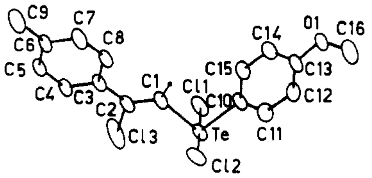
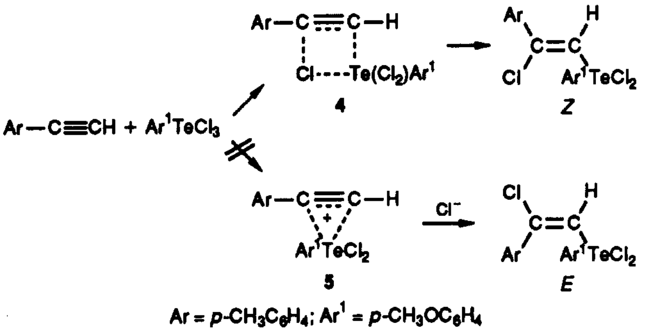


Figure 1. ORTEP drawing of **2b**.

Scheme I



by the inductive effect of the chlorine atoms linked to tellurium. When the chlorine atoms are removed, the C–Te bond polarization is reversed in view of the lower electronegativity of tellurium compared with that of carbon.[14] In this way the carbon atom is negatively polarized and the signal due to this carbon is shifted to higher field. The regiochemistry observed was confirmed by the presence of satellite bands to the signal at δ 125.44 in the ^{13}C NMR spectrum of **2b**. These satellite bands are due to the ^{125}Te–^{13}C coupling. In addition, in the cases where the olefin region of the ^{1}H NMR spectra of the tellurium dichlorides **2** and tellurides **3** was not crowded, it was possible to observe satellite bands due to ^{125}Te–^{1}H coupling. X-ray analysis of **2b**[15] confirmed this regiochemistry and also showed that the stereochemistry of this compound is *Z* (Figure 1). This latter fact is consistent with the four-membered cyclic transition state **4** and not with the telluronium ion intermediate **5**, which should lead to the *E* isomer (Scheme I). It must be pointed out that the reaction of tellurium tetrachloride with acetylenes and olefins[16] also leads to syn addition products, whereas the addition of aryltellurium trichlorides to olefins gives anti addition products.[16]

The results reported in this communication show that the addition of organyltellurium trichlorides to terminal acetylenes is an efficient method of synthesis of trisubstituted vinylic tellurides.

Acknowledgments. We thank the following agencies for support: FINEP, CNPq, FAPESP, and PADCT. We are grateful to Prof. V. Luchini for valuable suggestions.

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(14) Laitem, L.; Christiaens, L.; Renson, M. *Org. Magn. Reson.* **1980**, *13*, 319.

(15) Zuckerman-Schpector, J.; Comasseto, J. V.; Stefani, H. A. *Acta Crystallogr., Sect. C*, in press.

(16) Backvall, J. E.; Bergman, J.; Engman, L. *J. Org. Chem.* **1983**, *48*, 3918.

Articles

Selective Generation of Various Rhodium Carbonyl Cluster Anions in Aminated Polymers and Their Catalysts for the Water-Gas Shift Reaction and Deoxygenation of Various N–O Bonds

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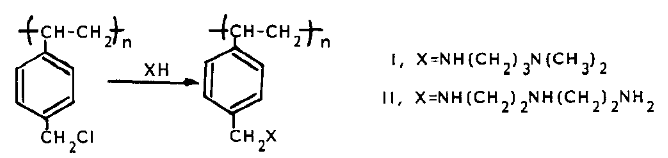
Aminated polystyrenes were prepared by amination of chloromethylated polystyrenes. Several Rh carbonyl cluster anions could be selectively generated in the aminated polymer with use of $Rh_6(CO)_{16}$. The reaction of $Rh_6(CO)_{16}$ with the aminated polystyrenes at 40 °C under 6 atm of CO gave a dark green polymer involving $[Rh_6(CO)_{15}H]^-$ and $[Rh_6(CO)_{15}]^{2-}$, while $[Rh_{14}(CO)_{25}]^{4-}$ was formed in the polymers at 100 °C. Treatment of the Rh_6 anion species with aqueous KOH solution gave a polymer-bound $[Rh_7(CO)_{16}]^{3-}$ complex. The Rh_6 anion species were catalytically active for the deoxygenation of N–O bonds, e.g., conversion of aliphatic nitro compounds to nitriles, *N*-oxides to amines, and hydroxylamines to amines. Rh_{14} species could be observed in the water-gas shift reaction. These isolated polymer-bound Rh carbonyl anion complexes were found to be reusable as catalysts for the above reactions.

