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Preparation of Polymer-Bound Dinitrogen Complexes by Direct Reactions of Polymer–Metal Complexes with Molecular Nitrogen

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ABSTRACT: Polymer-bound dinitrogen complexes were synthesized directly from the polymer-bound (η^5-vinylmethylcyclopentadienyl)tricarbonylmanganese analogues and molecular nitrogen in tetrahydrofuran (THF)/benzene (1 : 5 v/v) under 3 atm of N_2 at 2°C. Dinitrogen complexes were also prepared by the oxidation of the hydrazine coordinated to the polymer-bound manganese complexes with hydrogen peroxide in the presence of cupric ions. The polymer-bound dinitrogen complexes are considerably stable compared to that of the corresponding monomer model of (η^5-methylcyclopentadienyl)dicarbonyldinitrogenmanganese.

KEY WORDS Dinitrogen / Polymer Complex / Nitrogen Molecule / Manganese / Nitrogen Fixation /

A large number of dinitrogen complexes of transition metals have been synthesized and reduction of the coordinated nitrogen molecules to ammonia, hydrazine, and some organic nitrogen compounds have been investigated by many workers. Among these dinitrogen complexes, (η^5-cyclopentadienyl)dicarbonyldinitrogenmanganese ($CpMn(CO)_2N_2$)[1–3] is a remarkable compound having the potentiality for becoming a catalyst in nitrogen fixation.[4,5] Sellmann and Weiss[2] suggested that, in principle, an organic nitrogen compound such as azomethane can be synthesized from molecular nitrogen according to the catalytic cycle in which (η^5-cyclopentadienyl)tricarbonylmanganese ($CpMn(CO)_3$) is used as the catalyst. However, repetition of the catalytic cycle is prevented by side reactions which deactivate the catalyst. Some studies[5–10] have been reported on the reversible nitrogenation of transition-metal complexes. Catalytic reduction of the coordinated nitrogen molecules under mild conditions is not yet possible.[5]

We have investigated the chemical behavior of several polymer metal complexes.[11–18] In the course of investigation on certain synthetic polymer-metal complexes, electrostatic, hydrophobic, and neigbouring-group effect have been observed. It has been suggested by other workers[19,20] that active complex species fixed on the polymer chains are stabilized as a result of suppression of the side reactions in which active sites are decomposed.

This paper describes the preparation of some polymer bound dinitrogen complexes from (η^5-vinylmethylcyclopentadienyl)tricarbonylmanganese (VCM)–styrene (ST) and VCM–PY (PY = *N*-vinylpyrrolidone) copolymers and the characteristics of the dinitrogen complexes.

EXPERIMENTAL

Materials

Freshly-distilled styrene and *N*-vinylpyrrolidone were used for the copolymerizations. (η^5-methylcyclopentadienyl)tricarbonylmanganese (MCM) was purchased from Alfa Chemicals Co. and used after distillation under reduced pressure. Acetyl derivative of MCM was prepared in a manner similar to that for (η^5-acetylcyclopentadienyl)-tricarbonylmanganese reported by Kozikowski,[21] and Pittman, Jr. *et al.*[22] The light-yellow oily liquid of the acetyl derivative was obtained in a yield of *ca.* 80%. α-hydroxyethyl derivative of MCM was prepared by the reduction of the acetyl derivative with lithium aluminium hydride[22] (yield, *ca.* 75%). VCM was obtained by the dehydration of the α-hydroxyethyl derivative.[23] A mixture of the α-hydroxyethyl derivative (40 g, 150 mmol), $KHSO_4$ (2.4 g, 18 mmol), and *t*-butylcatechol (0.4 g, 4 mmol) was heated at 130—150°C and 9×10^{-2} atm for 20 min. Distillation of the reaction mixture at 80—84°C and 2×10^{-3} atm gave a light-yellow oily liquid of VCM (yield, *ca.* 90%). *Anal.* Calcd for $C_{11}H_{10}Mn$: C, 53.90%; H, 4.11%. Found: C, 54.28%; H, 3.73%.

