not by-produce hydrogen gas generated by the Water-Gas-Shift Reaction. Carbon monoxide is effectively consumed for the reduction in these catalysis.

5) An original reaction pathway might be considered for this almost exclusive reduction of aromatic nitro-group. This study is still now under investigation.

References and Notes

1) For example (Review),

a) R. M. Laine, E. J. Crawford, J. Mol. Catal., 1988, 44, 357.

b) P. C. Ford, A. Rokicki, Adv. Organomet. Chem., 1988, 28, 139.

2) For example (Review),

a) P. Escaffre, A. Thorez, P. Kalck, J. Mol. Catal., 1985, 33, 87.

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g) K. E. Hashem, J. F. Petrignani, H. Alper, J. Mol. Catal., 1984, 26, 285.

h) E. Alessio, G. Zassinovich, G. Mestroni, ibid., 1983, 18, 113.

i) E. Alessio, F. Vinzi, G. Mestroni, ibid., 1984, 22, 327.

j) M. Miura, M. Shinohara, M. Nomura, ibid., 1988, 45, 151.

4) It was already known that excess amount of NMe_3 aq. added $Ru_3(CO)_{12}$ in THF exhibited the catalytic activity for $PhNO_2$

reduction,[3b] however in this case, significant amount of dihydrogen (52% in the gas phase (300 cc autoclave) at the end of the reaction) was by-produced because this catalyst system also shows exceptionally high WGSR activity (W. A. R. Slegeir, R. S. Sapienza, and B. Easterling, ACS Symp. Ser., 1981, 152, 325).

5) For example, G. Mestroni, G. Zassinovich, E. Alessio, EP 97592 (1983).

6) We recently discovered new catalyst systems which show not only high catalytic activities but also markedly high nitro-group selectivities for the reduction of aromatic nitro compounds under the mild conditions of room temperature (25°C) and 1 atm of CO in the presence of 5N NaOH aq. solution: K. Nomura, M. Ishino, and M. Hazama, J. Mol. Catal., 1991, 65, L5; idem. ibid., 1991, 66, L1; idem. ibid., 1991, 66, L11; idem. ibid., 1991, 66, L19; idem. Bull. Chem. Soc., Jpn, 64, 2624 (1991); idem. J. Mol. Catal., in press.

7) Turnovers of 329 mol-cat^{-1} was obtained for the reduction of $PhNO_2$ (10mmol) using $Ru_3(CO)_{12}$ (0.01mmol) in 2-methoxy-ethanol/H_2O (15/5ml) under CO (20atm) at 150°C for 2 h.

8) The reduction was found to proceed at a significant rate under these conditions, resulting in obtaining the desired amine in high yield. It is to be noted that the rate was not retarded by the product aniline: this was confirmed by the reaction upon the addition of an excess amount of aniline, and by the time-course plot on this reaction.

9) The turnover numbers were also enhanced at low catalyst

concentrations in 2-methoxyethanol. The enhancement effect might be depend upon the solvents, suggesting the equilibrium between mononuclear and cluster ruthenium-carbonyl species may be important in these catalysis: K. Nomura, unpublished results.

10) We recently have discovered that diisopropylamine-added $Ru_3(CO)_{12}$ also exhibits both the remarkably high nitro-group selectivities and significant catalytic activities for the selective reduction of aromatic nitro compounds under CO/H_2O conditions: K. Nomura, Chem. Lett., 1679 (1991).

11) At the end of the reduction of 1-nitroanthraquinone (10.2mmol) affording 1-aminoanthraquinone (>10.0mmol, >98% yield) under CO (20atm), at 150°C for 5 h ($Ru_3(CO)_{12}$ 0.005mmol, NEt_3 1.5mmol, methanol/H_2O = 15/5 ml), ca. 30 mmol of CO_2 and quite a trace amount of H_2 (0.02mmol) were formed. Compared with ref.3b in the case using NMe_3-added Ru-carbonyl complexes, this result is very interesting and it is very important from the industrial viewpoints.

12) a) R. A. Sheldon,"Chemicals from Synthesis Gas," D. Reidel Publishing Co., Ltd. Dortrecht, 1981, pp. 181.

b) T. Ikariya, Shokubai(Catalyst), 1989, 5, 271.

13) As for the reduction of aromatic nitro compounds under CO/H_2O especially using ruthenium compounds, it has often been postulated that amines are produced by hydrogenation of the metal-nitrene species (eg. M=NAr) generated by the oxygentransfer reactions between aromatic nitro compounds and metal carbonyl.[10] However in our case, since hydrogen gas was not produced at the end of the reduction and the reduction

proceeded with remarkably high nitro-group selectivities as described in this paper, we believe, another reduction pathway can be considered for this novel reduction of aromatic nitro compounds.

2-2. Selective catalytic reduction of aromatic nitro compounds affording amines under CO/H_2O conditions using amine-added ruthenium-carbonyl complexes

Abstract

Remarkably high selectivities of nitro-group, as well as high catalytic activities, for the reduction of aromatic nitro compounds affording corresponding amines under CO/H_2O conditions have been found to be exhibited by using amine(HNR_2)-added ruthenium-carbonyl complexes; the reduction also proceeded without by-producing hydrogen gas which was formed by the Water-Gas-Shift Reaction.

Introduction

Water-Gas-Shift Reaction has been one of the most important processes from the aspect of industrial utilization of carbon monoxide and of a pure hydrogen source.[1] As one of its

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (1)$$

applications related to the WGSR, organic synthesis under CO/H_2O conditions,[2] especially the reduction of aromatic nitro compounds using homogeneous catalysts has also drawn considerable attention.[2,3]

Many studies have already been made for the reduction of aromatic nitro compounds using homogeneous catalysts,[3] especially in the case using ruthenium catalysts, the reduction using a catalyst comprised of $Ru_3(CO)_{12}$ complex in the presence of NMe_3-added,[3a] or 3,4,7,8-tetramethyl-1,10-phenanthroline[3d] have already been reported. However, the efficient reduction with high catalytic activity, as well as with high selectivity, has not so far been reported.[4]

$$ArNO_2 + 3CO + H_2O \longrightarrow ArNH_2 + 3CO_2 \qquad (2)$$

In this paper, we wish to present the efficient reduction which proceeds not only at significant rates, but also with remarkably high selectivities of nitro-group, catalyzed by ruthenium complexes in the presence of specified amines (HNR_2) under CO/H_2O conditions.[5]

Experimental

The reductions were typically carried out as follows: in an autoclave (110 or 50 ml) made of stainless steel (SUS 316) and equipped with a stirrer derivable by magnetic force, were charged $Ru_3(CO)_{12}$ (0.003 mmol), prescribed amount of amine, ethanol (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. The reaction product was then analyzed by GLC using an internal standard and was identified using GLC by co-injection with an authentic sample (column OV-225, 3m) and GC-MS (QP-1000, Shimazu Co., Ltd.). The reaction product was only aniline from nitrobenzene.

The reduction of 1-nitroanthraquinone and the other aromatic nitro compounds were also performed similarly. In the reduction of 1-nitroanthraquinone, a certain excess amount of water was added into the reaction medium after the reaction; a red precipitate which was obtained by filteration was dried and redissolved in N,N-dimethylformamide and was analyzed by GLC (column OV 210, 1m) using an internal standard or by liquid chromatography. Identification was made by comparison of the retention time of chromatogram, elemental analysis, and GC-MS. After the reduction, 1-aminoanthraquinone was obtained from 1-nitroanthraquinone and selectivity of nitro-group was almost 100 %.

Results and Discussion

The results for the reduction of $PhNO_2$ catalyzed by various amine-added $Ru_3(CO)_{12}$ complexes are summarized in Table 1.

<< Table 1 >>

The reduction proceeded at significant rates under the above mentioned reaction conditions. It should be noted that the rate remarkably increased upon the addition of small amount of amines (HNR_2);[6] especially, diisopropylamine and dibutylamine were preferred. The other amines such as pyrrolidine, piperidine were also effective. It was also revealed that effective ratio of amine additives were different. The important fact was also found that the rate markedly increased at higher reaction temperatures, much higher catalytic activity will be exhibited at higher reaction temperatures and under higher CO pressures.

