Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Kurimura, Yoshimi , Takagi, Yasuyuki and Tsuchida, Eishun(1987) 'Mechanism of the Direct Coordination of Acetylene to the Polymer-Bound Cyclopentadienyl Manganese Complex', Journal of Macromolecular Science, Part A, 24: 3, 419 — 430

To link to this Article: DOI: 10.1080/00222338708074458

URL: http://dx.doi.org/10.1080/00222338708074458

J. MACROMOL. SCI.—CHEM., A24(3 & 4), pp. 419-430 (1987)

MECHANISM OF THE DIRECT COORDINATION OF ACETYLENE TO THE POLYMER-BOUND CYCLOPENTADIENYL MANGANESE COMPLEX

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ABSTRACT

On irradiation by visible light in acetylene, polymer-bound (methylcyclopentadienyl)tricarbonylmanganese membrane, P-MeCpMn$(CO)_3$, was found to react with acetylene to give its acetylene complex, P-MeCpMn$(CO)_2(C_2H_2)$. The reaction mechanism of the coordination and elimination of acetylene was investigated by means of resolution of the electronic absorption bands and IR spectra, and gas chromatographic analysis. Reversible coordination of acetylene was also studied by using divinylbenzene crosslinked polymer-bound (methylcyclopentadienyl)tricarbonylmanganese resin particles.

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INTRODUCTION

A wide variety of the chemistry of coordinatively unsaturated species of $RCpMn(CO)_2$ (R = H and CH_3, Cp = cyclopentadienyl ring), which were prepared by the photolysis of the corresponding tricarbonyl complexes, is currently being investigated [1, 2]. The fragments $RCpMn(CO)_2$ will generally strongly interact with solvents. When an appropriate ligand L (L = THF, N_2, CO, SO_2, amines, phosphines, and pyridines) is present in the solution, stable complexes of the type $RCpMn(CO)_2(L)$ are formed by irradiation with UV light under an inert gas [1-4]. It seems likely that the $RCpMn(CO)_2$ fragment has potential as catalyst for a wide variety of reactions involving ligand L. The $RCpMn(CO)_3$ catalyzed formation of carbon-nitrogen compounds and hydrogenation of carbon monoxide have been reported [5, 6].

In a previous paper [7] we reported that the polymer-bound dinitrogen complex of manganese, P-$MeCpMn(CO)_2(N_2)$ (MeCp = methylcyclopentadienyl ring, P = polymer backbone), can be prepared from P-$MeCpMn(CO)_3$ membranes or resin beads by a one-step reaction under moderate conditions [7]. In the case of the corresponding low molecular weight complex, $RCpMn(CO)_3$, direct synthesis of the dinitrogen complex, $RCpMn(CO)_2(N_2)$, has so far not been possible [5, 8]. Recently, we have also shown that an inert and stable polymer-bound η^2-acetylene complex is formed by direct photochemical reaction of $MeVCpMn(CO)_3$-*co*-St ($MeCpMn(CO)_3$ = (methylvinylcyclopentadienyl)tricarbonylmanganese, St = styrene) membrane with acetylene [9]. The corresponding low molecular weight η^2-acetylene complexes, $RCpMn(CO)_2(C_2H_2)$, are rather instable. Though they are the primary products, they isomerize to give the vinylidene complex and/or μ_2-dimer [1, 10].

The object of the work described here was an attempt to clarify the detailed reaction mechanism of the light-induced coordination of acetylene with the polymer-bound cyclopentadienylmanganese complexes $MeVCpMn(CO)_3$-*co*-St and $MeVCpMn(CO)_3$-*co*-VPRo (VPRo = vinylpyrrolidone).

EXPERIMENTAL

Freshly distilled styrene, *N*-vinylpyrrolidone (VPRo), and 1,4-divinylbenzene (DVB) were used for the copolymerization. (Methylvinylcyclopentadienyl)tricarbonylmanganese (MVCM) was prepared from (methylcyclopentadienyl)tricarbonylmanganese by the literature method [8, 11]. MVCM-*co*-St (PM-1), MVCM-*co*-VPRo (PM-2), and PM-2 crosslinked by

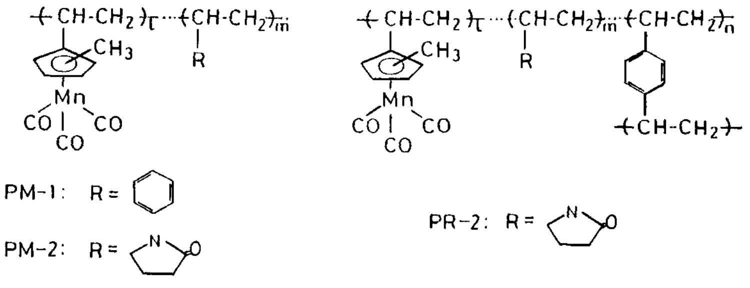


FIG. 1. Chemical structures of PM-1, PM-2, and PR-2.

