Selective Deoxygenation of Various N–O Bonds Catalyzed by Rhodium Carbonyl Clusters in the Presence of H₂O and CO and Their Heterogenization Using Amino-Substituted Polystyrenes

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Catalytic deoxygenation of various N–O bonds using rhodium carbonyl compounds under a water gas shift reaction was studied. A catalyst system of $Rh_6(CO)_{16}$ and N,N,N',N'-tetramethyl-1,3-propanediamine was found to have high activities for the following deoxygenations: 1) conversion of nitrobenzenes to anilines, 2) aliphatic nitro compounds to nitriles, 3) oximes to nitriles, 4) hydroxylamines to amines, and 5) amine oxides to amines. The above-mentioned rhodium catalyst system was heterogenized by using amino-substituted polystyrenes. Rh_6 and Rh_{14} carbonyl clusters of $[Rh_6(CO)_{15}H]^-$, $[Rh_6(CO)_{15}]^{2-}$, and $[Rh_{14}(CO)_{25}]^{4-}$, were formed on the polymer surface. The characteristic features of the catalysis of the polymer-bound rhodium cluster complexes are described in relation to the corresponding homogeneous ones.

Metal carbonyl clusters have generated interest as catalysts from the standpoint of faciliting new organic reactions and as a model for metal catalysts.[1] Various organic reactions explored by using metal carbonyl clusters (e.g., hydroformylation, reduction, and deoxygenation) have been carried out under a CO atmosphere since the labile cluster framework consisting of metal-metal bonds must be reinforced by CO molecules.[2] We also studied the application of the water gas shift reaction (WGSR) using CO and H₂O for organic syntheses in the presence of rhodium carbonyl clusters, and found that the rhodium clusters have unique reactivities for the reduction of carbonyl compounds (e.g., aldehydes and α,β-unsaturated carbonyl compounds), carbonylation of olefins, and deoxygenation of various N–O bonds.[3] In the above-mentioned organic reactions, the amines or pyridines are an essential additive to form active species of rhodium catalysts. In order to simplify the work-up procedure, we heterogenized the rhodium catalyst systems using amino-substituted polystyrenes and the rhodium cluster anions $[Rh_6(CO)_{15}H]^-$, $[Rh_6(CO)_{15}]^{2-}$, and $[Rh_{14}(CO)_{25}]^{4-}$ which formed as ammonium salts on the polymer. In this paper, we give a detailed account of the deoxygenation of nitro compounds, oximes, hydroxylamines, and amine oxides using CO and H₂O in the presence of rhodium carbonyl clusters, e.g., $Rh_6(CO)_{16}$ and $Rh_4(CO)_{12}$.[4] Furthermore, the characteristic features of the catalysis of polymer-bound rhodium cluster complexes are mentioned in relation to the corresponding homogeneous ones.

Results and Discussion

Deoxygenation of Aromatic Nitro Compounds. Rhodium carbonyl cluster-diamine catalyst systems showed high activity for WGSR under mild conditions.[5] In relation to WGSR, we have examined the reactivity of various amines and pyridines as additives for the deoxygenation of nitrobenzene to aniline using
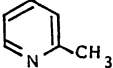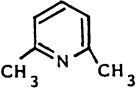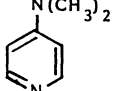
CO and H₂O at 80 °C. Results using CO of 700 mmHg (1 mmHg=133.322 Pa) and H₂O in the presence of the $Rh_6(CO)_{16}$ cluster are shown in Table 1 together with the activities of the corresponding WGSR. Aniline was the only deoxygenation product. The formation

$$\text{(NO}_2\text{-benzene)} + 3CO + H_2O \xrightarrow{Rh_6(CO)_{16}} \text{(NH}_2\text{-benzene)} + 3CO_2 \quad (1)$$
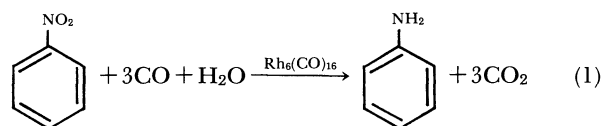
of other products (e.g., nitrosobenzene, phenylhydroxylamine, N,N'-diphenylurea, and cyclohexylamine) could not be observed under the reaction conditions.[6] The yields of aniline are also strongly dependent on various kinds of bases. It should be noted that there are sharp contrasts between the deoxygenation of nitrobenzene and WGSR regarding the effect of additives. The most effective additive in the deoxygenation reaction is N,N,N',N'-tetramethyl-1,3-propanediamine (TMPDA), which had no activity for generation of H₂ in WGSR. Among the diamine series of $-N(CH_2)_nN-$, increasing the number (n) of methylenes and the introduction of methyl substituents on the nitrogen atoms increase the yield of aniline, respectively, while decreasing H₂ generation from WGSR. For pyridine derivatives, the introduction of electron-releasing substituents on the γ-position of pyridines increases the yields of aniline; 4-(dimethylamino)-pyridine was the most effective additive. On the other hand, methyl substituents on the α-position of pyridines decrease the yield of H₂ while an α-substituent effect could not be observed in the nitrobenzene deoxygenation. The strong basicity of the pyridines with high pK_a value is an essential factor for attaining high yields of aniline in the deoxygenation of nitrobenzene.

The catalytic behavior for nitrobenzene deoxygenation using various metal complexes was examined in the presence of TMPDA as an additive. Typical

Table 1.   Additive Effect of Various Amines and Pyridines on Deoxygenation
of Nitrobenzene and the Water Gas Shift Reaction Using $Rh_6(CO)_{16}$[a]

| Base(pK_a)[b] | Deoxygenation | | WGSR |
| | Reaction time | Yield of aniline | Yield of H_2[c] |
	h	%	
$NH_2CH_2CH_2NH_2$(9.97)	10	34	75
$NH_2(CH_2)_3NH_2$(10.65)	10	45	32
$NH_2(CH_2)_4NH_2$(10.84)	10	50	6.4
$CH_3NHCH_2CH_2NHCH_3$(9.5)	10	45	69
$(CH_3)_2NCH_2CH_2N(CH_3)_2$(8.97)	4	>99	2.5
$(CH_3)_2N(CH_2)_3N(CH_3)_2$(10.2)	2.5	>99	0
(pyridine) (5.17)	10	79	22 3[d]
(2-methylpyridine) (5.97)	10	72	1
(2,6-dimethylpyridine) (6.75)	10	80	0
(4-dimethylaminopyridine) (9.70)	2.5	>99	2.8[d]
$N(C_2H_5)_3$(10.65)	10	83	0
(N-methylpyrrolidine) (10.1)	5	92	2.3

a) For deoxygenation; nitrobenzene 1.5 mmol, $Rh_6(CO)_{16}$ 0.05 mmol, base 15 mmol, H_2O 0.72
ml, 2-ethoxyethanol 3 ml, P_{co}=700 mmHg, 80 °C. For WGSR: $Rh_6(CO)_{16}$ 0.05 mmol, base 85
mmol, H_2O 0.72 ml, 2-ethoxyethanol [10-base]ml, P_{co}=700 mmHg, 4 h.[5]   b) The pK_a values
are cited from Ref. 44.   c) Yield of H_2=mol of H_2/mol of $Rh_6(CO)_{16}$ per 6 h.   d) Base 17
mmol, 2-ethoxyethanol 10 ml, 12 h, 100 °C.