Much attention has been paid to the metal cluster complexes because of their potential possibility as new catalysts and as the surface model compounds of metal catalysts.[1] We have studied the application of the

Scheme I. Preparation of Aminated Polystyrenes



water-gas shift reaction (WGSR) to functional group transformations utilizing Rh carbonyl cluster catalysts and have reported that the Rh clusters have extraordinary reducing ability for carbonyl and nitro functions.[2] However, the cluster frame consisting of metal–metal bonds is prone to decompose under the conditions of metal-catalyzed reactions. It is a challenging problem to prevent the decomposition of such metal–metal bonds in order to maintain high activity and high selectivity during the catalytic reactions. We tried to reinforce these weak metal–metal bonds by the use of bulky polymer ligands, where various Rh clusters could be generated as stable species in the polymer resins. In this paper, we wish to report the selective generation of various Rh carbonyl cluster anions on aminated polystyrenes and their use as catalysts in the WGSR.[3]

Results and Discussion

Aminated polystyrenes were prepared by amination of chloromethylated polystyrene (Scheme I). These polymers were initially 2% cross-linked with DVB and contained 21.4% Cl, which corresponds to 90% of the phenyl rings of the polymer substituted with chloromethyl groups.

The reaction of $Rh_6(CO)_{16}$ with aminated polystyrene I in H_2O and ethoxyethanol was carried out under 6 atm of CO at 40 °C. After 24 h, a dark green polymer was obtained by filtration under a CO atmosphere, along with a colorless filtrate. The reaction with $Rh_2(CO)_4Cl_2$ in place of $Rh_6(CO)_{16}$ gave the same result.

$$Rh_6(CO)_{16} \xrightarrow[40\ ^\circ C,\ 24\ h]{I,\ CO\ (6\ atm),\ H_2O} [Rh_6(CO)_{15}]^{2-} + [Rh_6(CO)_{15}H]^- \quad (1)$$

IR spectra of the dark green polymer complexes showed strong absorption bands at 2021, 1989, and 1780–1763 cm^{-1}. After scrutiny of absorption bands due to ν_{CO} of many Rh carbonyl compounds, the above spectra were assignable to a mixture of the two Rh carbonyl cluster anions $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_6(CO)_{15}H]^-$. Attack of OH^- at $Rh_6(CO)_{16}$ gives $[Rh_6(CO)_{15}H]^-$ via a Rh hydroxycarbonyl intermediate, which further reacts with OH^- to form $[Rh_6(CO)_{15}]^{2-}$.[4] Such Rh_6 cluster anions are bound as ammonium salts in the polymer support.[5] An equilibrium might exist between $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_6(CO)_{15}H]^-$ due to hydrogen abstraction from $[Rh_6(CO)_{15}H]^-$ by another amine moiety in the polymer to form an ion-pair complex of $Rh_6(CO)_{15}]^{2-}$.[6] A mixture of the two Rh_6 cluster species

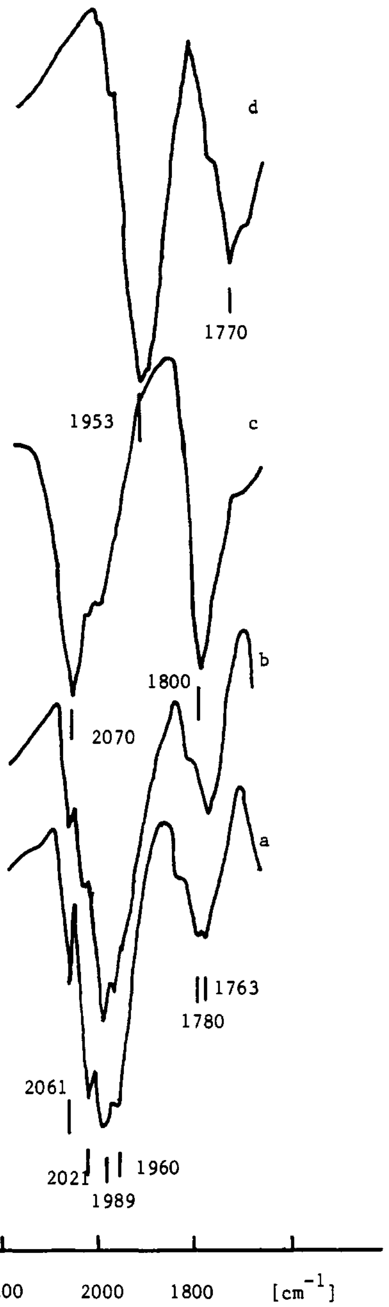


Figure 1. IR spectra of polymer-bound Rh complexes: (a) a dark green polymer of $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_6(CO)_{15}H]^-$ ($[Rh_6(CO)_{15}]^{2-}$ 1989, 1960, 1763 cm^{-1}; $[Rh_6(CO)_{15}H]^-$ 2061, 2021, 1780 cm^{-1}; (b) product of the exposure of the dark green polymer in a KBr disk to a CO atmosphere. $[Rh_6(CO)_{15}]^{2-}$; (c) product of the treatment of the dark green polymer with aqueous HCl solution, $Rh_6(CO)_{16}$; (d) product of the treatment of the dark green polymer with aqueous KOH solution, $[Rh_7(CO)_{16}]^{3-}$ (1953, 1770 cm^{-1}).