Table 2 shows the results for the reduction in the various solvents, in place of ethanol, under the same conditions in Table 1. Many kind of solvents were revealed to be effective on this catalytic reduction.

<< Table 2 >>

Table 3 summarizes the results for the reduction of various aromatic nitro compounds using CO and water using above described ruthenium-$HN(i\text{-}Pr)_2$ catalyst. It should also be paid particular attention that the reduction catalyzed by $Ru_3(CO)_{12}$ in the presence of $HN(i\text{-}Pr)_2$ proceeded with almost exclusive selectivities of nitro-group, resulting in affording the

Table 1. Amine-added $Ru_3(CO)_{12}$ catalyzed reduction of $PhNO_2$ under CO/H_2O conditions

No.	Amine	Molar ratio*	Temp. /°C	Turnovers /mol-cat^{-1}
1	pyrrolidine	5	150	1573
2	piperidine	3	150	1524
3	piperidine	3	180	3422[a)]
4	$HN(i\text{-}Pr)_2$	50	150	1683
5	$HN(i\text{-}Pr)_2$	50	180	3421[a)]
6	$HN(i\text{-}Pr)_2$	70	150	2016
7	$HNEt_2$	25	150	1510
8	$HNEt_2$	25	180	3448[a)]
9	$HNBu_2$	35	150	1833
10	$HN(c\text{-}C_6H_{11})_2$	50	150	1694

Reaction conditions: $Ru_3(CO)_{12}$ 0.003 mmol, $EtOH/H_2O$ = 10/4 ml, CO 20 atm, 100 min., $PhNO_2$ ca. 10 mmol. a) >98% yield.

*: molar ratio of amine/Ru

Table 2. $Ru_3(CO)_{12}$-$HN(i\text{-}Pr)_2$ catalyzed reduction of $PhNO_2$ using CO and water

No.	Solvents	Turnovers /mol-cat^{-1}
6	ethanol	2016
11	methanol	1707
12	3-methyl-2-butanol	1665
13	diglyme	1944
14	acetone	1919

Table 3. $Ru_3(CO)_{12}$-$HN(i\text{-}Pr)_2$ catalyzed reduction of aromatic nitro compounds using CO and water[a)]

Substrates	Products	Yield/%
o-chloronitrobenzene	o-chloroaniline	>99.9
o-bromonitrobenzene	o-bromoaniline	>99.9
p-chloronitrobenzene	p-chloroaniline	>99.9
p-cyanonitrobenzene	p-aminobenzonitrile	>99.9
p-nitrobenzophenone	p-aminobenzophenone	>99.9
1-nitroanthraquinone	1-aminoanthraquinone	>99.9
acetophenone	no reaction	
phenylacetylene	no reaction	
benzonitrile	no reaction	

a) Reaction conditions: $Ru_3(CO)_{12}$ 0.01 mmol, $HN(i\text{-}Pr)_2$ 1.5 mmol, diglyme/H_2O = 15/5 ml, $ArNO_2$ 5 mmol, CO 20 atm, 150 °C, 2 h.

corresponding aromatic amines in high yields. Halogen-substituted nitrobenzenes were found to be reduced to produce corresponding anilines; p-cyanonitrobenzene and p-nitrobenzophenone were also found to be reacted to afford p-aminobenzonitrile and p-aminobenzophenone, respectively, without reducing C=O and C≡N bond.[7)]

<< Table 3 >>

It should also be noted that the reduction of acetophenone, phenylacetylene and benzonitrile did not proceed under the same conditions in Table 3. These results, that aromatic nitro-group was reduced almost exclusively, are very important from both the synthetic and the industrial viewpoints.

Furthermore, considerable attention should be paid that stoichiometric amount of CO_2 (ca. 14.7 mmol) was formed at the end of the reduction of o-chloronitrobenzene without by-producing hydrogen gas (H_2 ca. 0.4 mmol), as described in eq. (3). No production of CO_2 and quite a trace amount of H_2 (ca. 0.4 mmol) were found to be detected in the reduction of benzonitrile under the same reaction conditions shown in Table 3 (eq.(4)).

$$o\text{-}ClC_6H_4NO_2 \text{ (5 mmol)} + CO/H_2O \xrightarrow[CO\ 20\ atm]{150°C,\ 2h} o\text{-}ClC_6H_4NH_2 \text{ (> 99.9 \%)} + CO_2 \text{ (14.7 mmol)} + H_2 \text{ (trace)} \quad (3)$$

$$\text{benzonitrile} + CO/H_2O \longrightarrow \text{no reaction} + H_2 \text{ (trace)} \quad (4)$$

This result, CO was effectively consumed without by-producing hydrogen gas, indicates that this catalytic reduction was not proceeded by the reaction of aromatic nitro compounds with the hydrogen gas which was formed by the WGSR.

A different reaction pathway can be considered in these catalysis;[9] further studies are now under investigation.

Summary

In this paper, the efficient catalytic reduction of aromatic nitro compounds, which shows both siginificant catalytic activities and almost exclusive selectivity of nitro-group under CO/H_2O conditions in the presence of homogeneous catalysts composed of ruthenium-carbonyl complexes and specified amines (HNR_2), can be presented, as summarized as follows.

1) The reduction catalyzed by homogeneous ruthenium complexes in the presence of specified amines proceeded at significant rates under CO/H_2O conditions; the rates increased upon the addition of small amounts of amines such as diisopropylamine, piperidine, dibutylamine, and others. The turnover numbers were also found to be increased at higher reaction temperatures under higher CO pressures.

2) The aromatic nirto group was reduced almost exclusively without other unsaturated group such as C=O, C≡N, and C≡C, being reduced in these catalysis, resulting in obtaining the desired amines in high yields. We believe that this result is potentially-important from both synthetic and industrial point of view.

3) Hydrogen gas which was generated from the Water-Gas-Shift Reaction did not formed at the end of these reductions. Carbon monoxide was effectively consumed in these catalysis.

4) Taking into account the above results, an another original reaction mechanism can be considered. This subject is now under investigation.

References and Notes

1) For example (Review),

a) R. M. Laine and E. J. Crawford, J. Mol. Catal., 44, 357 (1988).

b) P. C. Ford and A. Rokicki, Adv. Organomet. Chem., 28, 139 (1988).

2) For example (Review),

a) P. Escaffre, A. Thorez, and P. Kalck, J. Mol. Catal., 33, 87 (1985).

b) Y. Sugi, Shokubai (Catalyst), 25, 464 (1983).

3) For example using Ru catalysts,

a) K. Cann, T. Cole, W Slegeir, and R. Petit, J. Am. Chem. Soc., 100, 3969 (1978).

b) H. Alper and S. Amaratunga, Tetrahedron Lett., 21, 2603 (1980).

c) T. Okano, K. Fujiwara, H. Konishi, and J. Kiji, Chem. Lett., 1984, 1083.

d) E. Alessio, G. Zassinovich, and G. Mestroni, J. Mol. Catal., 18, 113 (1983).

4) We recently have discovered other new catalyst systems which show not only high catalytic activities but also markedly high selectivities of nitro-group for this reduction under the mild conditions of room temperature (25 °C) and 1 atm of CO in the presence of aqueous 5 N NaOH solution: K. Nomura, M. Ishino, and M. Hazama, J. Mol. Catal., 65, L5 (1991); idem. ibid., 66, L1, L11, L19 (1991); idem. Bull. Chem. Soc., Jpn., 64, 2624 (1991); idem. J. Mol. Catal., in press.

5) It was already known that $Ru_3(CO)_{12}$ complex containing an excess amount of aqueous NMe_3 solution in THF exhibited the catalytic activity for the $PhNO_2$ reduction,[3a] however in this case, significant amount of hydrogen gas (52% in the gas phase at the end of the reaction) was by-produced, because this catalyst also shows an exceptionally high WGSR activity (W. A. R. Slegeir, R. S. Sapienza, and B. Easterling, ACS Symp. Ser., 152, 325 1981)).

6) Turnovers of 329 mol-cat^{-1} was obtained for the reduction of $PhNO_2$ (10 mmol) using $Ru_3(CO)_{12}$ (0.01 mmol) in 2-methoxyethanol/H_2O (15/5 ml) under CO (20 atm) at 150 °C for 2 h.