Table 2.   Deoxygenation of Nitrobenzene with Various
Metal Carbonyl Compounds in the Presence
of H_2O and CO[a]

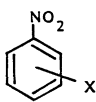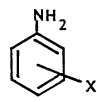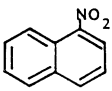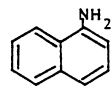| Catalyst | Aniline | |
	Time/h	Yield/%
$Rh_6(CO)_{16}$	2.5	>99
$Rh_4(CO)_{12}$	3.0	>99
$Rh_2(CO)_4Cl_2$	6.0	>99
$RhCl_3 \cdot 3H_2O$	10	20
$RhCl(PPh_3)_3$	10	17
Rh_2O_3	10	4
$Ru_3(CO)_{12}$	10	18
$Fe(CO)_5$	10	54
$W(CO)_6$	10	5

a) Reaction conditions were the same as used in Table 1.

examples are summarized in Table 2. Though Rh
carbonyl compounds (e.g., $Rh_6(CO)_{16}$, $Rh_4(CO)_{12}$, and
$Rh_2(CO)_4Cl_2$) are good catalysts, other Rh compounds
(such as $RhCl(PPh_3)_3$, $RhCl_3 \cdot 3H_2O$, and Rh_2O_3) have

low catalytic activities for deoxygenation. Other
transition metal carbonyl complexes of $Ru_3(CO)_{12}$,
$Fe(CO)_5$, and $W(CO)_6$ are poor catalysts under the
reaction conditions. All rhodium carbonyl com-
plexes having high activities were dark brown in
solution during deoxygenation. $Rh_2(CO)_4Cl_2$ had a
longer induction period for deoxygenation than the
Rh_6 and Rh_4 carbonyl clusters did. This phenom-
enon supports the idea that these rhodium com-
plexes were changed into a common active Rh species
during nitrobenzene deoxygenation.

The deoxygenation of various aromatic nitro com-
pounds using the catalyst system of $Rh_6(CO)_{16}$ and
TMPDA under 4 atm of CO is shown in Table 3,
together with that in the amino-substituted polymer
system. Details concerning the heterogeneous deox-
ygenation of nitro compounds are discussed in a latter
section. In a series of p-substituted nitrobenzenes,
electron-donating substituents decrease their reactivity
for deoxygenation, which became more clear by using
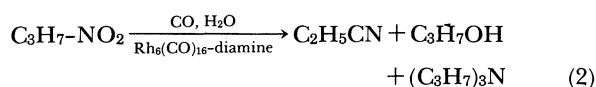competitive reactions to unsubstituted nitrobenzene

Table 3. Deoxygenation of Various Nitro Compounds Using Rh6(CO)16 in the Presence of CO and H2O[a]

Nitro compound	Amino-substituted product Yield[b]/%	k_X/k_H[c]
X=H	>99(>99)	1
4-Cl	>99(>99)	5.3(4)
4-CH3	>99(65)	0.40(0.36)
4-OCH3	65(21)	0.15(0.22)
3-CH3	73(54)	
2-CH3	42(23)	
2,4-CH3	76(23)	
2,6-CH3	10(trace)	
	61 (60)	

a) Rh6(CO)16 0.05 mmol, substrate 5 mmol, H2O 2.88 ml, 2-ethoxyethanol 2 ml, P_{co}=4 atm, 80 °C, N,N,N'N'-tetramethyl-1,3-propanadiamine (TMPDA) 5 mmol, 5 h.   b) Values of parentheses are for the polymer system. Amino-substituted polymer (Ia, 0.8 mg-atom of N), 48 h.   c) Relative rates were calculated by initial product ratios of substituted anilines to aniline.
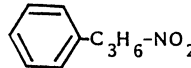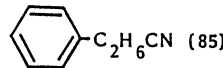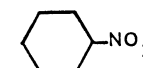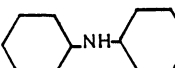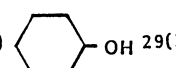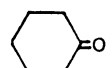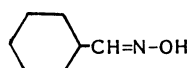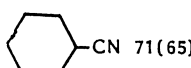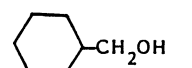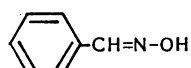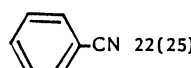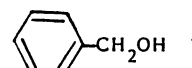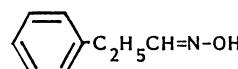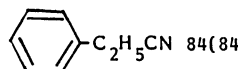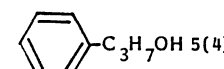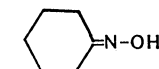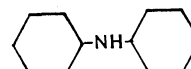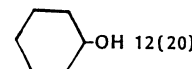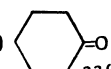
(ρ=2.75). A similar electronic effect of substituents has been reported in the phase-transfer catalyst of Ru3(CO)12[2d] and Ru(CO)3(Ph4C4CO),[7] while in the case of [Ru(cod)py4]$^{2+}$, electron-donating substituents accelerate the yield of aniline derivatives.[8] Nitro-naphthalene also gave naphthylamine in a 61% yield under the above-mentioned conditions.[9]