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(1) For reviews, see: (a) Muetterties, E. L.; Rhodin, R. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91. (b) Pittmann, C. U., Jr. Polymer Supported Catalysts. In *Comprehensive Organometallic Chemistry*; Stone, F. G. A., Abel, E., Eds.; Pergamon Press: New York, 1982; Chapter 55. (c) Hartley, F. R. *Supported Metal Complexes*; Reidel: Dordrecht, The Netherlands, 1985.

(2) (a) Kaneda, K.; Yasumura, M.; Imanaka, T.; Teranishi, S. *J. Chem. Soc., Chem. Commun.* **1982**, 93. (b) Kaneda, K.; Hiraki, M.; Imanaka, T.; Teranishi, S. *J. Mol. Catal.* **1981**, *12*, 385. (c) Kaneda, K.; Mori, T.; Kobayashi, M.; Imanaka, T.; Teranishi, S. *Chem. Lett.* **1985**, 1339.

(3) Recently these have been two reports concerning the generation of metal carbonyl cluster anions on MgO supports. (a) For $[Rh_6(CO)_{15}]^{2-}$: Dufour, P.; Huang, L.; Choplin, A.; Sanchez-Delgado, S. G.; Theolier, A.; Basset, J. M. *J. Organomet. Chem.* **1988**, *354*, 243. (b) For $[Os_5C(CO)_{14}]^{4-}$ and $[Os_{10}C(CO)_{24}]^{2-}$: Lamb, H. H.,; Fung, A. S.; Tooley, P. A.; Puga, J.; Krause, T. R.; Kelley, M. J.; Gates, B. C. *J. Am. Chem. Soc.* **1989**, *111*, 8367.

(4) On formation of $[Rh_6(CO)_{15}]^{2-}$ on an MgO support, Basset et al., have proposed $[Rh_6(CO)_{15}H]^-$ species as an intermediate in ref 3a.

(5) For formation of such ion-pair polymer-bound metal cluster complexes; see: (a) Jurewicz, A. T.; Rollman, L. D.; Whitehurst, D. D. *Adv. Chem. Ser.* **1974**, *132*, 240. (b) Kitamura, T.; Joh, T.; Hagihara, N. *Chem. Lett.* **1975**, 203. (c) Ryan, R. C.; Wilemon, G. M.; Dal Santon, M. P.; Pittman, C. U. *J. Mol. Catal.* **1979**, *5* 319. (d) Effa, J. B. N.; Lieto, J.; Aune, J. P. *Inorg. Chim. Acta* **1982**, *65*, L105. (e) Marrakchi, H.; Effa, J. B. N.; Haimeur, M.; Lieto, J.; Aune, J. P. A. *J. Mol. Catal.* **1985**, *30*, 101. (f) Marrakchi, H.; Haimeur, M.; Escalant, P.; Lieto, J.; Aune, J. P. A. *Nouv. J. Chim.* **1986**, *10*, 1. (g) Bhaduri, S.; Sharma, K. R. *J. Chem. Soc., Dalton Trans.* **1984**, 2309.

(6) For Rh_{14} species, see: Vidal, J. L.; Schoening, R. C. *Inorg. Chem.* **1982**, *21*, 438.

Table I. Stretching Frequencies in the ν_{CO} Region of Rh Carbonyl Compounds

Rh compd	ν_{CO}, cm^{-1}	ref
$[Rh_6(CO)_{15}]^{2-}$/polymer[a]	2043 w, 1989 s, 1960 (sh), 1815 w (br), 1763 s	this work
$[Rh_6(CO)_{15}]^{2-}$	2048 w, 1990 s, 1960 s, 1815 w (br), 1760 s	7a
$[Rh_6(CO)_{15}H]^-$/polymer[a]	2061 m, 2021 s, *b*, 1780 s	this work
$[Rh_6(CO)_{15}H]^-$[c]	2060 m, 2020 s, 1995 w, 1783 s	*e*
$[Rh_7(CO)_{16}]^{3-}$/polymer[a]	2020 w (sh), 1998 w (sh), 1953 s, 1942 w (sh), 1810 w, 1770 s, 1740 w (br)	this work
$[Rh_7(CO)_{16}]^{3-}$	2020 w (sh), 1995 w (sh), 1955 w (sh), 1955 s, 1945 w (sh), 1810 w, 1770 s, 1738 w (br)	7a
$[Rh_{14}(CO)_{25}]^{4-}$/polymer[a]	1969 s, 1940 w (sh), 1814 s, 1780 w (sh)	this work
$[Rh_{14}(CO)_{25}]^{4-}$[c]	1964 s, 1932 w (sh), 1809 s, 1784 w (sh)	*e*
$[Rh_{14}(CO)_{25}]^{4-}$	1966 s, 1810 s	8
$[Rh_{14}(CO)_{25}H]^{3-}$/polymer[a]	1990 s, 1833 s	this work
$[Rh_{14}(CO)_{25}H]^{3-}$	1988 s, 1835 s	9
$[Rh_6(CO)_{15}(CONH)]$/polymer[a]	2069 w (sh), 2044 s, 2000 w, 1835 w (sh), 1777 s, 1747 w (sh)	this work
$[Rh_6(CO)_{15}(CONH^iPr)$[d]	2073 w, 2040 s, 2012 w (sh), 1837 w, 1777 s, 1746 w	*e*