7) 1-Nitroanthraquinone was also reduced to afford 1-aminoanthraquinone almost exclusively without reducing C=O bond. Turnovers of 1416 and 1516 mol-cat^{-1} were obtained by using diisopropylamine-added, and piperidine-added(molar ratio of amine/Ru were 20 and 3, respectively) $Ru_3(CO)_{12}$ (0.005 mmol) in methanol/H_2O (15/5 ml) under CO (20 atm) at 150 °C for 2 h (1-nitroanthraquinone 10.2 mmol).

8) The similar result was also obtained in the reduction of 1-nitroanthraquinone (10.2 mmol) to produce 1-amino-anthraquinone (yield >99.9%) using $Ru_3(CO)_{12}$ (0.005 mmol)-pyrrolidine (0.015 mmol) catalyst in methanol/H_2O (15/5 ml) under CO (20 atm) at 150 °C for 5 h. After the reaction, the stoichiometric amount of CO_2 (34.2 mmol) and a trace amount of H_2 (0.08 mmol) were obtained.

9) For example,

a) R. A. Sheldon,"Chemicals from Synthesis Gas," D. Reidel Publishing Co., Ltd., Dordrecht, pp. 181 (1981).

b) T. Ikariya, Shokubai (Catalyst), 5, 271 (1989).

2-3. Selective reduction of nitroanthraquinones affording aminoanthraquinones using CO and water by homogeneous rhodium or ruthenium catalysis

Abstract

Aminoanthraquinones, which are important key materials used as dyes and their intermediates, are produced by the selective reduction of nitroanthraquinones under CO/H_2O conditions using homogeneous catalysts comprised of ruthenium or rhodium complexes. Aromatic nitro group was reduced almost exclusively without any other unsaturated groups such as C=O being reduced: the rate increased upon the addition of small amount of amines. The effects of additives (cocatalysts), such as other transition metal compounds, were also described briefly in this paper.[1)]

Introduction

- Back ground of invention -

Aminoanthraquinones, especially 1-aminoanthraquinone has been one of the most important key materials as dyes and their intermediates. Many studies have therefore already been made for the practical production of these compounds.

One of the conventional processes is amination before sulfonating anthraquinone, another process is the stoichiometric reduction of nitroanthraquinones with sulfides, such as alkali metal sulfides, alkali metal hydrogen sulfides. And another is the catalytic hydrogenation with, such as, palladium carbon.

However, many difficulties are encountered in the conventional production of aminoanthraquinones. One of the processes where anthraquinone is sulfonated and then aminated has problems, i.e. low yield and reactivity, in addition to trouble on catalysts, i.e. toxicity of mercury compounds and after-treatments of the wasted water. Problems in which a treatment of inorganic salts by-produced and contamination of the products with the inorganic salts are accompanied in the stoichiometric reduction with sulfides, and the catalytic hydrogenation with palladium carbon causes various side-reactions, such as reduction of carbonyl groups as well as nitro groups, thereby decreasing yield of the desired aminoanthraquinone: furthermore, separation of the catalyst from the reduction product needs so much labor that the reduction as a whole, is not economical.[1)]

The Water-Gas-Shift Reaction has been one of the most important processes from the aspect of industrial utilization of

carbon monoxide: it is now commercially used to produce pure hydrogen. A lot of studies have therefore been made in this

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (1)$$

subject especially in the field of catalysis.[2] As one of applications related to the WGSR, organic syntheses under CO/H_2O conditions, especially the reduction of aromatic nitro compounds has also been paid considerable attention.[3]

$$ArNO_2 + 3CO + H_2O \longrightarrow ArNH_2 + 3CO_2 \qquad (2)$$

We recently reported that the reduction proceeded at remarkable rates, as well as with high selectivities of nitro-group, under the mild CO/H_2O conditions by using rhodium, or ruthenium catalysts in the absence,[4] or in the presence of NaOH aqueous solution.[5]

In this paper, we wish to describe briefly the results for the production of aminoanthraquinones by catalytic reduction of nitroanthraquinones using homogeneous rhodium or ruthenium catalysts under CO/H_2O conditions.[1]

$$\text{1-nitroanthraquinone} + 3CO + H_2O \longrightarrow \text{1-aminoanthraquinone} + 3CO_2 \qquad (3)$$

Experimental

Catalytic reductions of 1-nitroanthraquinone were typically carried out as follows: in an autoclave (110 cc) made of stainless steel (SUS 316) and equipped with a stirrer derivable by magnetic force, (Apparatus A), were charged $Ru_3(CO)_{12}$, prescribed amount of amine, solvent, water and 1-nitroanthraquinone (Tokyo Kasei Co., Ltd., purity 86.2 %, anthraquinone 13.8 %). The contents were stirred under CO (20 atm) at 150 °C for 2 hours.

The catalytic reductions were also performed by using an autoclave (260 ml) made of stainless steel and equipped with a thermometer, a stirrer with turbin blades, cooling pipes and a CO gas feeder at the bottom (Apparatus B).

A certain excess amount of water was added into the reaction medium after the reaction: a red precipitate which was obtained by filteration was dried and redissolved in N,N-dimethylformamide and was analyzed by GLC (column OV 210, 1 m) using an internal standard, or by liquid chromatography. Identification was made by comparison of the retention time of the chromatogram, elemental analysis, and GC-MS. 1-Aminoanthraquinone was obtained almost exclusively from 1-nitroanthraquinone (selectivity of nitro group was almost 100 %) in these catalysis.

The reduction of nitroanthraquinones (mono- and dinitroantharquinones) were also carried out under the same conditions (Apparatus A or B), except that the mixture composed of mononitroanthraquinones (1-, and 2-nitroanthraquinone: 74.9 %

) and di-nitroantharquinones (1,5-, and 1,8-dinitroanthraquinone and others: 23.5 %) and anthraquinone (1.6 %) was used in place of 1-nitroantharquinone of reagent grade (Tokyo Kasei, Co., purity 86.2 %, anthraquinone 13.8 %). The corresponding aminoanthraquinones were obtained in high yield and with almost exclusive selectivities of nitro-group (almost 100 %), after the above procedures.

Results and Discussion

1. Reduction of 1-nitroanthraquinone affording 1-aminoanthraquinone using amine-added ruthenium complexes under CO/H_2O conditions

1-1. Effect of amine additives

The results for the reduction of 1-nitroanthraquinone using ruthenium complexes in the presence of various amines under CO/H_2O conditions are summarized in Table 1.

<< Table 1 >>

In these conditions, it is to be noted that the reduction proceeded not only at remarkable rates, but also with almost exclusive selectivity of nitro group: the desired 1-aminoanthraquinone was, consequently, obtained in high yield from 1-nitroantharquinone without other unsaturated groups such as C=O being reduced. We believe that this fact is potentially-important from both synthetic and industrial viewpoints.

It was also revealed from Table 1 that the rate increased upon the addition of small amounts of amines, especially piperidine, triethylamine, diisopropylamine, 1,8-bis(dimethylamino)naphthalene are preferred. The addition of 1-aminoanthraquinone was also effective,[6] and many kind of solvents were also found to be effective on this reduction.

Table 1. Amine-added $Ru_3(CO)_{12}$ catalyzed reduction of 1-nitroanthraquinone affording 1-aminoanthraquinone under CO/H_2O conditions

amine	molar ratio	solvent	turnovers /mol-cat^{-1}
none	---	methanol	969
pyrrolidine	6	methanol	1222
piperidine	3	methanol	1560
$HNEt_2$	100	methanol	1354
NEt_3	50	methanol	1141
NEt_3	100	methanol	1453
NEt_3	100	ethanol	1362
$N(n\text{-}Pr)_3$	10	methanol	1252
$HN(i\text{-}Pr)_2$	10	methanol	1340
$HN(i\text{-}Pr)_2$	20	methanol	1416
1,8-bis(dimethyl-amino)naphthalene	20	methanol	1538
N,N,N',N'-tetramethyl-o-phenylenediamine	1.5	diglyme	1384
4-cyanopyridine	3	diglyme	1242

Reaction conditions: $Ru_3(CO)_{12}$ 0.005 mmol, solvent/H_2O = 15/5 ml, 1-nitroanthraquinone 10.2 mmol, CO 20 atm, 150 °C, 2 hours. (Reaction apparatus A)

1-2. Time-course and effect of CO pressure

Table-2 shows the results under various CO pressures on this reduction. It was revealed that the reduction proceeded with high selectivity in a liquid phase, keeping a catalytic activity at high level, resulting in obtaining the desired aminoanthraquinone in high yield.