Aliphatic Nitro Compounds and Oximes. The reaction of 1-nitropropane in place of aromatic nitro compounds was performed by the catalyst system of Rh6(CO)16 and TMPDA at 40 °C under 16 atm of CO. Unexpectedly, propionitrile was obtained as the main product, accompanied by 1-propanol and tripropyl-amine without propylamine. Typical results of ali-

$$C_3H_7\text{-}NO_2 \xrightarrow[Rh_6(CO)_{16}\text{-diamine}]{CO, H_2O} C_2H_5CN + C_3H_7OH + (C_3H_7)_3N \quad (2)$$

phatic nitro compounds are listed in Table 4, together with those of amino-substituted polymer systems. A nitro function on the primary carbon atoms in various nitro compounds was deoxygenated to give the corresponding nitriles as the main product, respectively,

Table 4. Deoxygenation of Various Aliphatic Nitro Compounds and Oximes Using Rh6(CO)16 in the Presence of CO and H2O

Nitrogen compound	Deoxygenated products Yield[b]/%
C2H5-NO2	CH3CN 69 C2H5OH 10 2-butanone 7
C3H7-NO2	C2H5CN 71(72) C3H7OH 15(19) (C3H7)3N 4(3)
	C2H6CN (85)
	NH 33(30) OH 29(27) =O trace(trace)
CH3CH=N-OH	CH3CN 64(68) C2H5OH 11(14) trace(trace)
C2H5CH=N-OH	C2H5CN 61(62) C3H7OH 20(20)
CH=N-OH	CN 71(65) CH2OH 12(25)
CH=N-OH	CN 22(25) CH2OH 75(65)
C2H5CH=N-OH	C2H5CN 84(84) C3H7OH 5(4)
=N-OH	NH 28(21) OH 12(20) =O 22(30)

a) Substrate 5 mmol, Rh6(CO)16 0.05 mmol, 2-ethoxyethanol 2 ml, H2O 2.88 ml, N,N,N'N'-Tetramethyl-1,3-propanamine (TMPDA) 5 mmol, P_{co}=16 atm, 40 °C, 24 h. For oximes: P_{co}=8 atm, 5 h.   b) Values of parentheses are for the polymer system. Amino-substituted polymer (Ia, 0.8 mg-atom of N), 48 h.

while amines, alcohols, and ketones were formed in the case of secondary nitro compounds. The formations of these products are discussed (vide infra). During the initial stage of these deoxygenations, trace amounts of oximes were detected, respectively. The reaction of a prepared propionaldehyde oxime was carried out under the same conditions as in the above 1-nitropropane to give propionitrile as the main product. From the above results, a possible path for the formation of propionitrile via an oxime intermediate can be considered in Scheme 1; the deoxygenation of

$$C_3H_7\text{-}NO_2 + CO \longrightarrow C_3H_7\text{-}NO \rightleftharpoons C_2H_5\text{-}CH=N\text{-}OH + CO_2$$
$$C_2H_5\text{-}CH=N\text{-}OH + CO \longrightarrow C_2H_5\text{-}CN + CO_2 + H_2$$
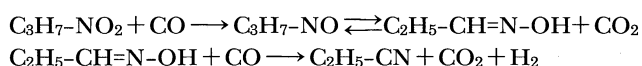
Scheme. 1.　Deoxygenation of 1-nitropropane via an oxime intermediate.

1-nitropropane occurs to give 1-nitrosopropane, which is tautomerized to propionaldehyde oxime, and dehydration of the oxime affords propionitrile with generation of H_2 and CO_2. 1-Propanol originated from hydrolysis of propionaldehyde oxime to give propionaldehyde, followed by a reduction. We have already found that a catalyst system consisting of $Rh_6(CO)_{16}$ and TMPDA has a high catalytic activity for the reduction of formyl groups under WGSR conditions.[3b]

The results of various oximes under 8 atm of CO are also included in Table 4. Aldoximes, except for benzaldehyde oxime, were deoxygenated to selectively give the corresponding nitriles; benzaldehyde oxime afforded benzyl alcohol as the main product, because of its facile hydrolysis to benzaldehyde under the reaction conditions. Deoxygenation with a protected oxime of propionaldehyde O-methyloxime did not occur and the starting material was recovered. Interestingly, this nitrile synthesis from oximes is regarded as being a formal dehydration, which occurs with the formation of CO_2 and H_2 (Eqs. 3 and 4).[10]

$$R\text{-}CH=N\text{-}OH \longrightarrow R\text{-}CN + H_2O \qquad (3)$$

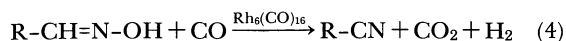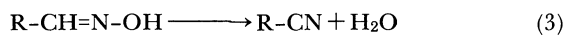$$R\text{-}CH=N\text{-}OH + CO \xrightarrow{Rh_6(CO)_{16}} R\text{-}CN + CO_2 + H_2 \qquad (4)$$

Next, the reaction of ketoximes was performed, leading to complicated product distributions of amines, alcohols, and ketones; for example, cyclohexanone oxime gave dicyclohexylamine, cyclohexanone, and cyclohexanol in 28, 22, and 12% yields, respectively. The formation of dicylohexylamine can be explained by the following paths. The hydrogenolysis of cyclohexanone oxime yields cyclohexylamine, followed by the dehydration of cyclohexylamine with cyclohexanone to afford N-cyclohexylidenecyclohexylamine, which is further reduced to dicyclohexylamine. In a separate experiment, the Schiff base of N-cyclohexylidenecyclohexylamine could be con-

(5)

83%
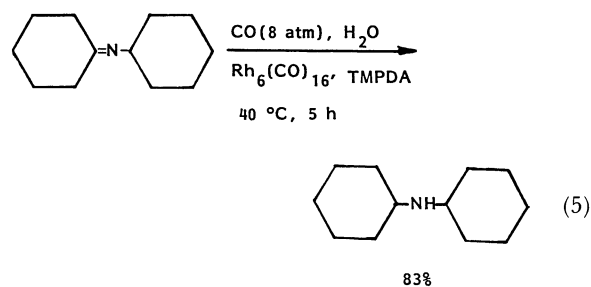
Table 5.　N-Alkylation of Amines with Ketones Using $Rh_6(CO)_{16}$ in the Presence of CO and H_2O[a]
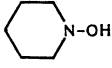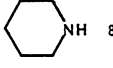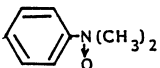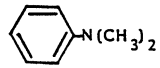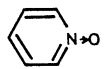
Amine	Ketone	N-Alkylated product Yield[b]/%
(cyclohexyl)NH₂	(cyclohexanone)	(dicyclohexylamine) 80
(cyclohexyl)NH₂	$C_2H_5\text{-}\overset{O}{\underset{\|\|}{C}}\text{-}CH_3$	$\text{(cyclohexyl)}NH\text{-}\underset{CH_3}{\overset{\|}{C}H}\text{-}C_2H_5$ 65
(cyclohexyl)NH₂	$CH_3\text{-}\overset{O}{\underset{\|\|}{C}}\text{-}C_7H_{15}$	$\text{(cyclohexyl)}NH\text{-}\underset{CH_3}{\overset{\|}{C}H}\text{-}C_7H_{15}$ 60
$C_6H_{13}NH_2$	(phenyl)$\overset{O}{\underset{\|\|}{C}}\text{-}CH_3$	$C_6H_{13}\text{-}NH\text{-}\underset{CH_3}{\overset{\|}{C}H}\text{-}\text{(phenyl)}$ 70