[a] In Nujol. [b] A weak absorption near 1995 cm^{-1} might be overlapped by a strong band at 1990 cm^{-1} due to $[Rh_6(CO)_{15}]^{2-}$. [c] CH_3CN. [d] THF. [e] Personal communication from Dr. S. Martinengo.

in the polymer was treated with aqueous HCl solution under a CO atmosphere to produce $Rh_6(CO)_{16}$ in the polymer, while use of aqueous KOH solution gave $[Rh_7(CO)_{16}]^{3-}$. The observations with acidic and basic media similar to those for analogous homogeneous $[Rh_6(CO)_{15}]^{2-}$ systems have been reported by Martinengo and co-workers.[7]

$$Rh_6(CO)_{16} \xleftarrow{HCl(aq)} [Rh_6(CO)_{15}]^{2-} + [Rh_6(CO)_{15}H]^- \xrightarrow{KOH(aq)} [Rh_7(CO)_{16}]^{3-} \quad (2)$$

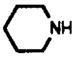
In the treatment of the Rh_6 polymer with a CO atmosphere, the equilibrium between two Rh_6 cluster anions bound to the polymer could be shifted to a mono species of $[Rh_6(CO)_{15}]^{2-}$ at room temperature. This behavior of the IR spectra of the polymer-bound Rh complexes is shown in Figure 1. Values of the above absorption bands due to ν_{CO} are summarized in Table I together with those of the corresponding homogeneous Rh carbonyl cluster anions.[7a,8,9] Under a CO atmosphere, the polymer-bound Rh_6 complexes were stable. The color of the polymer obtained gradually discharged to pale yellow on exposure to air. The pale yellow Rh complex showed high stretching frequencies due to the terminal CO moieties, compared with those of the original dark green polymer.[10]

The reaction of $Rh_6(CO)_{16}$ with aminated polystyrene II in a mixed solvent of H_2O and ethoxyethanol was carried out under 1 atm of CO at 100 °C. After 24 h, a brown polymer was obtained and its IR spectrum had strong absorption bands at 1969 and 1814 cm^{-1} in the CO stretching region, which shows the formation of $[Rh_{14}(CO)_{25}]^{4-}$ in the polymer. When a large amount of H_2O was used, new strong bands at 1990 and 1833 cm^{-1} assignable to $[Rh_{14}(CO)_{25}H]^{3-}$ appeared, with decreasing intensity of the 1969- and 1814-cm^{-1} bands. In the treatment of the polymer containing a mixture of $[Rh_{14}(CO)_{25}]^{4-}$ and $[Rh_{14}(CO)_{25}H]^{3-}$ with aqueous Na_2CO_3, the $[Rh_{14}(CO)_{25}H]^{3-}$ species was partly converted into the $[Rh_{14}(CO)_{25}]^{4-}$ species.[11] Vidal and Schoening have reported that reaction of $Rh(CO)_2(acac)$ with CO and H_2 under basic conditions gave $[Rh_{14}(CO)_{25}]^{4-}$ species directly.[8] We could also obtain the $[Rh_{14}(CO)_{25}]^{4-}$ complex from treatment of $Rh(CO)_2(acac)$ with the aminated polymer II under the same conditions as those for $Rh_6(CO)_{16}$.

$$Rh_6(CO)_{16} \text{ or } Rh(CO)_2(acac) \xrightarrow{II,\ CO\ (1\ atm),\ H_2O} [Rh_{14}(CO)_{25}]^{4-} + [Rh_{14}(CO)_{25}H]^- \quad (3)$$

