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Aminated Polystyrene-Bound Rhodium Carbonyl Clusters as a Catalyst for Deoxygenation of Various N-O Bonds

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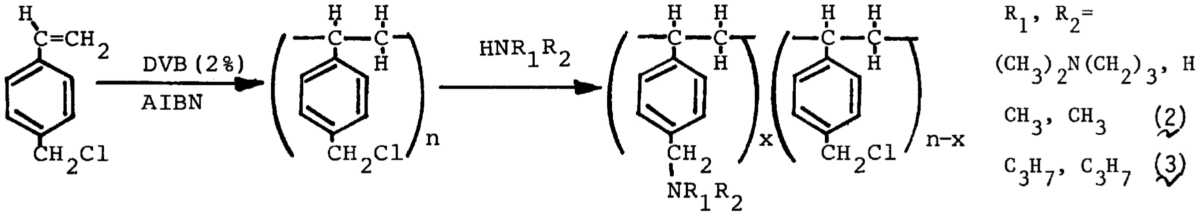
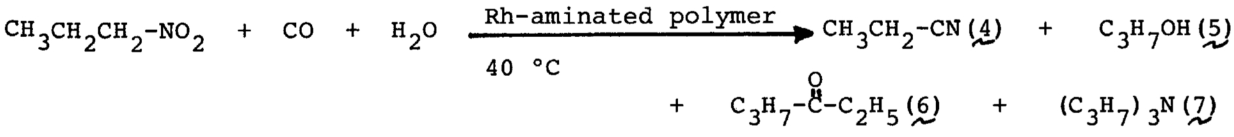
Aminated polystyrene-bound rhodium carbonyl cluster complexes are prepared by treatment of $Rh_6(CO)_{16}$ with various aminated polystyrenes. The polymeric rhodium complexes show a catalytic activity for deoxygenation of nitro compounds, oximes, hydroxylamines, and N-oxides under the conditions using CO and H_2O. The recovered rhodium complexes maintain the deoxygenation ability with a small loss of the selectivity.

Recently we have studied application of the water gas shift reaction to organic synthesis. Rh carbonyl clusters catalyze the reduction of carbonyl compounds,[1)] carbonylation of olefins,[2)] and deoxygenation of N-O bonds.[3)] In these reactions, amines and pyridines are essential additives for attaining high yield of products. These additive bases play an important role in the following steps; 1) attack of OH^- on coordinated CO to form Rh-carbonyl cluster anions as active species, 2) stabilization of the cluster anions with counter-cation of ammonium and pyridinium, and 3) controlling reaction course through coordination of the base to Rh clusters. In order to easily separate products from the reaction mixture and to reuse the Rh catalysts, we tried to heterogenize the Rh carbonyl clusters using aminated polystyrenes. Aminated polystyrene-bound Rh complexes showed catalytic activity for above organic reactions. In this paper, we wish to report the deoxygenation of various N-O bonds catalyzed by the aminated polystyrene-bound Rh complexes. To our knowledge, there are few examples concerning preparation of polymer-bound metal cluster complexes with forming ionic pair.[4)]

Aminated polystyrenes were synthesized by polymerization of *p*-chloromethylstyrene, followed by amination using various amines. *p*-Chloromethylstyrene was provided by Seimi Co., LTD. The degree of amination was calculated by elemental analysis. The amination degree in the range of about 50 to 90% showed the similar effect on the following deoxygenations. Residual chloromethyl moieties after the amination were converted into methyl group during the following deoxygenation. In a separate experiment, we found that the polymeric Rh complexes reduced benzyl chloride to toluene under the conditions using CO and H_2O.



The reaction of nitropropane with CO and H_2O was carried out in the presence of $Rh_6(CO)_{16}$ and various aminated polymers. Typical results for the deoxygenation of nitropropane together with those of homogeneous Rh systems are summarized in Table 1. Propionitrile (4) is a major product accompanied by propanol (5), 3-hexanone (6), and tripropylamine (7). 3-(N,N-Dimethylamino)propylamino polymer (1) is



$$CH_3CH_2CH_2\text{-}NO_2 + CO + H_2O \xrightarrow[40\ ^\circ C]{\text{Rh-aminated polymer}} CH_3CH_2\text{-}CN\,(4) + C_3H_7OH\,(5) + C_3H_7\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_2H_5\,(6) + (C_3H_7)_3N\,(7)$$

an excellent additive, compared with dialkylamino polymers (2 and 3). Such effect of various amines is also observed in the homogeneous $Rh_6(CO)_{16}$-amine systems.[3b] The homogeneous systems need higher concentration of the amines to attain high yield of the nitrile (4) than the polymeric Rh systems, which might be due to concentration effect of amine moieties on the polymer. It can be said that the present heterogenization of amines does not lose the character of the corresponding soluble amines for the deoxygenation.