a) Amine 5 mmol, ketone 5 mmol, $Rh_6(CO)_{16}$ 0.05 mmol, 2-ethoxyethanol 2 ml, H_2O 1.4 ml, P_{co}=8 atm, 80 °C, 5 h.　b) Isolated yield.

verted into dicyclohexylamine in 83% yield under the same conditions as in the oxime reactions. We planed one-pot N-alkylation of amines with ketones via Schiff base intermediates. The reaction of primary amines with ketones was carried out in the presence of $Rh_6(CO)_{16}$ under WGSR conditions. The expected N-alkylated products of the amines were obtained in moderate yields, which is shown in Table 5.[11]

Hydroxylamines and Amine Oxides. In previous sections it was revealed that a catalyst system of $Rh_6(CO)_{16}$ and TMPDA was effctive for the deoxygenation of various nitro compounds and oximes. In order to develop the deoxygenation ability of the rhodium catalyst to other nitrogen compounds having N–O bonds, many reactions of hydroxylamines and amine oxides were carried out under conditions similar to those of the above-mentioned oximes. The results are shown in Table 6. Various hydroxylamines and amine oxides were easily deoxygenated to give the corresponding amines in high yields, respectively.[12] The deoxygenation of pyridine N-oxide did not occur under the present conditions and the N-oxide was recovered quantitatively. Although there are many reagents and catalysts for the deoxygenations of oximes, hydroxylamines, and amine oxides,

Table 6. Deoxygenation of Hydroxylamines and Amine Oxides Using $Rh_6(CO)_{16}$ in the Presence of CO and H_2O[a]

Nitro compound	Amine product yield[b]/%
$(C_2H_5)_2N-OH$	$(C_2H_5)_2NH$ 93(89)
N-OH	NH 82(75)
$(CH_3)_3\overset{H}{C}N-OH$	$(CH_3)_3CNH_2$ 70(80)
$(C_3H_7)_3N\rightarrow O$	$(C_3H_7)_3N$ 91(84)
$-N(CH_3)_2$ $\overset{}{O}$	$-N(CH_3)_2$ 99(75)
$N\rightarrow O$	No reaction

a) Substrate 5 mmol, $Rh_6(CO)_{16}$ 0.05 mmol, 2-ethoxyethanol 2 ml, H_2O 2.88 ml, TMPDA 5 mmol, P_{co}=8 atm, 40 °C, 5 h. b) Values of parentheses are for the polymer system. Amino-substituted polymer (1a, 0.8 mg-atom of N), 5 h (hydroxylamines), 24 h (amine oxides).

little has been known about such deoxygenations using a reducing agent of CO in organic synthesis.[13] It should be noted that our system of Rh carbonyl clusters and TMPDA can catalyze the deoxygenation of various nitrogen compounds using CO as an inexpensive reducing agent.

$$(C_2H_5)N-OH + CO \xrightarrow[H_2O,\ 40°C,\ 5\ h]{Rh_6(CO)_{16}-diamine} (C_2H_5)_2NH + CO_2 \quad (6)$$
$$93\%$$

$$(C_3H_7)_3N\rightarrow O + CO \xrightarrow[H_2O,\ 40°C,\ 5\ h]{Rh_6(CO)_{16}-diamine} (C_3H_7)_3N + CO_2 \quad (7)$$
$$91\%$$
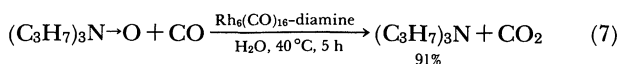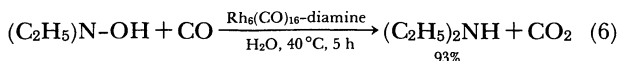
Polymer System in Deoxygenation of N–O Bonds. The most practical advantage of using insoluble polymer-bound metal complexes is to simplify the work-up procedure in organic synthesis.[14] Amines and pyridines are an essential additive in the above-mentioned deoxygenations, and act as a base to induce

the formation of active species of Rh carbonyl cluster anions and as an ammonium counter ion to stabilize the Rh cluster anions in an aqueous media (vide infra). We had a plan to heterogenize the $Rh_6(CO)_{16}$ catalyst system by using amino substituted organic polymers in place of TMPDA. The amino-substituted polymers were prepared by the following procedures: 1) polymerization of p-(chloromethyl)-styrene, followed by its treatment with amines, and 2) amination of p-(chloromethyl)styrene, followed by its polymerization. The above-mentioned synthetic routes are summarized in Scheme 2.

The catalytic behavior of our homogeneous $Rh_6(CO)_{16}$-amine systems is strongly dependent on various kinds of the amines, which was described in a previous section regarding nitrobenzene deoxygenation. It has been of interest whether polymer-heterogenized metal systems keep their instinctive catalytic activities of the corresponding homogeneous systems. Table 7 shows the effect of various amines on the 1-nitropropane reduction in the cases of poly-
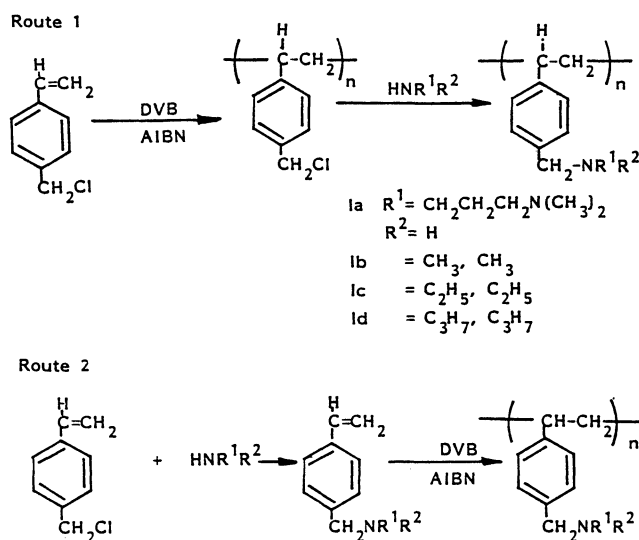
Scheme. 2. Synthetic routes of amino-substituted polystyrenes.