<< Table 2 >>

It should also be noted that the stoichiometric amount of CO_2 (30.2 mmol) was detected at the end of the reaction, whereas no production of hydrogen gas (0.02 mmol) or others, as shown below.

1-nitroantharquinone (10.2 mmol) $\xrightarrow[150°C,\ 5\ h]{CO\ 20\ atm,}$ > 98% conv. $\longrightarrow$ 1-aminoanthraquinone (1-AAQ) > 98% yield + CO_2 + H_2 (trace amount)

Products distribution after the reaction

Catalysts	Products/ mmol		
	1-AAQ	CO_2	H_2
$Ru_3(CO)_{12}/NEt_3$	10.2	30.2	0.02
$Ru_3(CO)_{12}$/pyrrolidine	10.2	34.2	0.08

$Ru_3(CO)_{12}/NEt_3$ = 0.01/1.5 mmol,
$Ru_3(CO)_{12}$/pyrrolidine = 0.005/0.015 mmol.

Table 2. Time-course and effect of CO pressure

CO/atm	time/h	turnovers/mol-cat^{-1}
20	1.5	852
20	2	1453
20	5	2040 (>99 % yield)
10	1.5	643
20	1.5	852
30	1.5	1162

$Ru_3(CO)_{12}$ 0.005 mmol, NEt_3 1.5 mmol, $MeOH/H_2O$ = 15/5 ml, 1-nitroanthraquinone 10.2 mmol, 150 °C. (Reaction apparatus A)

The result, that the reduction proceeded at remarkable rate without by-producing hydrogen gas, is very important from the industrial point of view, since CO was effectively consumed for the production of the desired amine. It also indicates that this type of reduction was not proceeded by the reaction of aromatic nitro compounds and hydrogen gas that was formed by the Water-Gas-Shift Reaction.

It was also revealed that the rate also increased under higher CO pressures, however, the reduction proceeded with high catalytic activities even under lower CO pressure.

1-3. Effect of temperature, catalyst concentration

As summarized in Table 3, the reduction rate markedly increased at higher reaction temperature: the reduction almost completed at high temperature (180 °C, $Ru_3(CO)_{12}$ 0.005 mmol, 2 hours).

<< Table 3 >>

It was also revealed that larger turnover numbers were found to be exhibited under the lower catalyst concentration region: turnovers of 2705 mol-cat^{-1} was attained at higher reaction temperature (180 °C), under these conditions (0.002 mmol, 2 hours). Much higher catalytic activities in these catalysis will be achieved at higher reaction temperatures under higher CO presures.

Table 3. Effect of temperature and catalyst concentration

cat. conc. /mmol	temp. /°C	turnovers /mol-cat^{-1}
0.005	120	622
0.005	150	1453
0.005	180	1971 (96.6 % yield)
0.002	180	2705
0.002	180	2348 (diglyme solv.)

NEt_3 1.5 mmol, $MeOH/H_2O$ = 15/5 ml,

1-nitroanthraquinone 10.2 mmol, CO 20 atm,

2 hours. (Reaction apparatus A)

2. $Rh_6(CO)_{16}$ complexes in the presence of various amines catalyzed reduction of 1-nitro-anthraquinone yielding 1-amino-anthraquinone under CO/H_2O conditions

Table 4 shows the results for the reduction of 1-nitro-anthraquinone using amine-added $Rh_6(CO)_{16}$ catalysts.

<< Table 4 >>

It was also found that 1-aminoanthraquinone was obtained in high yield and with high selectivities of nitro-group using these catalysts;[7] the rate also increased upon the addition of amines, especially diisopropylamine. The catalytic activities (efficiency of the catalyst) shown here using rhodium catalysts were not so high as those obtained using ruthenium-amine catalysts, however, more active catalysts will be discovered in the near future.

Table 4. $Rh_6(CO)_{16}$-amine catalyzed reduction of 1-nitroanthraquinone yielding 1-aminoanthraquinone under CO/H_2O conditions

amine	molar ratio	solvent	turnovers /mol-cat^{-1}
none	---	methanol	1224
none	---	diglyme	1158
imidazole	1	diglyme	1356
9,10-diamino-phenanthrene	10	diglyme	1422
NEt_3	50	diglyme	1506
$N(n\text{-}Pr)_3$	10	diglyme	1500
$HN(i\text{-}Pr)_2$	50	diglyme	1824

Reaction conditions: $Rh_6(CO)_{16}$ 0.005 mmol, solvent/H_2O = 15/5 ml, 1-nitroanthraquinone 10.2 mmol, CO 20 atm, 150 °C, 2 hours.

(Reaction apparatus A)

3. Further studies for the reduction of nitroanthraquinones using homogeneous ruthenium catalysts under CO/H_2O conditions

As described above, aminoanthraquinones were obtained in high yield with almost exclusive selctivity of nitro group by catalytic reduction using homogeneous rhodium or ruthenium catalysts under the CO/H_2O conditions. In order for this reduction to discover more active catalysts, or to improve, or to construct good processes, we examined the effect of additives and the factors affecting the reaction rate. In this part, we would like to introduce our results briefly for this catalytic reduction of nitroanthraquinones affording aminoanthraquinones.

3-1. Factors affecting the reaction rates. - Effect of ruthenium compounds, solvents, and additives[8] -

Studies concerning the factors affecting the reduction rate were carried out under the conditions using an autoclave, equipped with turbin blades, cooling pipes and a CO gas feeder at the bottom (800 rpm, CO 20 atm, 500 ml/min.).

It was revealed from the results under the above described conditions[9] that the reduction also proceeded at significant rates in various solvents, especially ethyleneglycol monoehtyl ether acetate and n-butanol were found to be preferred in these catalysis.

It was also revealed that the other ruthenium compounds, such as $Ru(acac)_3$, RuO_2, $[RuCl_2(COD)]_n$, or $RuCl_2(CO)_2(PPh_3)_2$, in place of $Ru_3(CO)_{12}$, were also effective on this reaction; the

rates were also found to be increased at higher reaction temperatures under higher CO pressures.[8)]

Importantly, the rates were found to be increased upon the addition of organophosphine, or organophosphite compounds, such as PPh_3, $P(OPh)_3$ or others; the rates were also found to be increased upon the addition of phase-transfer catalysts, such as TBAB (tetra-n-buthylammoniumbromide), or BAC (benzyl(triethyl) ammoniumchloride).[10)] The reduction of other nitro-anthraquinones, such as 2-nitroanthraquinone, 1,5-, 1,8-dinitro-anthraquinones were also found to be reduced to produce the corresponding aminoanthraquinones, respectively with exclusive selectivities of nitro-group (almost 100 %).

3-2. Effect of cocatalyst

In order to discover the more active catalyst system under the CO/H_2O conditions, many screening of cocatalyst were carried out for the reduction of nitro-anthraquinones using catalysts composed of ruthenium-carbonyl complexes in the presence of various transition metal compounds in diglyme or ethyleneglycol monoethyl ether aceate (Apparatus A).