The isolated polymer-bound $[Rh_{14}(CO)_{25}]^{4-}$ was treated with a mixed solvent of 2-ethoxyethanol and H_2O at 40 °C under 6 atm of CO to give the Rh_6 anion species. Interconversion among the Rh_6, Rh_7, and Rh_{14} species in the polymer resins is reversible with use of CO and H_2O. Treatment of $Rh_6(CO)_{16}$ with aminated polymer II under a nitrogen atmosphere at room temperature gave an Rh amide cluster complex, $[Rh_6(CO)_{15}CONH]$–Ⓟ.[7a] The Rh amide cluster polymer could be converted into $[Rh_{14}(CO)_{25}]^{4-}$ with use of 1 atm of CO and H_2O at 100 °C. In Rh cluster chemistry, increasing the reaction temperature tends to increase the cluster nuclearity.[12] It can be thought that $[Rh_{14}(CO)_{25}]^{4-}$ is derived from dimerization of the Rh_7 species in the above reaction. The WGSR occurred to generate hydrogen in the above reactions with use of polymer II at 100 °C.[13] We examined the time course of the hydrogen evolution, which is shown in Figure 2. There was an induction period for both evolution of hydrogen and formation of the Rh_{14} species. The above phenomenon suggests that the Rh_{14} compound and/or its closely related Rh species might be an active species for the WGSR.

Table II. Deoxygenation of Various N–O Bonds with Use of CO and H_2O in the Presence of $Rh_6(CO)_{16}$–Aminated Polystyrene Catalyst[a,b]

substrate	reaction time, h	products [yield, %]
$(C_2H_5)_2NOH$	5 (5)	$(C_2H_5)_2NH$ [89 (93)]
	5 (5)	 [75 (62)]
$(CH_3)_3CHNOH$	5 (5)	$(CH_3)_3CNH_2$ [96 (70)]
$(C_3H_7)_3N\rightarrow O$	24 (5)	$(C_3H_7)_3N$ [84 (91)]
Ph-N(→O)$(CH_3)_2$	24 (5)	$PhN(CH_3)_2$ [99 (75)]
$C_2H_5CH{=}NOH$[c]	48 (5)	C_2H_5CN [61 (61)], C_3H_7OH [20 (20)]
cyclohexyl-CH=NOH[c]	48 (5)	c-$C_6H_{11}CN$ [65 (77)], c-$C_6H_{11}CH_2OH$ [35 (12)]
$PhCH_2CH_2CH{=}NOH$[c]	48 (5)	$PhCH_2CH_2CN$ [83 (84)]
$C_3H_7NO_2$[c]	48 (24)	C_2H_5CN [72 (71, 44[d])], C_3H_7OH [19 (15, 20[d])]
$PhCH_2CH_2CH_2NO_2$[c]	48 (24)	$PhCH_2CH_2CN$ [85 (84)]

[a] Conditions: $Rh_6(CO)_{16}$, 0.05 mmol; aminated polymer I, 0.16 g (0.8 mmol of N); substrate, 5 mmol; 2-ethoxyethanol, 2 mL; H_2O, 2.08 mL; P_{CO} = 8 atm; 40 °C. [b] Values in parentheses are for the corresponding homogeneous $Rh_6(CO)_{16}$ system, and the same reaction conditions as for the heterogeneous system were used except for the addition of *N,N,N',N'*-tetramethyl-1,3-propanediamine (5 mmol). [c] P_{CO} = 16 atm. [d] The propanediamine (0.4 mmol).

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(7) (a) Chini, P.; Martinengo, S.; Giordano, G. *Gazz. Chim. Ital.* **1972**, *102*, 330. (b) Martinengo, S.; Chini, P. *Gazz. Chim. Ital.* **1972**, *102*, 344.

(8) Vidal, J. L.; Schoening, R. C. *Inorg. Chem.* **1981**, *20*, 265.

(9) Ciani, G.; Sironi, A.; Martinengo, S. *J. Organomet. Chem.* **1980**, *192*, C42.

(10) Collman et al., have reported that treatment of $Rh_6(CO)_{16}$ on phosphinated polystyrene with O_2 formed metallic Rh species without CO moieties: Collman, J. P.; Hegedus, L. S.; Cooke, M. P.; Norton, J. R.; Dolcetti, G.; Marquardt, D. N. *J. Am. Chem. Soc.* **1972**, *94*, 1789.

(11) Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37.

(12) Vidal, J. L.; Schoening, R. C. *J. Organomet. Chem.* **1983**, *241*, 395.

(13) The aminated polymer I was not an effective catalyst for the WGSR, and a similar substituent effect of amines was also observed in the corresponding homogeneous systems: Kaneda, K.; Hiraki, M.; Sano, K.; Imanaka, T.; Teranishi, T. *J. Mol. Catal.* **1980**, *9*, 227.