Table 7. Effect of Amines and Amino-Substituted Polymers on Deoxygenation of 1-Nitropropane[a]

Amine	Products yield[b]/%			
	C_2H_5CN	C_3H_5OH	3-Hexanone	$(C_3H_7)_3N$
Ⓟ-$NHC_3H_6N(CH_3)_2$ **1a**	72	19	0	3
$(CH_3)_2NC_3H_6N(CH_3)_2$	71(44)[b]	15(20)	0(5)	4(7)
Ⓟ-$N(CH_3)_2$ **1b**	55	32	0	3
$N(CH_3)_3$	55(48)	15(20)	0(5)	8(9)
Ⓟ-$N(C_2H_5)_2$ **1c**	53	29	5	0
$N(C_2H_5)_3$	40	19	4	9
Ⓟ-$N(C_3H_7)_2$ **1d**	31	7	18	4
$N(C_3H_7)_3$	39(35)	16(24)	5(5)	—

a) Reaction conditions were the same as in Table 4. b) Values in parentheses are for the amine monomers of 0.4 mmol used, respectively.

mer and homogeneous systems. Both of the systems gave similar product distributions for a variety of amine additives; the use of a polymer having the diamino moiety (**Ia**) led a high yield of propionitrile, and TMPDA was the most effective additive in homogeneous systems. Various heterogeneous systems of the amino-substituted polymers showed lower reaction rates for the 1-nitropropane deoxygenation than the corresponding homogeneous ones did; the reaction times for heterogeneous reactions had to be prolonged for up to 48 h in order to attain high nitrile yields. However, a relatively small amount of the amino moiety (0.8 mg-atom of N) can cause the selective formation of nitriles, compared with homogeneous systems (10 mg-atom of N). This might be due to the location of amino moieties within a relatively small volume of the polymers;[15] the high concentration of the amines on the polymer surfaces increases the basicity of the reaction media near the polymer surfaces, which facilitates the formation of Rh carbonyl cluster anions as an active species, and also promotes the stability of the Rh cluster anions through ammonium ions.

The effect of the various polymerization degrees of polystyrene supports on the deoxygenation was examined by using polymers prepared from route 1 with N,N-dimethyl-1,3-propanediamine. In the cases of polystyrenes with M_w=7600, 8600, and 52700, heterogeneous polymer-bound Rh complexes were formed in the above-mentioned deoxygenation, and gave similar yields of the nitrile in 69, 73, and 71%, respectively. The difference of the polymerization degree did not

remarkably change the product distribution of 1-nitropropane. Furthermore, the use of amino-substituted polymers having the diamino moiety (**Ia**) prepared from routes 1 and 2 gave similar yields of the nitrile of 70 vs. 75% under the conditions with an equivalent amino amount. We think that the structure of amino moieties on polymers is the crucial factor in the design of a suitable polystyrene support for the selective deoxygenation of 1-nitropropane to propionitrile.

Heterogeneous deoxygenations of nitropropane using Ia were carried out in the presence of various solvents. Since large amounts of water were required for the selective formation of the nitrile, the solvents used here had to be well miscible with organic compounds and water. These results are shown in Table 8. Alcohols having an ether function (e.g., 2-ethoxyethanol and 2-methoxyethanol) were good solvents. Although THF and dioxane have a high swelling ability for polystyrene supports,[16] the use of THF, dioxane, and a mixed solvent of 2-ethoxyethanol–THF did not lead to high yields of propionitrile in a polymer system. It seems that the swelling ability of solvents might not play an important role in the selective formation of the nitrile in the present aqueous systems.

Recycling of the polymer-bound Rh cluster catalyst was examined in the deoxygenation of 1-nitropropane. After deoxygenation, a dark-green polymer was filtered, and was then reused for deoxygenation under the same conditions as in a former reaction. The results are shown in Table 9. Reused Rh com-

Table 8.   Solvent Effect of Deoxygenation of 1-Nitropropane Using Polymer-Bound Rh Complex[a]

Solvent	Products yield/%			
	C_2H_5CN	C_3H_7OH	3-Hexanone	$(C_3H_7)_3N$
2-Ethoxyethanol	72	19	0	3
2-Ethoxyethanol[b]	53	9	0	5
2-Methoxyethanol	67	17	1	4
Ethylene glycol	56	25	4	3
THF/2-ethoxyethanol	56	28	1	3
Methanol	52	19	0	3
THF	27	29	1	0

a) Nitrobenzene 5 mmol, $Rh_6(CO)_{16}$ 0.05 mmol, H_2O 2.88 ml, polymer (Ia, 0.8 mg-atom of N), P_{co}=16 atm, 40 °C, 48 h.   b) H_2O 1.44 ml.

Table 9.   Recycling of Polystyrene-Bound Rh Cluster Complex in Deoxygenation of 1-Nitropropane[a]

Reused number	Products yield/%			
	C_2H_5CN	C_3H_7OH	3-Hexanone	$(C_3H_7)_3N$
Fresh	72	19	0	3
1	57	20	6	2
2	53	14	9	2
3	54	28	9	1

a) Initial conditions were the same as in Table 8. In the recycling study, the polymer-bound Rh catalyst filtered under an atmosphere were used and other conditions were the same as in the fresh reaction.

plexes kept their catalytic activity to give propionitrile as the main product as well as a small amount of new 3-hexanone.[17] In separated experiments, the reaction of 1-nitropropane was interrupted after 5h. A colorless filtrate was separated from the resulting heterogeneous mixture under a CO atmosphere, which did not further show any catalytic activity for deoxygenation under the same conditions as in the above 1-nitropropane reaction. It can be said that deoxygenation proceeds on polymer-bound Rh complexes.