Particular attention should be paid that the rates markedly increased upon the addition of the other transition metals, such as metal carbonyl compounds of Co, Mo, W which show no catalytic activities under these conditions, as shown in Table 5.[11)]

<< Table 5 >>

In particular, the siginificant turnover numbers under these

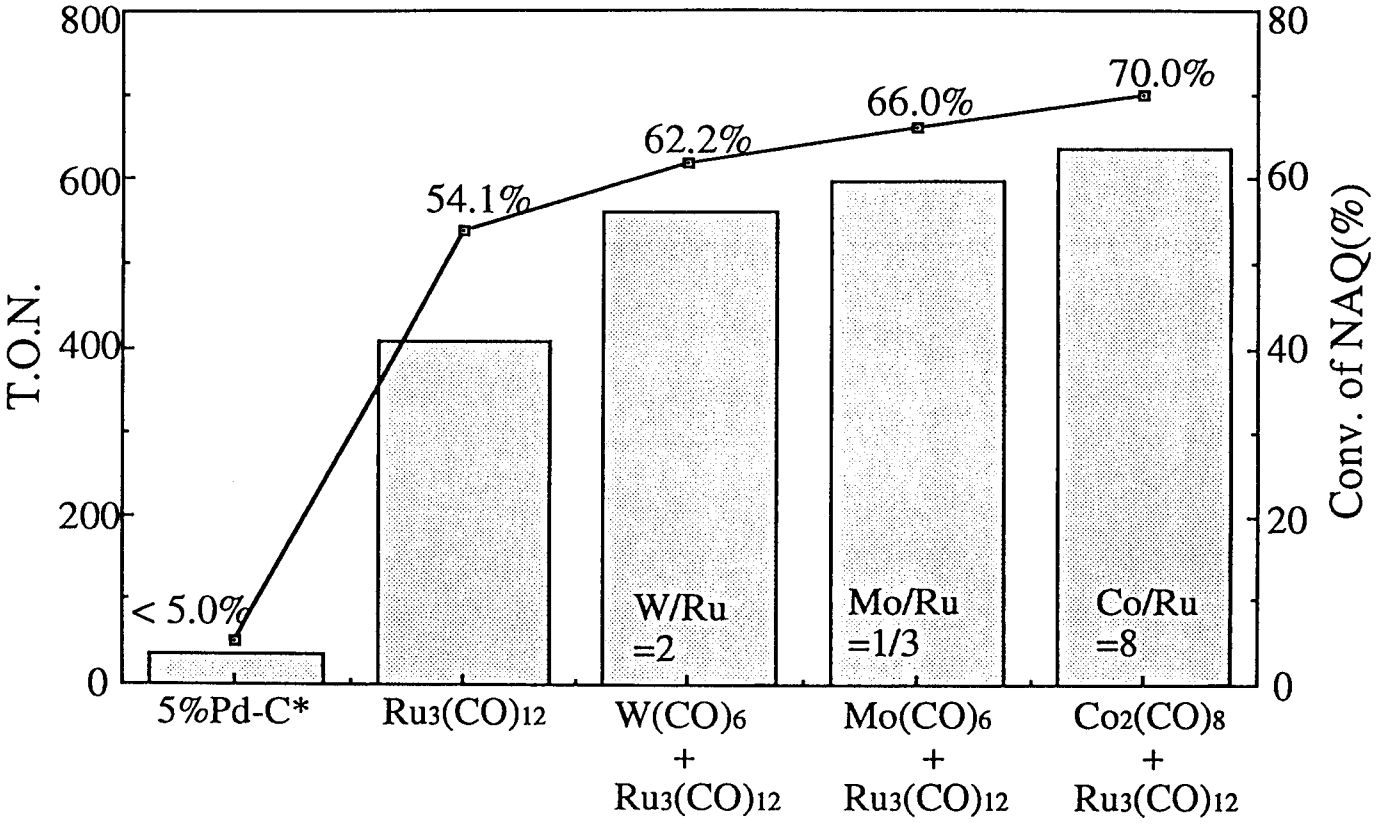
CO/H_2O conditions were found to be attained upon the addition of Cu compounds, especially cupric oxides, copper carbonates, cupric bromide, and copper acetate; the rates were also found to be markedly increased at higher reaction temperatures under higher CO pressures, as shown in Table 7. The remarkable selectivity of nitro-group did not change under these conditions. The mixed Ru-Cu catalyst was very effective to exhibit the significantly high catalytic activities for this selective reduction of nitroanthraquinones under the CO/H_2O conditions.[8)]
We believe that these results are very imortant from both synthetic and industrial viewpoints.

<< Table 6 >> <<Table 7 >>

Highly efficient process can be demonstrated for the production of aminoanthraquinones by the selective catalytic reduction of nitroanthraquinones using a homogeneous catalyst, which are comprised of ruthenium compounds and additives, such as Cu compounds, under CO/H_2O conditions, since aromatic nitro-group are reduced almost exclusively without other unsaturated groups such as C=O being reduced, and aminoanthraquinones are readily separated by filteration as a red precipitate from the catalysts which are recycled because of the poor solubilities in solvents of aminoanthraquinones. We believe this catalytic process will be applied to produce an aromatic amines commercially in the near future.

Table 5

Reduction of Nitroanthraquinones under CO/H_2O Conditions : Effect of Co-Catalysts

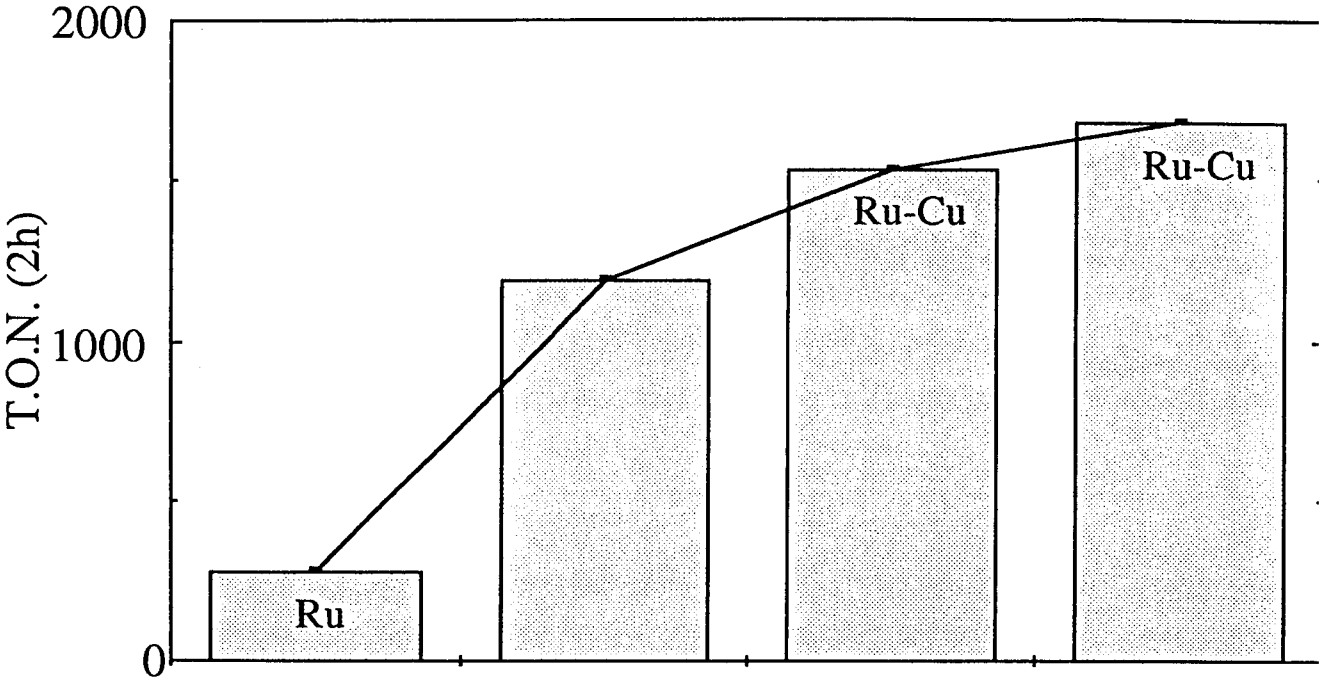


Conditions : $Ru_3(CO)_{12}$ 0.01 mmol, CO 20 atm, 150°C, 2h, diglyme-H_2O
Nitroanthraguinones (mono-and di-nitro), 2g

* 5% Pd-C 0.2g, MeOH, 1-Nitroanthraquinone 2g
H_2 30 atm, 120°C, 4.5h

Table 6

Selective Reduction of Nitroanthraquinones Affording Aminoanthraquinones Using Ru-Cu Catalys under CO-H_2O Conditions