TABLE 1. Mole Fractions of the Monomers in the Copolymers

Copolymer	VMCM (l)	ST (BPRo) (m)	DVB (n)
PM-1	0.364	0.636	–
PM-2	0.580	(0.420)	–
PR-2	0.466	(0.524)	0.010[a]

[a] Mole fraction of DVB in the copolymer was assumed to be equal to that in the monomer mixture.

DVB (PR-2) were synthesized from the corresponding monomers by the methods described elsewhere [8, 11]. The chemical structures and the copolymer compositions of PM-1, PM-2, and PR-2 are represented in Fig. 1 and Table 1, respectively.

The PM-1 and PM-2 membranes were prepared as follows: Benzene solutions of the copolymers were spread with a small brush on a quartz plate (10 X 40 mm, 1 mm thick) and dried in vacuo. The contents of the monomeric units of the tricarbonyl manganese complex in the membranes were 0.6-1.0 μmol/cm^2 [12]. The PR-2 copolymer blocks were ground with a mechanical grinder and the grains were separated with a sieve. The crude resins were swollen in benzene, washed with large amounts of benzene, and dried in vacuo. Resins of 50-100 mesh were used for the experiments.

The amounts of coordinated acetylene were determined as follows. The polymer-bound acetylene complex resins (~100 mg) were kept in a 7.7-mL glass tube sealed with a small rubber cap under argon, at 60°C for 12 h. The amount of acetylene gas evolved from the complex was determined by gas chromatography (Hitachi Model 163) with a TCD detector and a column (200 cm length) filled with Gasukuro Pack 54 (Gasukuro Kogyo Co.).

Visible light irradiations were carried out by using a slide projector with a UV cut-off filter (Kenko SL-39), which was used because the spectral changes of the membranes were so rapid that the spectral analyses were difficult. A 100-W high-pressure mercury lamp (Richoh Kagaku Model UVL 100P) was used for UV irradiation. The IR and electronic absorption spectra were recorded on a Hitachi 200-10 infrared spectrometer and a Hitachi 320 recording spectrophotometer, respectively.

RESULTS AND DISCUSSION

Preliminary study [9] showed that the photolysis of MeVCpMn$(CO)_3$-*co*-St (PM-1) and MeVCpMn$(CO)_3$-*co*-VPRo (PM-2) membranes under acetylene give an acetylene complex, P-MeCpMn$(CO)_2(C_2H_2)$ under moderate conditions. In the present study, PM-1 and PM-2 were used in the form of membranes and DVB-crosslinked MeVCpMn$(CO)_3$-*co*-VPRo (PR-2) in the form of small particles. The PM-1 and PM-2 membranes were prepared in order to resolve the electronic spectra of the membranes, and PR-2 was used to investigate the reversible coordination of acetylene to the manganese center. Unfortunately, the complete resolution of the absorption spectra of the PM-2 membranes prepared by irradiation under Ar and acetylene has not yet been achieved because of the complexity of these spectra. Therefore, the results obtained with PM-1 membranes and the reversible coordination of acetylene by PR-2 resins are reported in the present paper.

Coordination of Acetylene in the PM-1 Membrane System

On irradiation of PM-1 membrane with visible light under Ar, two isosbestic points were observed at 320 and 350 nm (Fig. 2a), indicating formation of one chemical species (abbreviated X). This species is suggested to be a phenyl-ring-coordinated complex or a dimerized one having a Mn—Mn bond [12].

The changes in the electronic spectra of the PM-1 membrane on irradiation with visible light under acetylene are shown in Fig. 2(b) which shows no isosbestic point, but increasing absorbance at ~320 nm due to the formation of the acetylene complex.