Polymeric Rh complexes could be easily separated from the reaction mixture. The filtrate was colorless and IR analysis of the condensed filtrate gave no spectra characteristic to Rh carbonyl complexes. The isolated polymeric Rh complexes showed dark green color and their IR spectra indicate formation of Rh carbonyl cluster anions of $[Rh_6(CO)_{15}H]^-$ and $[Rh_6(CO)_{15}]^{2-}$.[5] The pathway to two Rh_6 carbonyl anions can be thought as follows. The reaction of $Rh_6(CO)_{16}$ with OH^-

Table 1. Reaction of Nitropropane Using CO and H_2O in the Presence of $Rh_6(CO)_{16}$-Amine Systems[a)]

Amine additive	Products Yield/% Propionitrile (4)	Propanol (5)	3-Hexanone (6)	Tripropylamine (7)
$(CH_3)_2N(CH_2)_3$-NH-CH_2-Ⓟ (1)	72	19	0	4
1[b)]	57	20	6	2
1[c)]	54	28	9	1
$(CH_3)_2N$-CH_2-Ⓟ (2)	55	32	0	3
$(C_3H_7)_2N$-CH_2-Ⓟ (3)	31	7	18	4
$(CH_3)_2N(CH_2)_3N(CH_3)_2$	47(71)[d)]	14(19)	5(0)	8(3)
$(CH_3)_3N$	40(55)	16(19)	7(0)	8(7)
$(C_3H_7)_3N$	28(43)	14(14)	5(5)	-

a) Nitropropane, 5 mmol; $Rh_6(CO)_{16}$, 0.05 mmol; amine, 0.8 mg-atom; H_2O, 0.16 mol; ethoxyethanol 2ml; 16 atm of CO; 48 h; 24 h for soluble amines; Ⓟ: polystyrene support. b) First recycle. c) Third recycle. d) Parentheses denote 5 mg-atom of N_2.

forms $[Rh_6(CO)_{15}H]^-$ species with generation of CO_2, while $[Rh_6(CO)_{15}]^{2-}$ species is obtained from OH^- attack on the $[Rh_6(CO)_{15}H]^-$ and/or from dimerization of the $[Rh_6(CO)_{15}H]^-$ to give $[Rh_{12}(CO)_{30}]^{2-}$ species, followed by OH^- attack. Ammonium cations on bulky polymeric support can stabilize the Rh_6 clusters. Recovered Rh complexes had the catalytic activity, but gave rise to lowering the selectivity for the nitrile formation.

The polymeric Rh complexes catalyzed not only the nitrile synthesis from various nitro compounds, but also other deoxygenation of oximes, hydroxylamines, and N-oxides. The reaction of propionaldoxime gave propionitrile in 62% accompanied by formation of H_2 and CO_2.[6)] Hydroxylamines were deoxygenated to give the corresponding amines. In gas phase, CO_2 could be detected without formation of H_2. Hydroxylamines were recovered almost quantitatively under a

$$(C_2H_5)_2N\text{-}OH \quad + \quad CO \quad \xrightarrow[\substack{H_2O\text{-}C_2H_5OC_2H_4OH \\ 40\ °C,\ 5\ h}]{\text{Rh-aminated polymer (1)}} \quad \underset{(89\%)}{(C_2H_5)_2NH} \quad + \quad CO_2$$

nitrogen atmosphere. In the case of N-oxides, propylamine-N-oxide gave 84% of propylamine, while pyridine-N-oxide was not deoxygenated under the present reaction conditions. It should be noted that the CO ligand bound to Rh clusters has high ability for deoxygenation of various N-O bonds.

A typical experiment of the deoxygenation is for 3-phenylnitropropane. A stainless autoclave containing $Rh_6(CO)_{16}$(106 mg, 0.10 mmol) and the amino polymer (1, 0.32 g, 1.60 mg-atom of N) was evacuated and flushed three times with CO. 3-Phenylnitropropane(1.8 g, 10 mmol), H_2O(5.76 g, 0.32 mol) and ethoxyethanol (4 ml) was added. The reaction was carried out under 16 atm of CO at 40 °C. After 48 h, polymeric Rh complex was separated by filtration and the filtrate was analyzed by GLPC to give 85% yield of 3-phenylpropionitrile. Kugelrohr distillation afforded 0.97 g of the pure nitrile.

In conclusion, the amine additives act as an activating agent for Rh clusters and this heterogenization of the soluble amines does not lose their essential functions for the deoxygenation. Using the polymeric ligands, isolation of products is much more facile than that with soluble amines.

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