Copolymerizations

All copolymerization reactions were carried out in benzene using azobisisobutyronitrile (AIBN) as the radical initiator at 60°C under nitrogen atmosphere. The amount of initiator added was 2 mol% of the total monomer. VCM–ST (1A) and VCM–PY (1B), where A and B represent the copolymers of the styrene and *N*-vinylpyrrolidone, respectively, were purified by being precipitated twice from petroleum ether and dried *in vacuo*.

Monomeric Dinitrogen Complex

$MeCpMn(CO)_2N_2$ was prepared from $MeCpMn(CO)_3$ in a manner similar to that for the preparation of $CpMn(CO)_2N_2$.[3] A THF solution of $MeCpMn(CO)_3$ (0.5 g, 2 mmol) in THF (100 ml) was illuminated with ultraviolet (UV) lamp at 0°C for 2 h. The solution turned from light yellow to deep wine red. To this solution was added a solution of anhydrous hydrazine (0.48 ml, 15 mmol in 2 ml THF) at 2°C. After standing for 2 h, 0.05 M $CuSO_4$ (0.05 ml) and 30% H_2O_2 solution (3.4 ml, 30 mmol) were added and the reaction mixture was kept at −40°C for 1 h. The solution was evaporated to dryness at 0°C under reduced pressure. $MeCpMn(CO)_2N_2$ was sublimed from the residue at 20°C and 10^{-3} atm. A light-yellow oily product of $MeCpMn(CO)_2N_2$ was obtained in a yield of about 20%. *Anal.* Calcd for $C_8H_7N_2O_2Mn$; C, 44.05%; H, 3.24%; N, 12.84%. Found: C, 44.52%; H, 3.65%; N, 12.51%. Key bands of the infrared (IR) spectra (neat) in cm^{-1} were 3101 (Cp ring CH str), 2160 (N_2 str), 2002, 1910 (CO str), 672, 638 (Mn–CO bands).

Polymer-Bound Dinitrogen Complexes

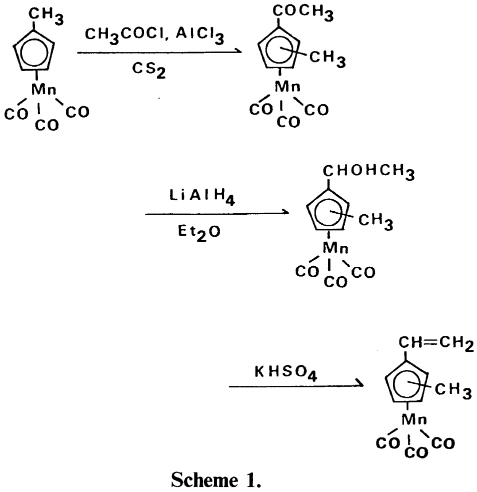
The polymer-bound dinitrogen complexes, 4A and 4B, were prepared from the mono-substituted tetrahydrofuran (THF) derivatives of 1A and 1B, respectively. Molarities of the polymer complexes are represented by unit moles of the manganese in the copolymer. The THF derivative of 1A(2A) and that of 1B(2B) were obtained by substitution of one of the carbonyl groups by a THF molecule with illumination. An argon-saturated solution of 1A or 1B (3.5 mmol) in 50 ml of THF was illuminated for 2 h at 2°C. With the illumination of light, the initially-light-yellow solution turned to deep wine red. Molar fractions of the manganese complex unit and styrene or *N*-vinylpyrrolidone unit, represented by *m* and *n*, respectively, were determined by both elemental analysis and spectrophotometry: the value of *m* was determined spectrophotometrically, using the visible absorption spectra of argon-saturated THF solutions of the copolymers prepared under dim light in order to prevent a substitution reaction of the carbonyl group by the THF molecule. The visible absorption spectrum of 1A in the argon-saturated THF solution is shown in Figure 1 (curve a). The absorption peak of the band at 328 nm and its molar extinction coefficient of 1A are the same as those of 1B regardless of the value of *m*. Consequently, the value of *m* may be determined spectrophotometrically using $\varepsilon = 1330\ mol^{-1}\ dm^3$ at 328 nm. The methods for preparing the polymer-bound dinitrogen complexes were 1), oxidation of the coordinated hydrazine and 2) reaction of the THF derivatives, 2A and 2B, with nitrogen gas. These methods are simply represented by "indirect method" and "direct method," respectively. The indirect method was carried out as follows. To a THF solution of 1A or 1B (12 mmol in 50 ml) was added a small excess of anhydrous hydrazine (0.42 ml, 13 mmol) at 0°C. After 1 h, 30% H_2O_2 solution (3.0 ml, 26 mmol) and 0.05 M $CuSO_4$ (0.05 ml) were added successively and stirred at −40°C for 1 h. A crude-polymer-bound dinitrogen complex was precipitated by pouring the THF solution into petroleum ether. The product was purified by precipitation twice from petroleum ether. The polymer-bound dinitrogen complexes were obtained as a pale-yellow powder. The direct preparation was carried out as follows. The polymer 1A or 1B (3.5 mmol) was dissolved into 30 ml of Ar-saturated THF–benzene (1 : 5 v/v). The solution was illuminated with a UV lamp for 2 h at 2°C. The solution was kept under 3 atm of N_2 at 0°C for 10 h. The polymer-bound dinitrogen complex was precipitated from a large amount of petroleum ether and dried under nitrogen.