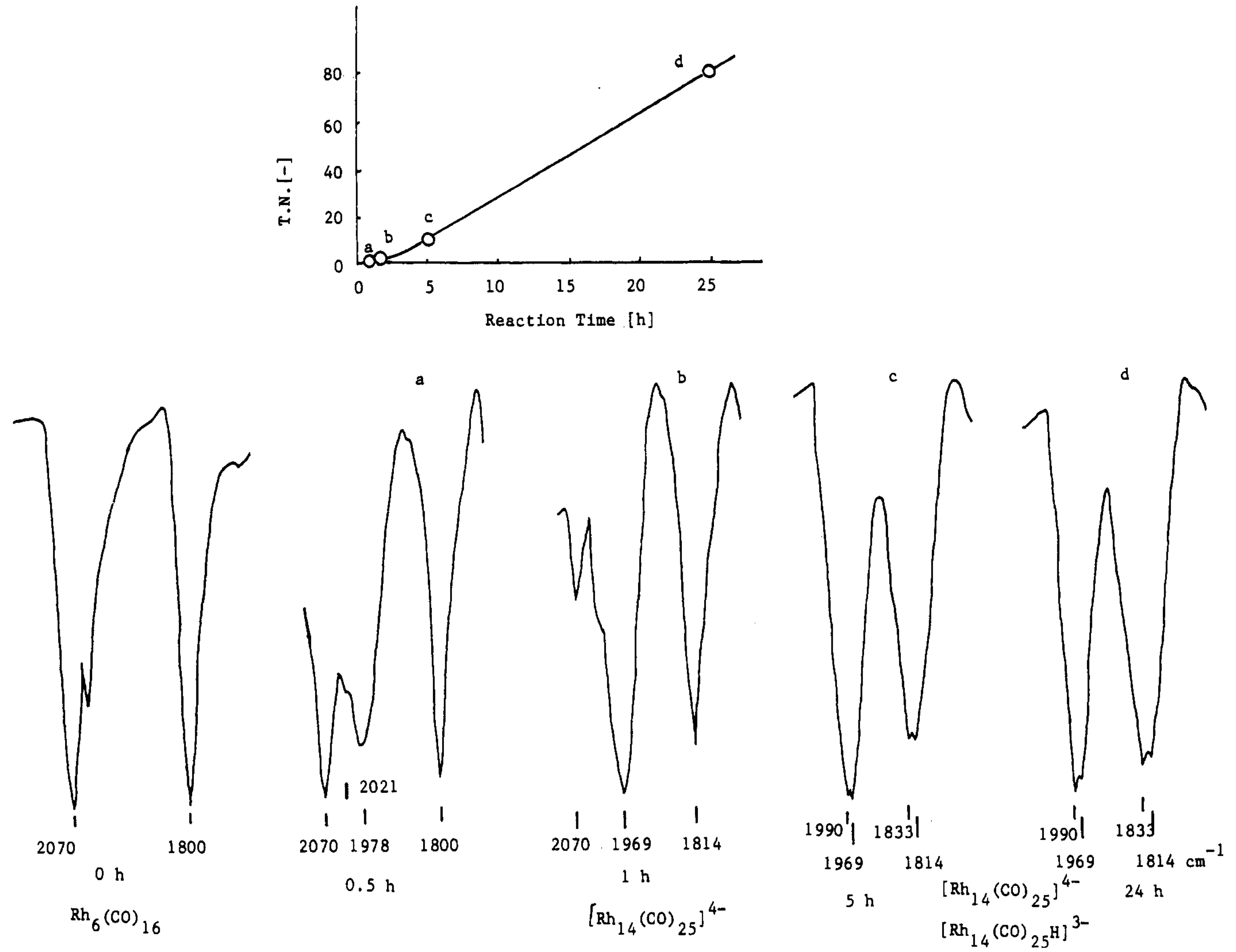

Figure 2. IR spectra of polymer-bound Rh cluster complexes and yield of H_2 (TN, equal to moles of H_2 per moles of $Rh_6(CO)_{16}$) in the course of the WGSR. Reaction conditions: $Rh_6(CO)_{16}$, 0.05 mmol; aminated polystyrene II, 5.0 mmol of N; P_{CO} 700 mmHg; H_2O, 2.16 mL; ethoxyethanol, 5.56 mL; 100 °C. Assignments: $[Rh_{14}(CO)_{25}]^{4-}$ 1969, 1814 cm^{-1}; $[Rh_{14}(CO)_{25}H]^{3-}$ 1990, 1833 cm^{-1}. An absorption band at 2021 cm^{-1} after 0.5 h might be due to the $[Rh_6(CO)_{15}H]^-$ species.

The polymer-bound Rh_6 complexes have demonstrated the deoxygenation of various N–O bonds at 40 °C under catalytic conditions in the conversion of (1) aliphatic nitro compounds to nitriles, (2) oximes to nitriles, (3) hydroxylamines to amines, and (4) *N*-oxides to amines. Typical examples of the above deoxygenations are shown in Table II together with analogous ones under homogeneous conditions.[14]