The deoxygenation of organic compounds with various N–O bonds in the presence of the diamino-substituted polymer (Ia) was carried out. The results for aromatic nitro compounds, aliphatic nitro compounds, and oximes appear together with the corresponding homogeneous compounds in Tables 3 and 4, respectively. The reactions of hydroxylamines and amine oxides are summarized in Table 6. In the deoxygenations of ortho-substituted nitrobenzenes, polymeric Rh catalyst systems showed extremely low catalytic activities (Table 3) since the approach of the substrates to active metal centers is strongly influenced by the steric hindrance of polymer surfaces. The heterogenization of soluble metal catalysts using organic polymers which leads to a decreasing of their catalytic activities has been reported in many polymer-bound metal catalysts.[18]

Reaction Mechanisms for Deoxygenations. Many of the reactions of aromatic nitro compounds using CO have been studied in the presence of various

transition metal carbonyl complexes, e.g., $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Rh_6(CO)_{16}$.[2] The reaction products from nitrobenzenes were anilines, isocyanides, carbamates, and ureas. All of the above-mentioned metal-catalyzed reactions proceed via nitrene species as a common intermediate derived from the deoxygenation of nitrobenzene with CO. The characterization of various isolated metal nitrene complexes and their reactivities have been actively examined.[19] The μ_3-coordination mode in nitrene complexes is the most common in low-valent organometallics and the phenylnitrene bound to metal clusters reacts with CO and hydrogen to give phenyl isocyanate and aniline, respectively. In our combined catalyst system of $Rh_6(CO)_{16}$ and diamines, aniline would be formed via the nitrene intermediate, as shown in Scheme 3: a phenylnitrene bound to Rh carbonyl clusters reacts with hydrogens generated from the water gas shift reaction to give aniline or reacts with CO to give phenyl isocyanate, followed by hydrolysis to aniline.

In the case of our Rh catalysts, primary aliphatic nitro compounds did not give amines but, rather, nitriles as the main product. As mentioned in a previous section, the deoxygenation of aliphatic nitro compounds affords oximes, which further react with CO to give nitriles with formations of H_2 and CO_2. One can image that the deoxygenation of oximes to nitriles is operated by a similar mechanism proposed for WGSR (Scheme 4);[20] a nucleophilic oxygen of oximes or H_2O attacks a carbonyl moiety on Rh clusters to form a metallocarboxyimine or metallocarboxylic acid intermediate, and their decarboxylation gives either nitrile and/or H_2, respectively. Since the reaction of an aldehyde O-methyloxime did not occur, oximes would be deprotonated by an amino moiety of additive bases to increase their nucleophilicity in the deoxygenation. The bonding mode of carbonyl moieties on Rh carbonyl clusters can be classified mainly into three types: terminal, edge-bridge, and face-bridge. A nucleophilic attack of oximes or H_2O might favor the terminal CO moiety because of the relatively weak back bonding of Rh metal to the
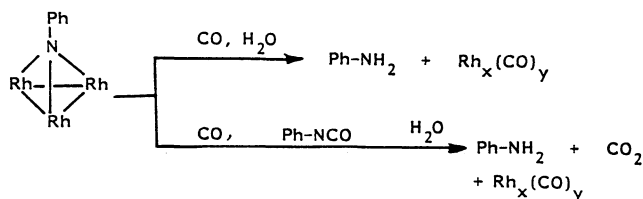
Scheme. 3. Formation of aniline via a nitrene intermeidate.
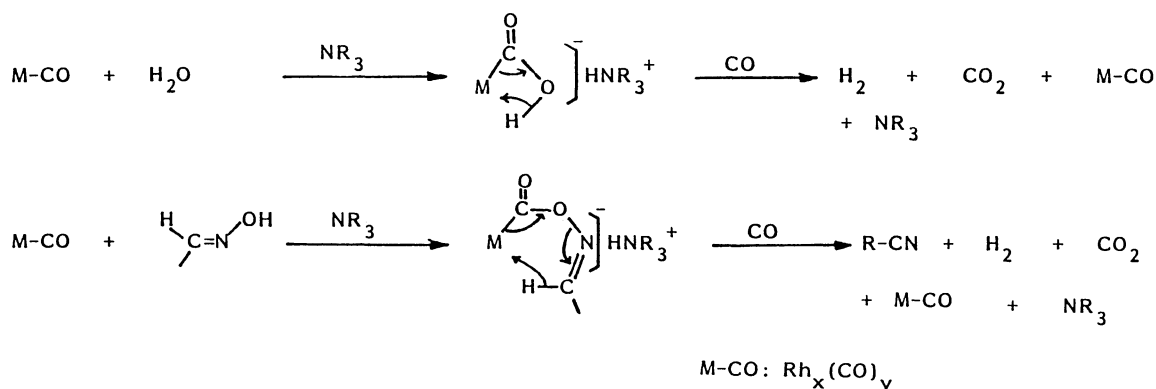
Scheme. 4. Mechanisms for the water gas shift reaction and deoxygenation of oximes.

$$\text{C=N}^{OH} \rightleftharpoons \text{C=N}^{O}_{H} \qquad (8)$$

$$R_2N\text{-OH} \rightleftharpoons R_2NH\text{>}O \qquad (9)$$
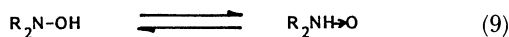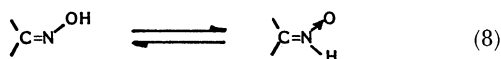
terminal CO.[21]

Next, the amine oxide forms can be thought as being the corresponding tautomers of oximes and hydroxylamines according to Eqs. 8 and 9, respectively. Recently, Basolo and co-workers have studied the mechanism for a stoichiometric deoxygenation of tertiary alkylamine N-oxides with $M_3(CO)_{12}$ (M= Fe,Ru,Os);[13] a nucleophilic oxygen of amine oxides attacks a carbonyl moiety on the metal clusters to give the corresponding amines and CO_2. Therefore, the amine oxide intermediates might also participate in the present deoxygenation of nitro compounds, oximes, and hydroxylamine using the present Rh cluster catalysts.

In the homogeneous deoxygenation of N–O bonds, e.g., aliphatic nitro compounds, oximes, hydroxylamines, and amine oxides at 40 °C, the reaction solutions had a dark-green color which changed instantly to dark brown upon exposure to air. In polymer systems (Ia), polymer-bound Rh complexes isolated from reaction mixtures were stable as dark-green powders in air for several hours.[22] The IR spectrum of the dark green powder showed the formation of $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_6(CO)_{15}H]^-$ on the polymer.[23] Treatment of the Rh_6 species with aqueous KOH at room temperature gave the $[Rh_7(CO)_{16}]^{3-}$ anion. In Rh cluster chemistry, increasing the reaction temperatures tends to increase the cluster nuclearity.[24] Probably, the Rh_{14} species might be derived from a dimerization of the Rh_7 species during the nitrobenzene reaction.