Instruments

A 100 W high-pressure mercury lamp was used as the light source for UV illumination. The distance between the reaction vessel (100 ml round bottomed pyrex flask) and the lamp was kept at 35 cm. The infrared spectra were measured in KBr disks or neat liquid films on a Hitachi Model 200—10 spectrometer. Absorption spectra were measured on a Hitachi Model 320 spectrophotometer. Viscosities were measured in THF solutions, using a Ubbelohde-type viscometer at 25 ± 0.1°C.

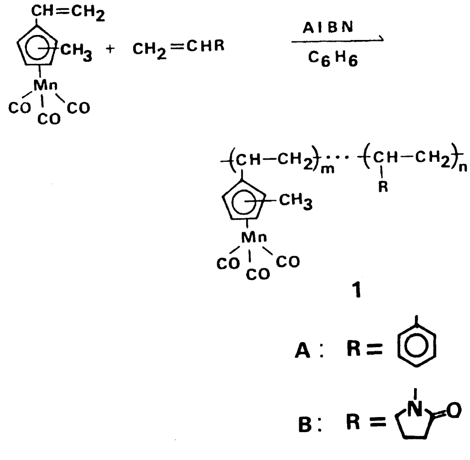
RESULTS AND DISCUSSION

The acetyl derivative of MCM was prepared by the aluminium chloride-catalyzed acetylation of MCM with acetyl chloride in carbon disulfide. Reduction of the acetyl derivative with lithium aluminium hydride in diethyl ether yielded the α-hydroxyethyl derivative, and dehydration of it with potassium bisulfate gave VCM as a light-yellow oily product. Two isomers of the vinyl derivatives (1,2- and 1,3-substituents) of VCM presumably exist in the product and were used without being separated.



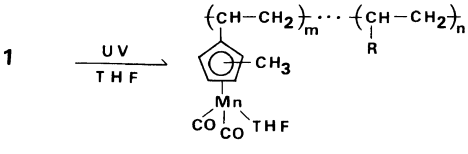
Scheme 1.

AIBN-initiated copolymerization reaction of VCM with ST or PY gave the copolymer 1A or 1B, respectively, as a pale yellow powder. The copolymers 1A and 1B are soluble in THF and other ordinary organic solvents. The values of *m* and *n* obtained by elemental analysis agree with those obtained by means of spectrophotometry within experimental error. The analytical data of the copolymers prepared are shown in Table I.



Scheme 2.