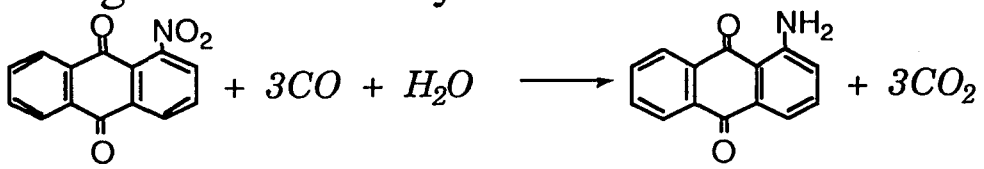


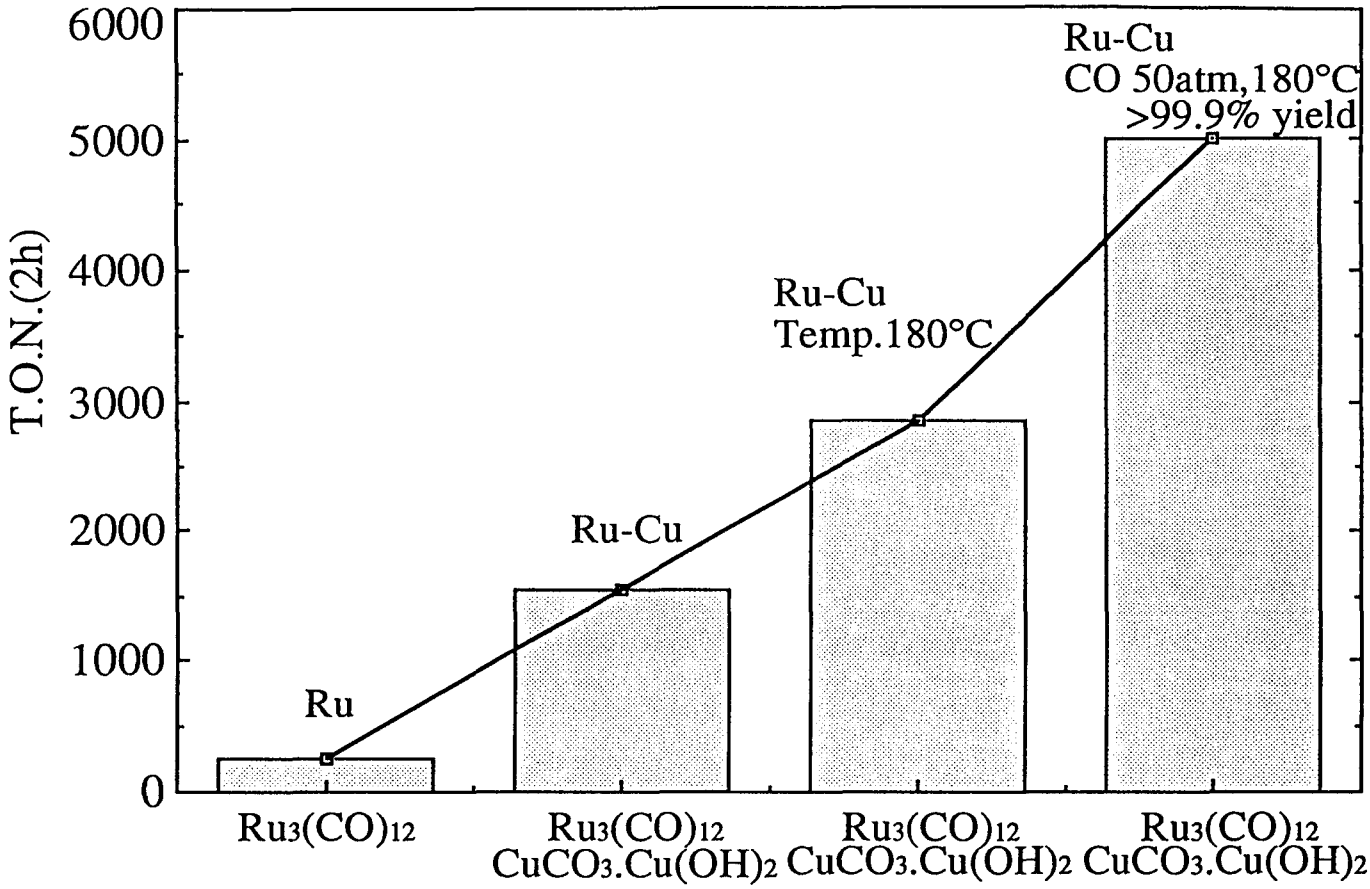
cat	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
Co-Cat	none	$Cu(CH_3CO_2)_2$	$CuCO_3.Cu(OH)_2$	CuO
Molar Ratio Cu/Ru	—	25	16	20

Conditions : $Ru_3(CO)_{12}$ 0.005 mmol, $EtOCH_2CH_2OAc$ / H_2O solv. Nitroanthraquinones (mono-, and, di-nitro) 2g, CO 20atm, 150°C

Table 7

Facile Selective Reduction of Nitroanthraquinones Using Ru-Cu Catalyst under CO / H_2O Conditions





Conditions : $Ru_3(CO)_{12}$ 0.00.-0.005 mmol, CO 20atm, 150°C
$EtOCH_2CH_2OAc$ / H_2O solv.
Nitroanthraquinones (mono-, and, di-nitro-) 2 or 3g

Summary

In conclusion, highly efficient practical process can be demonstrated for the production of aminoanthraquinones by selective reduction of nitroanthraquinones using the following homogeneous catalysts under CO/H_2O conditions:

1) ruthenium-carbonyl catalysts (and additives)

2) ruthenium-copper catalysts.

In this paper, the following important facts were also found for this catalytic reduction under the CO/H_2O conditions.

1) The reduction of nitroanthraquinones using a catalyst comprised of homogeneous rhodium or ruthenium compounds proceeded not only at remarkable rates, but also with almost exclusive selectivity of nitro-group under the CO/H_2O conditions. The rates were also found to be increased upon the addition of small amounts of amines such as triethylamine, diisoropylamine, or piperidine. The larger turnover numbers were also found to be attained at higher reaction temperatures under higher CO pressures.

2) The rates were also found to be increased upon the addition of organophosphine, or organophosphite compounds, such as PPh_3 or $P(OPh)_3$ or others. The increase on the reaction rates were also observed upon the addition of a phase-transfer catalyst such as TBAB, or BAC.

3) The more significant turnover numbers were found to be attained upon the addition of copper compounds such as cupric oxide, copper acetate, or copper carbonate for the reduction using a homogeneous ruthenium catalyst under the CO/H_2O conditions.

We believe that the above described facts are potentially-important from both synthetic and industrial viewpoints: this process will be applied in the near future.

References and Notes

1) K. Nomura, and M. Ishino, "Production of Aromatic Amines," to be published (for example USP 5112997 (1992)), and their references cited therein.

2) For example (Review),

a) R.M. Laine, E.J. Crawford, J. Mol. catal., 44, 357 (1988).

b) P.C. Ford, A. Rokicki, Adv. Organomet. Chem., 28, 139 (1988).

3) For example (Review),

a) P. Escaffre, A. Thorez, P. Kalck, J. Mol. Catal., 33, 87 (1985).

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b) idem. J. Mol. Catal., 73, L1 (1992).

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c) idem. ibid., 66, L11 (1991).

d) idem. ibid., 66, L19 (1991).

e) idem. Bull. Chem. Soc., Jpn., 64, 2624 (1991).

f) idem. J. Mol. Catal., in press.

6) Turnovers of 994 mol-cat^{-1} was obtained under the similar conditions (amine/Ru molar ratio of 20 in diglyme solvent).

7) It was already reported that benzylidene acetone was reduced to yield the corresponding saturated ketone using $Rh_6(CO)_{16}$-3,4,7,8-tetramethyl-1,10-phenanthroline catalyst under CO/H_2O conditions: E.Alessio, G. Zassinovich, G. Mestroni, J. Mol.

Catal., 22, 327 (1984).

8) The detailed results were already published in ref. 1 (for example USP 5112997 (1992)), and their references cited therein.

9) The rate, the yield was improved by using this apparatus.[1)]

10) K. Nomura, and M. Ishino, to be published.

11) K. Nomura, and M. Ishino, to be published.