Under WGSR conditions, hydridorhodium anions can be thought as being one of the important intermediates species which binds to ammonium ions to form an ion-pair complex (II) equilibrated with a dihydrido complex (III) , as shown in Eq. 10.[25] Additive bases having a strong coordinating ability, e.g. ethylenediamine, easily coordinate to Rh clusters to promote H_2 generation,[26] while additives with methyl groups on nitrogen atoms, e.g., TMPDA, can not greatly activate an intermediate species III, because of their weak coordination. Therefore, nitro compounds, oximes,
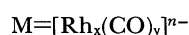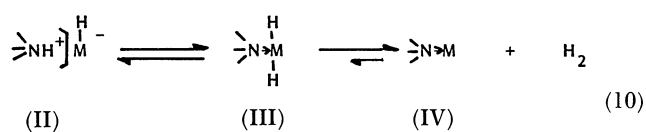
hydroxylamimes, and amine oxides can react with the carbonyl moiety on both species of II and/or III to give deoxygenated products. Presumably, a nucleophilic oxygen attack of N–O bonds might favor the species of III over the II because the carbon atom of the CO moieties within the III species are more cationic than that of II. In the course of the deoxygenation of nitrobenzene using TMPDA or 4-(dimethylamino)-pyridine at 80 °C under 700 mmHg of CO, H_2 could not be detected and WGSR did not occur without adding nitrobenzene. Furthermore, using the catalyst system of $Rh_6(CO)_{16}$ and 4-(dimethylamino)-pyridine, only 6% nitrobenzene was reduced at 80 °C during 4 h under 700 mmHg of H_2. It can be said that deoxygenation occurs mainly not with molecular hydrogen, but with $CO+H_2O$ acting as the reducing agent.[27]

Conclusions

The catalyst system of $Rh_6(CO)_{16}$ N,N,N',N'-tetramethy-1,3-propanediamine shows high activity for the deoxygenation of various N–O bonds, e.g., nitro compounds, oximes, hydroxylamines, and amine oxides in the presence of H_2O and CO. Notably, a formal dehydration of oximes to nitriles occurred selectively, even in aqueous media. The unique deoxygenation is due to the strong deoxygenating ability of the CO moiety within the Rh clusters. The Rh catalyst system can be heterogenized by using amino-substituted polystyrenes. The functions of the amines on the polymer are summarized as follows: 1) generation of OH^- in aqueous media to yield Rh-cluster anions, 2) stabilization and heterogenization of the Rh-cluster anions by forming ion-pairs, and 3) control for the reaction course through coordination of amines to Rh clusters. On the basis of the present study, we are now developing a new methodology of organic synthesis in aqueous media.

Experimental

$RhCl_3 \cdot 3H_2O$, $Fe(CO)_5$, $Mo(CO)_5$, $W(CO)_6$ were commercially available. $RhCl(PPh_3)_3$,[28] $Rh_2(CO)_4Cl_2$,[29] $Rh_4(CO)_{12}$,[30] $Rh_6(CO)_{16}$,[31] and $Ru_3(CO)_{12}$[32] were prepared by methods described in the literature. 3-Phenyl-1-nitropropane,[33] tripropylamine N-oxide,[34] N,N-dimethylaniline N-oxide,[35] all oximes,[36] propionaldehyde O-methyloxime,[37] and N-cyclohexylidenecyclohexylamine[38] were prepared according to published procedures. Other nitro compounds, hydroxylamines, and amine oxides were commercially available. All amines and pyridines used were also commercially available. Chloromethylated polystyrenes with M_w=7600, 8600, and 52700 were available from Toso Chemical Co. Elemental analyses were performed by Yanagimoto CHN-CORDER MT-III. The ^1H NMR spectra were recorded at 100 MHz with a Nihondenshi-JEO-JNM 4H-100 spectrometer. Infrared spectra were obtained with a Hitachi EPI-G spectrometer. Analytical GLPC was performed with a Shimadzu GC-3BT or a Shimadzu GC-8A

$$\geq NH^+ \overset{H}{\underset{M}{|}} {}^- \rightleftharpoons \geq N \text{>} \underset{H}{\overset{H}{M}} \rightleftharpoons \geq N\text{>}M + H_2 \qquad (10)$$

(II)   (III)   (IV)

$$M=[Rh_x(CO)_y]^{n-}$$

with a flame ionization detector,a linear temperature programe, and a Shimadzu CHROMATOPAC CR-3A integrator. The columns used were ASC-H, Apiezon L, and OV-17 for the analysis of liquid products.

Preparation of Amino-Substituted Polystyrenes. Typical examples for the title preparation are shown below. For route 1: bulk polymerization of p-(chloromethyl)styrene and divinylbenzenes (98/2, v/v) was carried out at 100 °C using AIBN, followed by amination with N,N-dimethyl-1,3-propanediamine in dioxane at room temperature. The MeOH treatment gave an amino-substituted polymer with N 8.7%. Chloromethylated polystyrenes (Toso) were aminated with N,N-dimethyl-1,3-propanediamine in dioxane at room temperature, which is a simiar method to that of Lieto:[39] N, 7.1% for M_w=7700; N, 9.0% for M_w=8600; N, 7.0% for M_w=52700. For route 2: reaction of p-(chloromethyl)styrene (Seimi Chemical) with N,N-dimethyl-1,3-propanediamine gave N,N-dimethyl-N'-(4-vinylphenylmethyl)-1,3-propanediamine which was identified by elemental analysis, IR, and NMR. ^{1}H NMR (CDCl${}_3$) δ=1.5—1.9 (2H, m, CH${}_2$), 2.16 (1H, s, NH), 2.20 (6H, s, N(CH${}_3$)${}_2$), 2.34 (2H, t, J=6.5 Hz, NCH${}_2$), 2.68 (2H, t, J=6.5 Hz, NCH${}_2$), 3.77 (2H, s, Ph-CH${}_2$) 5.1—5.9 (2H, m, =CH${}_2$), 6.4—7.0 (1H, m, HC=), and 7.3 (4H, s, phenyl). Bulk copolymerization of the amino-substituted styrene and divinylbenzene (98/2, v/v) was carried out at 100 °C using AIBN. After a MeOH treatment, the obtained polymer showed 11.4% of N. The above-mentioned procedures are described in the literature.[40,41] Polymers having other amino moieties (**Ib—Id**) were prepared only by the method of route 1. **Ib**; N, 7.4%, **Ic**; N, 6.6%, **Id**; N, 5.3%.