Solutions of the mono THF-coordinated derivatives of 1A and 1B, represented by 2A and 2B, respectively, were obtained by illumination of the THF solutions of 1A and 1B, respectively, under an argon atmosphere. Spectral change of 1A in the THF solution during UV illumination is shown in Figure 1. With illumination of the UV lamp, the color of the solution turned from light yellow to deep wine red. Similar color changes were observed in THF solutions of 1B and $MeCpMn(CO)_3$ and are attributed to the substitution of the carbonyl group by the THF molecule.[1,2] In the spectral change



(1)

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Scheme 3.

Table I. Copolymerization of (η^5-vinylmethylcyclopentadienyl)tricarbonylmanganese (M_1) with styrene or *N*-vinylpyrrolidone[a]

Copolymer	Found (Calcd)/%			Mole fraction of M_1 in feed	Mole fraction of M_1 in copolymer	$[\eta]^b$
	C	H	N			dl g^{-1}
1A-1	69.18 (70.04)	5.14 (5.40)		0.50	0.37	0.0788
1A-2	79.74 (80.99)	6.69 (6.55)		0.33	0.15	0.114
1B-1	56.94 (56.87)	5.69 (4.85)	3.14 (3.23)	0.33	0.57	0.0628
1B-2	57.99 (58.76)	6.38 (5.64)	6.47 (5.45)	0.17	0.37	0.102

[a] 1A and 1B represent the VCM–ST and VCM–PY copolymers, respectively.

[b] Intrinsic viscosities in THF solutions at 25±0.1°C.

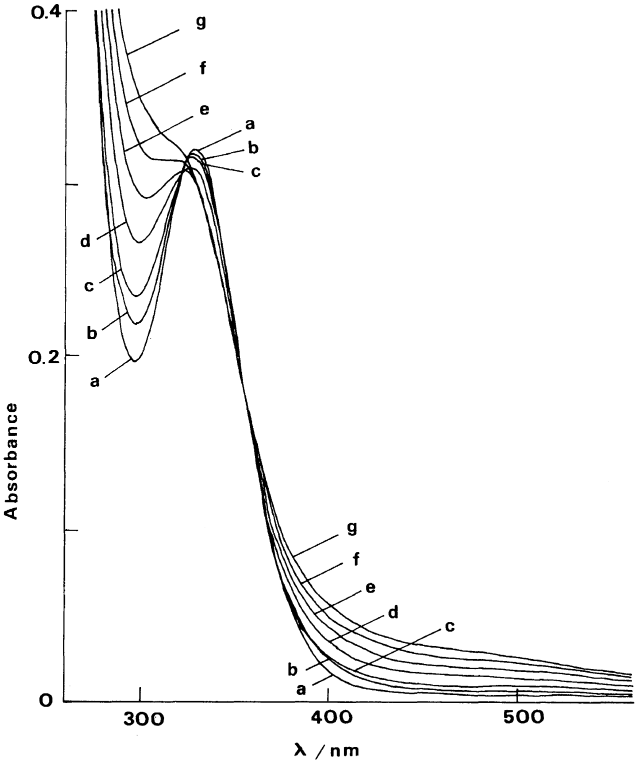
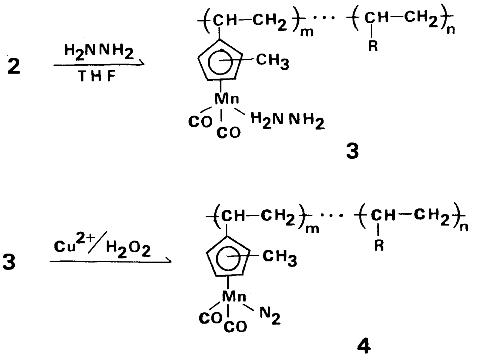


Figure 1. Spectral change in the THF solution of 2.50×10^{-4} mol l^{-1} 1A with UV illumination at 2°C under argon. Illumination time / min: a, 0; b, 20; c, 40; d, 120; e, 160; f, 220; g, 280.

