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Efficient Selective Reduction of Aromatic Nitro Compounds Affording Aromatic Amines under CO/H_2O Conditions Catalyzed by Amine-Added Rhodium-Carbonyl Complexes

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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 5 equiv 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.

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

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

using both homogeneous and heterogeneous catalysts.[2]

As one of its applications related to WGSR, organic synthesis under CO/H_2O conditions using a 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 an also very attractive subject, and many studies have already been made.[2,3] Alper found that the reduction proceeded under atmospheric

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

pressure of CO and room temperature by using $Ru_3(CO)_{12}$ in a benzene–2-methoxyethanol–5 equiv NaOH aqueous solution in the presence of a phase-transfer catalyst ($PhCH_2N(C_2H_5)_3^+Cl^-$)[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 describe that amine-, diamine-added rhodium carbonyl complexes shows 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 5 equiv NaOH aq solution.[4]

Experimental

General Procedure. All manipulations were carried out under a nitrogen atmosphere, or in vacuo. Water and 2-methoxyethanol, diglyme (diethylene glycol 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 5 equiv-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, 3 m) and GC-MS (QP-1000, Shimadzu 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 1 m) 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–5 equiv NaOH aqueous solution under 1 atm of CO and room temperature (25 °C) for 3 h are summarized in 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. It was revealed that the reaction proceeded at a significant rate during the initial stage (72 turnovers for 1 h), but that the 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 5 equiv NaOH aqueous solution used was thought to play an important role in this reaction to proceed with a significant rate. 2-methoxyethanol was also favorable as a solvent.

Table 1. The Reduction of Nitrobenzene Catalyzed by Amine-Added $Rh(CO)_2(acac)$ Complexes — The Effect of Amine Additives —

Amine	Molar ratio[a)]	Turnovers[d)]
None[b)]	—	<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[c)]
1,8-Diaminonaphthalene	1.5	68
Pyridine	3.0	61
NEt_3	3.0	66

Reaction conditions: 2-methoxyethanol/5 equiv NaOH aq=15/5 (ml), $Rh(CO)_2(acac)$ 0.02 mmol, $PhNO_2$ 5 mmol, 25 °C, CO 1 atm, 3 h. a) Molar ratio of amine/Rh. b) H_2O (5 ml) was used instead of 5 equiv NaOH aq solution. c) $Rh(CO)_2(acac)$ 0.01 mmol. d) 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 conditions: $Rh(CO)_2(acac)$/9,10-diaminophenanthrene (0.02/0.03 mmol), 2-methoxyethanol/5 equiv NaOH aq=15/5 (ml), $PhNO_2$ 5 mmol, CO 1 atm, 25 °C.

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.

The results for the reduction of various substituted nitrobenzenes using the $Rh_4(CO)_{12}$–9,10-diaminophenanthrene catalyst system for 90 min. are summarized in

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)	1.5 equiv NaOH aq (5)	64
2-Methoxyethanol (15)	3 equiv NaOH aq (5)	94
2-Methoxyethanol (15)	5 equiv NaOH aq (2.5)	78
2-Methoxyethanol (15)	5 equiv NaOH aq (5)	122
2-Methoxyethanol (8)	5 equiv NaOH aq (5)	79
2-Propanol (15)	5 equiv 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, 3 h.

Table 4. Reduction of Nitrobenzene Catalyzed by 9,10-Diaminophenanthrene-Added $Rh_4(CO)_{12}$ Complex under CO/H_2O

Molar ratio[a)]	Turnovers/mol-cat^{-1}
0	108
1.09	200
2.25	225
1.50	610[b)]

Reaction conditions: $Rh_4(CO)_{12}$ 0.02 mmol, 2-Methoxyethanol/5 equiv NaOH aq=15/5 (ml), $PhNO_2$ 5 mmol, CO 1 atm, r.t. (25 °C), 3 h. a) Molar ratio of 9,10-diaminophenanthrene/Rh. b) $Rh_4(CO)_{12}$ 0.005 mmol.

Table 5. It should be noted that these reductions proceeded not only with significant rates but also with high nitro-group selectivities. 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 $Rh_4(CO)_{12}$–dppe (dppe: $Ph_2P(CH_2)_2PPh_2$) catayst 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).

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 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 nitroanthraquinone 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 reduction of aromatic nitro compounds after much further development of this subject.

The results for the reduction of 1-nitroanthraquinone with various amine-added $Rh_4(CO)_{12}$ are summarized in in Table 7. The reduction rate increased upon the addition of only a small amount of amines, especially NEt_3 and 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

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[a)]
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/5 equiv NaOH aq=15/5 (ml), aromatic nitro compounds 5 mmol, CO 1 atm, r.t. (25 °C), 3 h. a) >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/5 equiv NaOH aq=15/5 (ml), aromatic nitro compounds 5 mmol, CO 1 atm, r.t. (25 °C), 10 h.

Table 7. Reduction of 1-Nitroanthraquinone Affording Added $Rh_4(CO)_{12}$ Complexes

Amine	Molar ratio[a)]	Turnovers/mol-cat^{-1}
None	—	373
9,10-Diaminophenanthrene	1.5	419
NEt_3	3.0	554
4-(Dimethylamino)pyridine	3.0	529
1-Aminoanthraquinone	3.0	469

Reaction conditions: Diglyme (diethylene glycol dimethyl ether)/5 equiv 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. a) Molar ratio of amine/Rh.

Table 8. Catalytic Reduction of Nitrobenzene under CO/H_2O or under H_2 Conditions

Catalyst	Conditions	Temp/°C	Time/h	Turnovers[a]
$Rh(CO)_2(acac)$–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) undr CO/H_2O; $Rh(CO)_2(acac)$/diamine=0.02/0.03 (mmol), 2-methoxyethanol/5 equiv aq=15/5 (ml), nitrobenzene 5 mmol, CO 1 atm. b) under H_2; the same reaction conditions except that 5 equiv NaOH aq was not added. a) 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[a]	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(dimethylamino)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)[b]

Reaction conditions: $Rh_6(CO)_{16}$ 0.001 (mmol), 2-methoxyethanol/5 equiv NaOH aq=15/5 (ml), nitro compounds 5 mmol, CO 1 atm, r.t. (25 °C), 1 h. a) Amount of amine or diamine (mmol)/amount of catalyst metal (mmol). b) $Rh_6(CO)_{16}$ 0.001 mmol, 5 h.

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 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 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)]

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-5 equiv-NaOH aqueous solution under 1 atm of CO at room temperature (25 °C) for 1 h (summarized in 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 be noted that the 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 presence 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; this subject is now under investigation.

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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).

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)–5 equiv NaOH aq solution (5 ml) under CO (1 atm) at 25 °C for 4 h. This result, that the reduction proceeded without by-producing dihydrogen that was formed by 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, should 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., Dordrecht, Netherland (1981), p. 181; T. Ikariya, *Shokubai,* **5**, 271 (1989).