2-4. Chapter 2 Discussion (Tentative mechanism)

As described above in 2-1, 2-2, and 2-3, significant catalytic activities as well as exclusive selectivities of nitro-group were found to be exhibited for the reduction of aromatic nitro compounds using catalysts composed of ruthenium-carbonyl complexes in the presence of small amount of the specified amines under CO/H_2O conditions.

$$ArNO_2 + 3CO + H_2O \longrightarrow ArNH_2 + 3CO_2$$

The reduction using amine-added ruthenium-carbonyl catalysts under CO/H_2O conditions, presented in this chapter, can be summarized as follows:

a) The reduction proceeded not only with remarkably high selectivities of nitro-group, but also at significant rates.

b) The reduction proceeded without by-producing hydrogen gas which was formed by the Water-Gas Shift Reaction; CO was effectively consumed for the production of the desired amines.

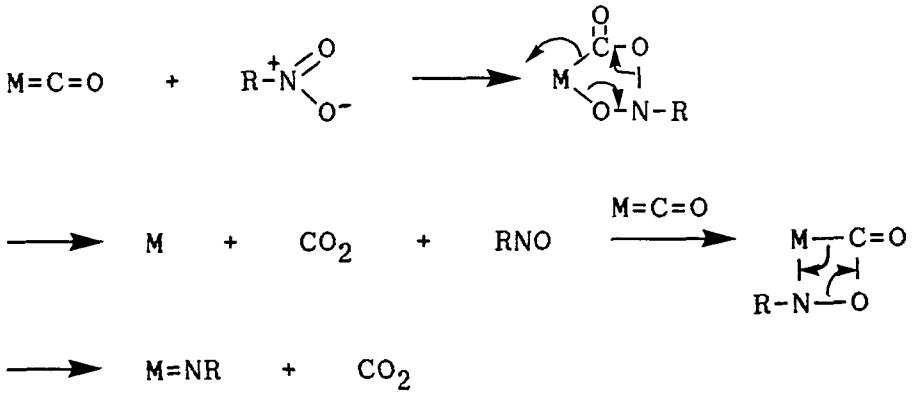
c) The catalysts will be easily recycled by filteration or extraction, therefore this catalytic reduction process will be more economical, and cleaner than the other conventional methods, such as stoichiometric reduction using alkali metal sulfides, or catalytic hydrogenation using iron, or palladium-carbon.

In this part, I wish to present a tentative reaction pathway in these catalysis on the basis of previous reports and our experimental results.

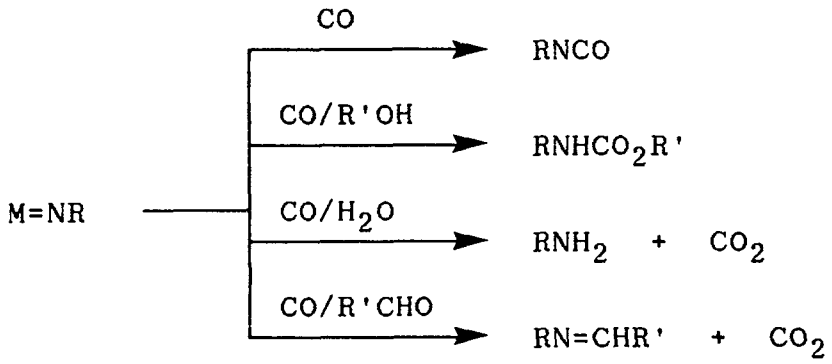
It has been postulated by R.A. Sheldon and others that the reaction of aromatic nitro compounds involves successive oxygen transfer reactions between the nitro compound and coordinated metal-carbonyl ligand.[1] And this can be conveniently envisaged as formally involving cycloaddition of $ArNO_2$ and ArNO to a metal-carbonyl double bond and subsequent extrusion of carbon dioxide, as shown in Scheme I.

And the further reactions, such as carbonylation etc., are considered to be proceeded by the scheme outlined in Scheme II.

Scheme I

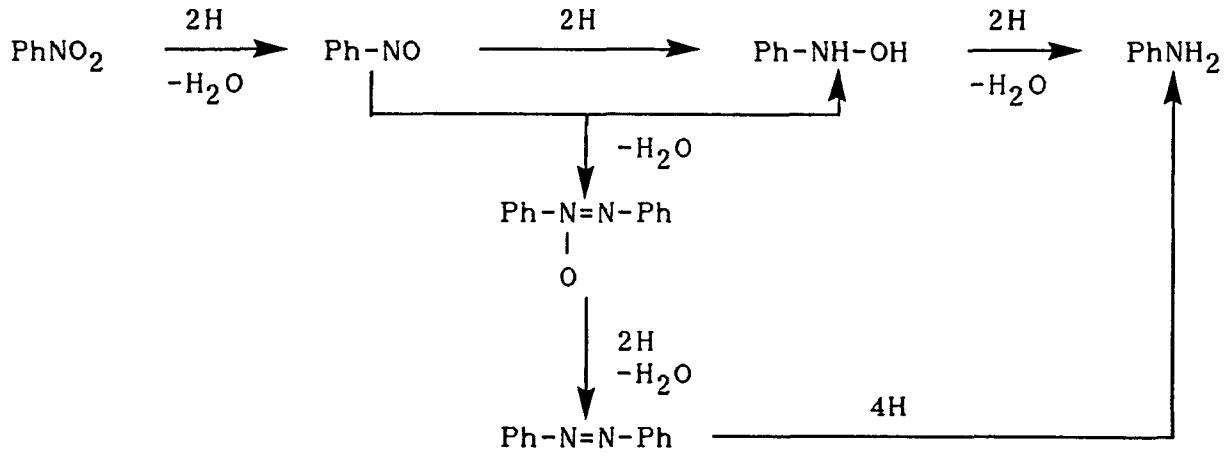


Scheme II



E. Alessio et al. also proposed another possibility in J. Mol. Catal. that the reduction of nitrobenzene using 3,4,7,8-tetramethyl-1,10-phenanthroline-added $Ru_3(CO)_{12}$ complex was proceeded by the simple hydrogenation of aromatic nitro compounds with hydrogen which was formed by the Water-Gas Shift Reaction, as shown in Scheme III.[2)]

Scheme III

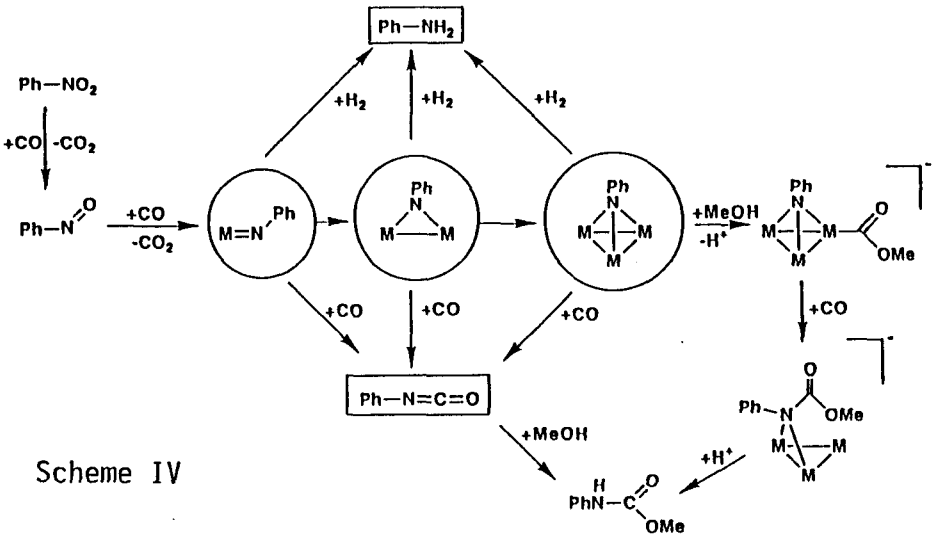


In our case, as mentioned above, the reduction proceeded at remarkable rate without by-producing hydrogen gas. And this result clearly indicates that the reduction was not proceeded by the scheme shown in Scheme III. And therefore, we believe it clear that the reduction of aromatic nitro compounds using our specified amine-added ruthenium-carbonyl complexes under CO/H_2O conditions is considered to proceed via metal-nitrene intermediate (Ru=NAr) which is formed by the oxygen transfer reaction between aromatic nitro group and metal carbonyl ligand, shown in Scheme I.