caused by illumination of 1A and 1B solutions, isosbestic points could be observed at 324 nm and 352 nm within an irradiation time of 2 h. The spectral changes within 2 h are caused by the exchange of one of the carbonyl groups by a THF molecule. These isosbestic points, however, could not be observed when the irradiation time was prolonged. This is presumably due to the replacement of the second carbonyl group. It may be concluded that about one Mn-bound carbonyl group on each polymer complex is substituted by the solvent molecule during 2 hours of irradiation under the conditions employed. The polymeric THF complexes, 2A and 2B are fairly stable compared to the monomeric THF complex, $MeCpMn(CO)_2$–THF. No appreciable spectral change in 2A and 2B in THF solution was observed during 100 minutes of standing at 2°C under Ar. On the other hand, when $MeCpMn(CO)_2$–THF was allowed to stand under the same conditions a rapid spectral change was observed within several minutes.

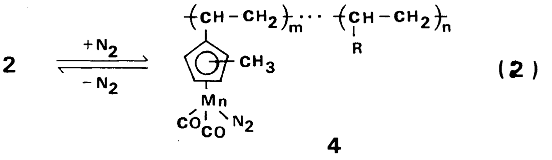
The polymer-bound dinitrogen complexes (4A and 4B) were prepared by 1) oxidation of the coordinated hydrazine (indirect method) and 2) a direct reaction between nitrogen molecule and the THF complexes, 2A or 2B (direct method).

The polymeric hydrazine complexes, 3A and 3B, were obtained by the reaction of 2A and 2B, respectively, with hydrazine in THF at 2°C. As a result of the formation of the hydrazine derivative, the color of the solution turned from wine red to orange. The oxidation reaction of the coordinated hydrazine to dinitrogen was carried out using the two-electron oxidizing agent, H_2O_2–Cu^{2+}, at −40°C.



Scheme 4.

Preparation of the N_2-coordinated polymer complexes by the direct method was carried out in THF–benzene (1 : 5 v/v). The substitution reaction of the THF by nitrogen molecule proceeded under relatively mild conditions. Solid-polymer-bound dinitrogen complexes were obtained by precipitation from petroleum ether and dried under nitrogen stream. The IR spectra of the polymer-bound dinitrogen complexes showed a characteristic ν_{N_2} band at 2160 cm^{-1}.



Scheme 5.

A possible structure for the polymer-bound dinitrogen complexes in THF solution is given in Figure 2.

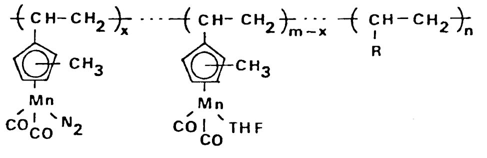


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Figure 2. Possible structure of the polymer-bound dinitrogen complex in the THF solution.

When the polymer-bound dinitrogen complexes are obtained as a solid, a part of the THF and/or nitrogen molecules coordinated to the manganese atoms are presumably released during the process of the precipitation and drying under nitrogen. The precipitates of the polymer-bound dinitrogen complexes were dried *in vacuo* for several hours. The resulting powder became less soluble in THF and other ordinary organic solvents.

It was reported[3] that the characteristic ν_{N_2} band was observed for the product obtained by the reaction of $CpMn(CO)_2$–THF with nitrogen molecule in the following manner. Nitrogen gas was pressurized at 150 atm into a solution of $CpMn(CO)_2$–THF for 24 h and the THF was then removed at room temperature *in vacuo*. The solid products were obtained by sublimation of the residue. $CpMn(CO)_2N_2$ in the products was iden-

Table II. IR frequencies (cm^{-1})[a]

Compound	ν_{C-H}(Cp)	ν_{N_2}	ν_{CO}	ν_{C-C} (Ph)	ν_{C-C} (PY)	ν_{Mn-CO}
1A-1[b]	3070sh 3045sh		2002vs 1920vs	1601s 1490s		662s 638s
4A-1[c]	3070sh 3050	2160s	2002vs 1920vs	1598s 1492s		660s 637s
1B-1[b]	3070 3050sh		2002cs 1920vs		1285	660s 637s
4B-1[c]	3070sh 3050sh	2160s	2003vs 1918vs		1282	662s 640s
$MeCpMn(CO)_3$	3102		2005vs 1910vs			670s 640s
$MeCpMn(CO)_2N_2$	3101	2160s	2002vs 1910vs			672s 638s

[a] KBr disks, except those for $MeCpMn(CO)_3$ and $MeCpMn(CO)_2N_2$. vs, very strong; s, strong; sh, shoulder.