The IR data in Table 2 also account for the formation of the acetylene com-

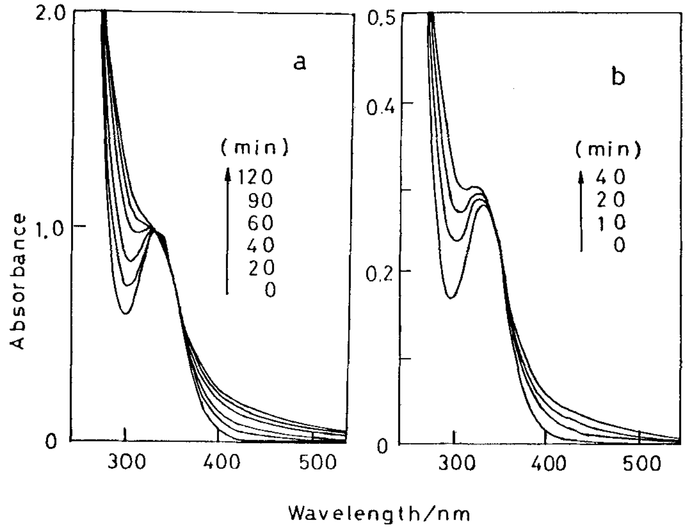


FIG. 2. Absorption spectrum changes of PM-1 membranes irradiated with visible light under argon (a) and acetylene (b).

plex. Side-on type coordination of acetylene was confirmed by the characteristic $\nu_{C\equiv C}$ absorption peak at 1 740 cm^{-1} [9] and the band shift of ν_{CO} from 1 920 cm^{-1} for –MeCpMn(CO)$_3$ to ~1 830-1 850 cm^{-1} (shoulder) for that of –MeCpMn(CO)$_2$(C$_2$H$_2$). No distinct IR band shift from one of the ν_{CO} bands for the tricarbonyl compound (2 009 cm^{-1}) to that for X and/or MeCpMn(CO)$_2$-(C$_2$H$_2$), which was expected at ~1 970 cm^{-1}, was observed, probably due to the presence of the strong band at 1 920 cm^{-1} for ν_{CO} of the tricarbonyl complex moieties. The IR frequency of the $\nu_{C\equiv C}$ band for P-MeVCpMn(CO)$_2$-(HC≡CH) is similar to those for CpMn(CO)$_2$(HC≡Cph) (1 840 cm^{-1}) [13] and CpMn(C$_6$H$_6$)Mo(HC≡CH) (1 689 cm^{-1}) [14].

In Fig. 3(a) the resolved spectrum of the nonirradiated PM-1 membrane, an end-absorption band (A$_1$) and a visible-region band (A$_2$) at 328 nm are seen.

On irradiation of PM-1 under Ar, three resolved bands were obtained at 270 (B$_1$), 285 (B$_2$), and 400 nm (B$_3$) in addition to the two bands for the starting material (A$_1$ and A$_2$) (Fig. 3b).

On the other hand, the resolution of the spectrum on PM-1 membrane irradiated under acetylene gives four absorption bands at 270, 285, 400, and 310 nm, besides A$_1$ and A$_2$ (Fig. 3c). The former three peaks were assigned to the same

TABLE 2. IR Frequencies[a] of PM-1, PM-2, and PR-2

	ν_{CO} (carbonyl)				$\nu_{C=O}$ (pyrrolidone)	$\nu_{C \equiv C}$
			Nonirradiated			
PM-1	2009(vs)	1920(vs)	–	–	–	–
PM-2	2008(vs)	1920(vs)	–	–	1655(vs)	–
PR-2	2009(vs)	1919(vs)	–	–	1654(vs)	–
			Irradiated under Ar			
PM-1	2008(vs)	1920(vs)	1970(sh)	1895(sh)	–	–
PM-2	2009(vs)	1920(vs)	–	1840(sh)	1654(vs)	–
PR-2	2009(vs)	1920(vs)	–	1840(sh)	1655(vs)	–
			Irradiated under C_2H_2			
PM-1	2009(vs)	1920(vs)	1970(sh)	1895(sh)	–	1740(w)
PM-2	2009(vs)	1920(vs)	–	1840(sh)	1655(vs)	1740(w)
PR-2	2009(vs)	1920(vs)	–	1840(sh)	1655(vs)	1740(w)

[a] In cm^{-1}.

chemical species formed by the irradiation of PM-1 under argon, i.e., B_1, B_2, and B_3. The peak at 310 nm (C band) can be assigned to the acetylene complex moieties.