$$RCH_2NO_2 + 2CO \rightarrow RCN + 2CO_2 + H_2 \qquad (4)$$

$$RCH{=}NOH + CO \rightarrow RCN + CO_2 + H_2 \qquad (5)$$

$$R_2NOH + CO \rightarrow R_2NH + CO_2 \qquad (6)$$

$$R_3NO + CO \rightarrow R_3N + CO_2 \qquad (7)$$

The homogeneous Rh system showed higher reaction rates than heterogeneous ones but required higher concentrations of amine moieties to attain selective deoxygenations. This might be due to the occurrence of a high concentration of amine moieties in the polymer resins;[15] high concentrations of the amines increase the basicity of reaction media to facilitate the formation of Rh carbonyl cluster anions as active species and increase the stability of the Rh cluster anions through ammonium ions. Alkoxy alcohols such as ethoxyethanol are good solvents for the deoxygenations in both heterogeneous and homogeneous Rh catalyst systems. This facile deoxygenation of various N–O bonds is due to the strong deoxygenating ability of the CO moiety coordinated within the Rh clusters.[16] The deoxygenation process was interrupted, and the polymer solid was collected by filtration under the reaction conditions. Rh complexes could not be detected after evaporation of the filtrate to dryness. The IR spectrum of the dark green polymer showed formation of a mixture of two Rh_6 species, $[Rh_6(CO)_{15}H]^-$ and $[Rh_6(CO)_{15}]^{2-}$. In separate experiments, the recovered polymer and the filtrate were reused for the deoxygenation process under the same reaction conditions as for the above reaction, respectively. Only the recovered polymer had catalytic activity; deoxygenation of 3-phenylnitropropane gave an 82% yield of 3-phenylpropionitrile, which indicated activity like that of the fresh catalyst. Similar phenomena for the recovered catalysts were observed also in the WGSR.

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(14) For other reagents utilized in these transformations, see: March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; pp 930 and 1105.

(15) Whitehurst, D. D. *CHEMTECH* **1980**, 44.

(16) For examples of deoxygenation of these N–O bonds with use of homogeneous metal carbonyl clusters, see: (a) Alper, H.; Amaratunga, S. *Tetrahedron Lett.* **1980**, *21*, 2603. (b) Shen, J.-K.; Shi, Y.-L.; Gao, Y.-C.; Shi, Q.-Z.; Basolo, F. *J. Am. Chem. Soc.* **1988**, *110*, 2414. (c) Kaneda, K.; Doken, K.; Imanaka, T. *Chem. Lett.* **1988**, 285.

In conclusion, a suitable choice of reaction conditions, e.g., reaction temperature and H_2O and base concentrations, controls the size of several Rh carbonyl clusters in the aminated polymers. Use of the polymer ligands might be a promising route for increasing the robustness of metal frames, and such Rh clusters are active catalyst species for the WGSR and for the deoxygenation of various N–O bonds. Functions of amines in the polymer resins 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 of the reaction course through coordination of amines to Rh clusters.

Experimental Section

$Rh_2(CO)_4Cl_2$[17] and $Rh_6(CO)_{16}$[18] were prepared by literature methods. 3-Phenylnitropropane,[19] tripropylamine *N*-oxide,[20] dimethylaniline *N*-oxide,[21] and oximes[22] were prepared by published methods. Nitropropane and hydroxylamines were commercially available. All solvents and reagents were distilled as necessary. Elemental analyses were performed on a Yanagimoto MT-III CHN-CORDER. ^1H NMR spectra were recorded on 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 Shimazu GC-3BT or a Shimazu GC-8A instrument with a flame ionization detector, a linear temperature program, and a Shimazu CHROMATOPAC integrator. Columns were packed with ASC-H, Apiezon L, and OV-1 for analysis of liquid products.

Synthesis of Aminated Polystyrenes. Chloromethylated polymers were available from TOSO Chemical Co. A polymer having 2% of cross-linking degree and 21.4% of Cl was aminated with *N*,*N*-dimethyl-1,3-propanediamine in dioxane at room temperature, which is similar to the method of Lieto.[23] The aminated polymer I contained 8.7% of N and 8.7% of Cl. A polymer having $NHC_2H_4NHC_2H_4NH_2$ moieties (II) was also obtained by treatment of the chloromethylated polystyrene with $NH_2C_2H_4NHC_2H_4NH_2$ (15.0% N).

Preparation of Polymer-Bound $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_6(CO)_{15}H]^-$ Complexes. The reaction of $Rh_6(CO)_{16}$ (0.05 mmol) with aminated polystyrene (I, 0.8 mg-atom of N) in H_2O (2.88 mL) and ethoxyethanol (2 mL) was carried out under 6 atm of CO at 40 °C. After 24 h, a dark green polymer of $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_6(CO)_{15}H]^-$ was obtained by filtration and further washed with ethoxyethanol and ethyl ether successively under a CO atomosphere. The dark green polymer was treated with aqueous KOH (0.4 N) to give a green polymer of $[Rh_7(CO)_{16}]^{3-}$, while the reaction with aqueous HCl (1 N) gave a brown polymer of $Rh_6(CO)_{16}$ at room temperature for 24 h under a nitrogen atmosphere. The IR spectra of the above Rh complexes were measured in KBr under a nitrogen atmosphere. The results are summarized in Figure 1. The above Rh_6 species were extracted with tetrabutylammonium chloride in ethoxyethanol.[3a] The supernatant liquid was dark green, and its IR spectrum was compatible with that of the starting polymer-bound Rh complexes.