Tentative reaction pathway for amine-added ruthenium-carbonyl complexes catalyzed reduction of aromatic nitro compounds under CO/H_2O conditions

The mechanism by which aromatic nitro compounds is catalytically reduced to afford aromatic amines and carbonylated to form carbamates has never been fully elucidated, although the transformation like those shown in Scheme IV have often been suggested.[3] This scheme implies the stepwise deoxygenation of nitrobenzene to form nitrosobenzene followed by subsequent nitrosobenzene deoxygenation to form an imido ligand bound to one, two, or three metal atoms. It was also suggested that hydrogenation of the imido ligand would give aniline whereas carbonylation would yield phenyl isocyanate. However, it should be noted that there is no firm evidence that imido ligands and clusters are at all important in the catalytic chemistry, and other mechanisms have been suggested involving initial reduction of nitrobenzene to aniline via an electron transfer path.[4]

Proposed Reaction Scheme for Formation of Aniline, Isocyanate, Carbamates.



Scheme IV

We believe, however, we can't explain the mechanism in these catalysis by the scheme postulated above, in which aromatic amines are produced by hydrogenation of metal-nitrene species, because the reduction proceeded without by-producing hydrogen gas which was formed by the Water-Gas-Shift Reaction, and the reduction also proceeded with remarkably high selectivities of nitro-group. In particular, the result that CO was effectively consumed without by-producing hydrogen gas, is quite different from that for the reduction using trimethylamine-added $Ru_3(CO)_{12}$ catalyst which shows also exceptionally high catalytic activities for the Water-Gas Shift Reaction.[5)]

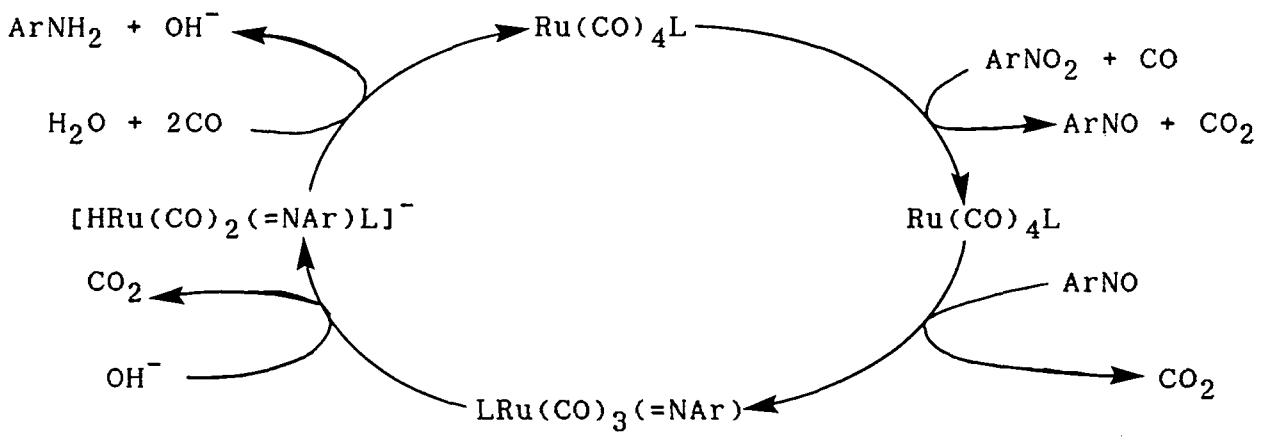
Taking into account the above described results, we consider that the reduction of aromatic nitro compounds using amine-added ruthenium-carbonyl complex catalysts presented in this paper proceeds via intramolecular hydrogen-transfer reaction of metal-nitrene intermediate as outlined in Scheme V. The results, that reduction proceeded with high nitro-group selectivity as well as without by-producing hydrogen gas, can be explained by using this scheme. An original reaction pathway for the selective reduction of aromatic nitro compounds can be demonstrated in these catalysis. Further studies are now actively investigated.

<< Intramolecular Hydrogen Transfer Reaction >>

$$L_m(CO)_nM{=}N{-}Ar \xrightarrow[-CO_2]{OH^-} [HL_m(CO)_{n-1}M{=}N{-}Ar]^-$$

$$\xrightarrow[-OH^-]{H_2O/CO} L_m(CO)_nM + ArNH_2$$

$$Ru_3(CO)_{12} + L \rightleftharpoons 3Ru(CO)_4L$$



Scheme V. Tentative Reaction Scheme for Ruthenium-Catalyzed Selective Reduction of Aromatic Nitro Compounds

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1) R.A. Sheldon,"Chemicals from Synthesis Gas," D. Reidel Publishing Co., Dortrecht, pp. 181 (1981).

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c) S. Bhauduri, K.S. Gopalkrishnan, W. Clegg, P.G. Jones, G.M. Sheldrick, and D. Stalke, J. Chem. Soc., Dalton Trans., 1765 (1984).

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CONCLUSING REMARKS

<< Conclusing Remarks >>

The present paper discloses the selective organic syntheses by homogeneous transition metal catalysis, in particular, selective reduction of aromatic nitro compounds under CO/H_2O conditions using transition metal complex catalysts. The important features presented in each chapters are summarized as follows.

A selective reduction of aromatic nitro compounds under CO/H_2O conditions using homogeneous transition metal catalysts has been described. Two types of new catalyst systems which exhibit both significant catalytic activities and almost exclusive selectivities of the nitro-group have been presented (chapter 1, chapter 2).

In chapter 1, the reduction was found to proceed at marked rates which were much higher than those previously reported even under the extremely mild conditions of room temperature and atmospheric pressure of carbon monoxide by using amine- or phosphine-added rhodium-, ruthenium-carbonyl complexes in the presence of NaOH aqueous solution. In particular, as the results of many screenings, the following catalyst systems were found to be preferred for this reduction:

1) $Rh(CO)_2(acac)$, $Rh_4(CO)_{12}$-9,10-diaminophenanthrene

2) $Rh(CO)_2(acac)$-PEt_3

3) $Rh_4(CO)_{12}$-dppm, dppe

4) $Rh_6(CO)_{16}$-amine, diamine

Both electronic and steric factor of phosphine ligand was also found to be important in order for the reduction using PR_3-added $Rh(CO)_2(acac)$ catalysts to proceed at a significant rate. Effect of NaOH aqueous solution was quite remarkable; metal-hydride species generated by the decarboxylation of metal-CO_2H plays an important role in these catalysis.

Remarkably high selectivities of nitro-group were also found to be exhibited in these catalysis: the aromatic nitro-group was reduced almost exclusively without other unsaturated groups such as C=O being reduced. The almost exclusive reduction by these catalysis is, we believe, very important from both synthetic and industrial viewpoints.

The reduction was also found to proceed without by-producing hydrogen gas which was formed by the Water-Gas-Shift Reaction.

As described in chapter 2, remarkably high selectivities of nitro-group as well as high catalytic activities were also found to be exhibited by using ruthenium-carbonyl complexes in the presence of small amounts of specified amines under CO/H_2O conditions (in the absence of NaOH aqueous solution). As the result of many screenings of the catalyst, diisopropylamine, piperidine, dibutylamine, and triethylamine were found to be

preferred in these catalysis. The turnover numbers were increased at higher reaction temperatures under higher CO pressures.

Aromatic nitro-group was reduced almost exclusively without other unsaturated groups such as C=O, C≡N, C=C, C≡C being reduced in these catalysis, resulting in obtaining the desired amines in high yields. The reduction was also found to proceed without by-producing hydrogen, suggesting that the reduction did not proceed by the reaction of aromatic nitro-group with hydrogen gas generated by the WGSR.

Aminoanthraquinones which are important key materials as dyes and their intermediates were also found to be produced in high yield by the selective reduction of nitroanthraquinones using the above-described practical homogeneous ruthenium, or rhodium catalysts. The effect of additives on this reduction was also explored; the rates were found to be increased upon the addition of additives such as organophosphine, organophosphite, or phase-transfer catalysts, or others. In particular, the remarkable increase on the reaction rate was found to be observed upon the addition of Cu compounds.

In both cases (chapter 1, 2), an original reaction pathway for the almost exclusive reduction of aromatic nitro-group, such as intramolecular hydrogen transfer between metal-nitrene and hydride, can be demonstrated in these catalysis from the above results.

Acknowledgements (謝辞)

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