The absorption maxima (λ_{max}) and relative molar absorptivities (R_ϵ) of typical resolved bands are summarized in Table 3. The resolved bands with absorption maxima lower than about 270 nm are omitted since they could not be analyzed accurately.

In all the cases studied, no appreciable changes in the resolved band maxima with time were observed up to ~60 min. As shown by the time dependence of the relative intensities (I_r) of the resolved bands in Fig. 4, the formation of both acetylene complex and product X is accompanied by a decrease in the amount of the tricarbonyl complex moieties.

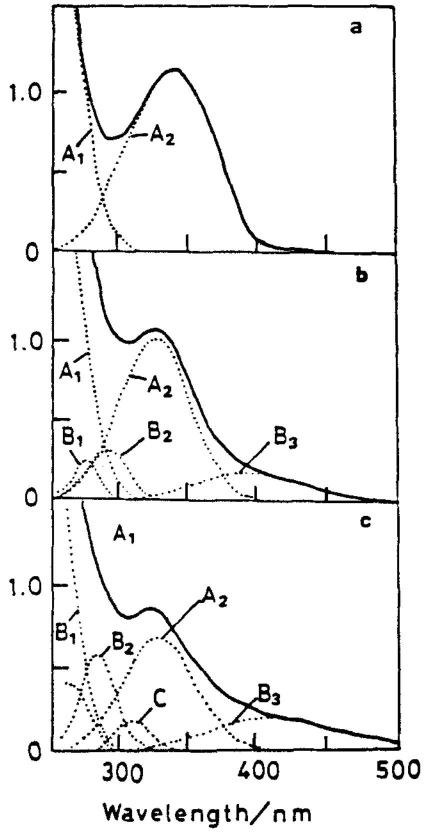


FIG. 3. Resolution of the absorption spectra of PM-1 membranes. (a) Non-irradiated; (b) irradiated under argon; (c) irradiated under acetylene.

In addition of the above results, the following additional observations were obtained in the present study: 1) The acetylene complex was stable at least for several days under air at room temperature; 2) no appreciable changes in the absorption spectra of X and the acetylene complex were observed on irradiation with visible light under carbon monoxide. These results seem to indicate that no appreciable reaction from X to the tricarbonyl complex and from the acetylene complex to the tricarbonyl complex takes place under the experimental conditions.

TABLE 3. Typical Resolved Absorption Spectral Bands

	Resolved band		
	A_2	B_2	C
Assignment	P-MeCpMn(CO)$_3$	X	P-MeCpMn(CO)$_2$(C$_2$H$_2$)
λ_{max}, nm[a]	328	285	310
R_ϵ[b]	1.0	9.1	13

[a] The errors of the values of λ_{max} were estimated to be ±5%.

[b] The errors of the values of the relative absorptivities were estimated to be ±10%.

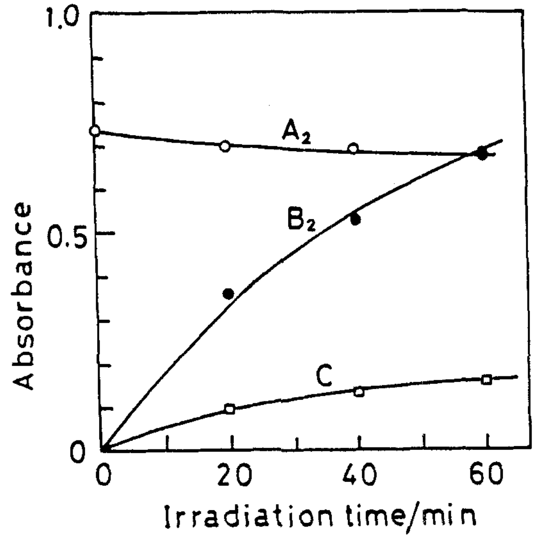
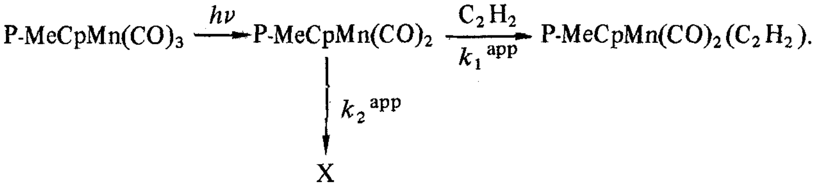


FIG. 4. Dependence of the absorbances of A_2, B_2, and C bands on the irradiation time for the PM-1 membrane.