General Procedure of the Water Gas Shift Reaction. The reaction vessel was a 25 ml flask with a sidearm sealed with silicone rubber. It was attached to a closed reaction system (510 ml) with a reflux condenser, a gas circulator, and a vent. The Rh compound was placed in the vessel. The reaction system was evacuated and flushed three times with CO and then charged at room temperature to an initial CO pressure of 700 mmHg. Amine, H${}_2$O, and 2-ethoxyethanol were added to the vessel. The solution was heated with stirring to 100 °C. The gas above the dark-brown solution was periodically sampled and analyzed by gas chromatography (3 m column of activated carbon).

General Procedure of Deoxygenation of Nitrobenzene under 700 mmHg of CO. The reaction apparatus was similar to that in the case of previous WGSR.[5] The Rh compound was placed in the vessel; the reaction system was then evacuated and flushed thee times with CO and charged at room temperature to an initial CO pressure of 700 mmHg. Nitrobenzene, 2-ethoxyethanol, amine, and H${}_2$O were successively added to the vessel. The solution was heated with stirring to 80 °C. Both the gas and liquid phases were sampled periodically and analyzed by gas chromatography. The results are shown in Tables 1 and 2.

General Procedure of Homogeneous Deoxygenation of Nitro Compounds, Oximes, Hydorxylamines, and Amine Oxides under CO Pressure. A stainless-steel autoclave containing a Rh complex and an amine additive was evacuated and flushed three times with CO. A substrate, H${}_2$O, and a solvent were added. The reaction was carried out with stirring under apropriate conditions (4—16 atm of CO). After the reaction, the liquid phase was analyzed by GLPC. The results are summarized in Tables 3, 4, 6, and 7.

General Procedure for the Heterogeneous Deoxygenation of Nitro Compounds, Oximes, Hydroxylamines, and Amine Oxides under CO Pressure. A method similar to the above-mentioned homogeneous reactions was used for the title heterogeneous reactions. Amino-substituted polymers (**I**) were used in place of the soluble amines. After the reaction, a polymeric Rh complex was separated by filtration. The filtrate was analyzed by GLPC and then distillated to give pure products. The Results are summarized in Tables 3, 4, 6, 7, 8, and 9. A typical isolation procedure was used for 3-phenyl-1-nitropropane. A mixture of 3-phenyl-1-nitropropane (1.65 g 10 mmol), Rh${}_6$(CO)${}_{16}$ (0.107 g, 0.10 mmol), and an amino-substituted polymer (1.6 mg-atm of N, 0.32g) in H${}_2$O (5.76 g) and 2-ethoxyethanol (4 ml) was stirred at 40 °C under 16 atm of CO for 48 h. After the polymer-bound Rh complex was removed by filtration, the filtrate was extracted with diethyl ether. The ether layer was washed with an aqueous NaCl solution and then dried. Kugelrohr distillation afforded 0.97 g of pure nitrile (74%).

IR Measurement of Polymer-Bound Rh Complexes. After deoxygenations, polymer-bound Rh complexes were filtered and washed with 2-ethoxyethanol. The Rh complexes in KBr were measured by IR spectroscopy. All of the above-mentioned procedure were carried out under a CO atmosphere. In the deoxygenation of nitrobenzene at 80 °C under 4 atm of CO, isolated dark-brown powders showed the formation of the [Rh${}_{14}$(CO)${}_{25}$]${}^{4-}$ species on the amino-substituted polymer (**Ia**). IR ν_{co} 1969, 1814 cm^{-1} for [Rh${}_{14}$(CO)${}_{25}$]${}^{4-}$.[42] In the deoxygenations of the aliphatic nitro compounds, oximes, hydroxylamines, and amine oxides at 40 °C under 8—16 atm of CO, dark-green polymer showed formations of [Rh${}_6$(CO)${}_{15}$]${}^{2-}$ and [Rh${}_6$(CO)${}_{15}$H]${}^-$ species. IR ν_{co} 1989, 1960, 1765 cm^{-1} for [Rh${}_6$(CO)${}_{15}$]${}^{2-}$;[43] 2063, 2019 cm^{-1} for [Rh${}_6$(CO)${}_{15}$H]${}^-$.[42] A treatment of the Rh${}_6$ species with KOH and HCl under a nitrogen atmosphere gave the [Rh${}_7$(CO)${}_{16}$]${}^{3-}$ and Rh${}_6$(CO)${}_{16}$ species, respectively. IR ν_{co} 1951, 1763 cm^{-1} for [Rh${}_7$(CO)${}_{16}$]${}^{3-}$.[43] The above-mentioned values due to the CO stretching frequencies were compatible with the corresponding homogeneous Rh cluster complexes.[42,43]

Reduction of N-Cyclohexylidenecyclohexylamine Using Rh${}_6$(CO)${}_{16}$ in the Presence of CO and H${}_2$O. A stainless-steel autoclave of 300 ml containing Rh${}_6$(CO)${}_{16}$ (0.05 mmol) and N,N,N',N'-tetramethyl-1,3-propanediamine (2 ml) was evacuated and flushed three times with CO. The titile Schiff base (5 mmol), H${}_2$O (2.8 g), and 2-ethoxyethanol (2 ml) were then added. The reaction was carried out with stirring under 8 atm of CO at 40 °C. After 5 h, the liquid phase was analyzed to give 83% of dicyclohexylamine by GLPC.

N-Alkylation of Amines with Ketones Using Rh${}_6$(CO)${}_{16}$ in the Presence of CO and H${}_2$O. The reaction of cyclohexylamine with cyclohexanone is typical. A stainless-steel autoclave (300 ml) containing a Rh complex (53 mg, 0.05 mmol) was evacuated and flushed three times with CO. Cyclohexylamine (0.496 g, 5 mmol), cyclohexanone (0.491 g, 5 mmol), H${}_2$O (1.40 g), and 2-ethoxyethanol (2 ml) were then added. The reaction was carried out with stirring at 80 °C under 8 atm of CO. After 5 h, the resulting mixture was subjected to chromatography with Silica gel (Wakogel 200). Dicyclohexylamine of 0.72 g (80%) was isolated from hexane-dichloromethane elution. The results are shown in Table 5.

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