[b] Except for the ν_{C-C}(ph) band, IR frequencies of the key bands of 1A-1, 1B-1, 4A-1, and 4B-1 are the same as the corresponding bands of 1A-2, 1B-2, 4A-2, and 4B-2, respectively.

[c] Prepared by the direct method in THF–benzene (1 : 5 v/v) at 3 atm of N_2 and 2°C. 4A-1 and 4B-1 were synthesized from 1A-1 and 1B-1, respectively.

tified by means of its characteristic IR band. However, our attempt to prepare pure $MeCpMn(CO)_2N_2$ by the direct reaction of $MeCpMn(CO)_2$–THF with N_2 was unsuccessful.

For the polymer-bound dinitrogen complexes, an end-on type coordination of the dinitrogen to the manganese is suggested from the intense ν_{N_2} band arround 2160 cm^{-1}.[1,2] The infrared frequencies of the main peaks of the polymer-bound dinitrogen complexes, copolymers 1A and 1B, $MeCpMn(CO)_2N_2$, and $MeCpMn(CO)_3$ are listed in Table II. The IR peaks of the ν_{N_2} bands of the polymer-dinitrogen complexes are the same as that of $MeCpMn(CO)_2N_2$.

A THF solution of the polymer-bound dinitrogen complexes, 4A and 4B, was made to stand for 3 h at room temperature under argon. The solution was poured into petroleum ether and the powder was collected. The IR spectra of the powder had no ν_{N_2} band and no appreciable change in the IR band was observed except for the ν_{N_2} band. This seems to indicate that the nitrogen molecules coordinated to the polymer complexes could be eliminated without appreciable decomposition of the polymer complexes.

A conventional method was employed for making a comparison of the stabilities of the dinitrogen complexes. The changes in the ν_{N_2} band strength of the dinitrogen complexes were followed as a function of the time. The polymer-bound dinitrogen complexes, 4A and 4B, were stable in air at room temperature for several days whereas the monomeric dinitrogen complex was air sensitive and the ν_{N_2} band of $MeCpMn(CO)_2N_2$ disappeared after 17 h at room temperature. The ν_{N_2} band strength of 4A hardly changed at 90°C for 6 h but that of 4B decreased appreciably under the same conditions. This indicates that the polymer-bound dinitrogen complex having styrene units is more stable thermally than that having *N*-vinylpyrrolidone units. The monomeric dinitrogen complex completely decomposed whithin several minutes under the same conditions.

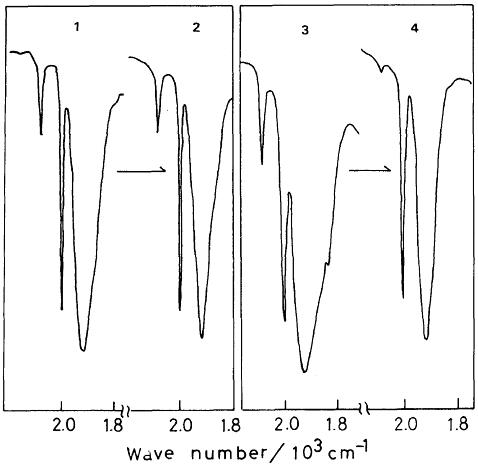

Figure 3. IR spectra changes of 4A and 4B at 90°C under air: 1, freshly-prepared sample of 4A; 2, 4A after 6 h; 3, freshly-prepared smaple of 4B; 4, 4B after 6 h.

We are now investigating the reactions of the coordinated nitrogen molecules using the polymer-bound manganese complexes.

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