Preparation of Polymer-Bound $[Rh_{14}(CO)_{24}]^{4-}$ and $[Rh_{14}(CO)_{24}H]^{3-}$ Complexes. The reaction of $Rh_6(CO)_{16}$ (0.05 mmol) with aminated polystyrene (II, 5 mg-atom of N) in a mixed solvent of H_2O (0.72 mL) and ethoxyethanol (7 mL) was carried out under 1 atm of CO at 100 °C. After 24 h, a brown polymer with $[Rh_{14}(CO)_{24}]^{4-}$ was obtained by filtration and further washed with ethoxyethanol and ethyl ether successively under a CO atmosphere. The isolated brown polymer was treated in a mixed solvent of H_2O and ethoxyethanol at 40 °C under 6 atm of CO for 24 h to give the dark green polymer of the Rh_6 species. In the presence of a large amount of H_2O (2.16 mL), a similar reaction with $Rh_6(CO)_{16}$ gave a mixture of $[Rh_{14}(CO)_{24}]^{4-}$ and $[Rh_{14}(CO)_{24}H]^{3-}$ after 24 h. In the treatment of the polymer containing a mixture of $[Rh_{14}(CO)_{25}]^{4-}$ and $[Rh_{14}(CO)_{25}H]^{3-}$ with aqueous Na_2CO_3, the $[Rh_{14}(CO)_{25}H]^{3-}$ species was partly converted into the $[Rh_{14}(CO)_{25}]^{4-}$ species. IR spectra of the above Rh_{14} and Rh_6 species were measured in KBr and are the same as in Figures 1 and 2.

Water-Gas Shift Reaction with Use of $Rh_6(CO)_{16}$ and Aminated Polymer II. The reaction vessel was a 25-mL flask with a side arm sealed with silicon rubber. It was attached to a closed reaction system with a reflux condenser, a gas circulator, and a vent. $Rh_6(CO)_{16}$ (0.05 mmol) and aminated polymer (II, 5 mg-atom of N) were 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. H_2O (2.16 mL) and ethoxyethanol (5.56 mL) were added to the vessel. The solution was heated with stirring to 100 °C. The gas phase was analyzed by gas chromatography (3-m column of activated carbon) at appropriate times, and then the polymers were collected by filtration. Their IR spectra were measured in KBr under a nitrogen atmosphere.

General Procedure of Deoxygenation of Nitro Compounds, Oximes, Hydroxylamines, and *N*-Oxides under CO Pressure. A stainless autoclave containing $Rh_6(CO)_{16}$ and the amine additive was evacuated and flushed three times with CO. Substrate, H_2O, and solvent were added. The reaction was carried out with stirring under appropriate conditions. After the reaction, the liquid phase was analyzed by GLPC. In the case of aminated polymer I, polymeric Rh complexes were separated by filtration. The filtrate was analyzed by GLPC and was distilled to give a pure product. Results of the above deoxygenations are summarized in Table II. A recycling study of polymer-bound Rh catalysts was carried out for 3-phenylnitropropane. After the above deoxygenation of 3-phenylnitropropane, the polymer was filtered and washed with 2-ethoxyethanol under a CO atmosphere. Reaction of 3-phenylnitropropane with the recovered polymer-bound Rh complexes was carried out anew under conditions similar to those for the above fresh-catalyst reaction. After 48 h, 3-phenylpropionitrile was obtained in 82% yield, which is similar to the 85% yield in the fresh-catalyst reaction. In a separate experiment, the deoxygenation of 3-phenylnitropropane was carried out for 8 h; the polymer solids were filtered under the conditions of 16 atm of CO and 40 °C. Aliquots of the filtrate were analyzed by GLPC to give a 40% yield of 3-phenylpropionitrile and the unreacted nitro compound. The filtrate was further treated under conditions similar to those for the above reaction over 48 h, but the yield of the nitrile was not increased.

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(17) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.

(18) Chini, P.; Martinengo, S. *Inorg. Chim. Acta* **1969**, *3*, 315.

(19) Bordwell, F. G.; Bratmess, J. E. *J. Org. Chem.* **1978**, *43*, 3101.

(20) Cunninghman, D. W.; Workman, M. O. *J. Inorg. Nucl. Chem.* **1971**, *33*, 3861.

(21) Wdward, J. T.; Whiting, J. *Can. J. Chem.* **1971**, *49*, 3502.

(22) Wieland, H. *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 1676.

(23) Lieto, J.; Milstein, D.; Albright, R. L.; Minliewiz, J. V.; Gates, B. C. *CHEMTECH* **1983**, 46.