The following reaction scheme for the photoinduced reaction of the PM-1 membrane under acetylene accounts for the experimental results:



$$\begin{tikzcd}
\text{P-MeCpMn(CO)}_3 \arrow[r, "h\nu"] & \text{P-MeCpMn(CO)}_2 \arrow[r, "C_2H_2", "k_1^{app}"'] \arrow[d, "k_2^{app}"] & \text{P-MeCpMn(CO)}_2(C_2H_2). \\
 & X &
\end{tikzcd}$$

The parameters k_1^{app} and k_2^{app} are the apparent rate constants for the formation of acetylene complex and of X species, respectively. They would be dependent on the partial pressure of acetylene and the composition of PM-1.

The ratio of formation of the acetylene complex from the coordinatively unsaturated species ($R_{C_2H_2}$) would be given by

$$R_{C_2H_2} = \frac{k_1^{app}C}{k_1^{app}C + k_2^{app}C} = \frac{1}{1 + (k_2^{app}/k_1^{app})}, \tag{1}$$

where C is the concentration of the coordinatively unsaturated complex. The values of $R_{C_2H_2}$ and k_1^{app}/k_2^{app} for PM-1 were about 0.22 and 0.28, respectively, in the initial stage of the reaction under the conditions employed. The degree of the coordination of acetylene was estimated to be ~18% for 60 min irradiation under acetylene at room temperature.

Reversible Coordination of Acetylene by Use of PR-2 Resin Particles

In this case, UV light was used for irradiation. Coordination of acetylene to the manganese center and substitution of the coordinated acetylene by carbon monoxide can be achieved repeatedly by use of PR-2 resin under suitable conditions. The coordination of acetylene took place under normal acetylene pressure at room temperature, and the substitution of the coordinated acetylene by carbon monoxide occurred under normal carbon monoxide pressure at room temperature for 10 h.

In our study of the reversible coordination of acetylene by means of gas chromatography, the coordination and elimination of acetylene were repeated,

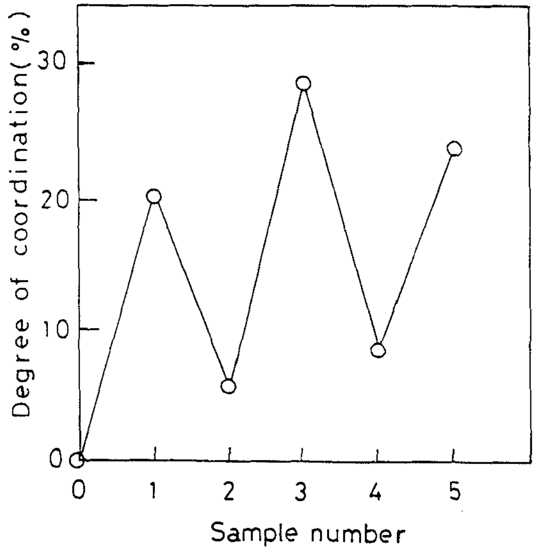


FIG. 5. Repetitive coordinations and eliminations of acetylene experiments for the PR-2 resins. Samples: (0) Nonirradiated PR-2; (1) UV irradiation under acetylene at room temperature for 50 min; (2) under CO at room temperature for 12 h; (3) UV irradiation under acetylene at room temperature for 50 min; (4) under CO at room temperature for 12 h; (5) UV irradiation under acetylene at room temperature for 50 min.

and the amount of coordinated acetylene in a small sample was determined. Figure 5 shows that about 70% of the coordinated acetylene molecules on the complex moieties could be eliminated by letting them stand under carbon monoxide at room temperature. However, it was found that presence of small amounts of the moisture prevents the coordination of acetylene. For PM-1 and PR-2, reversible coordination of acetylene was not successful, probably due to the substitution inertness of the phenyl ring in Compound X. As the pyrrolidone group coordinating to the manganese center has labile substitution, most of the coordinated pyrrolidone moieties are substituted by acetylene or CO molecules under suitable conditions.

The values of $R_{C_2H_2}$ for the PR-2 resins with 60 min irradiation under acetylene were estimated to be about 35% by gas chromatographic analysis of the coordinated acetylene. The high degree of coordination of acetylene for PR-2 may also account for the substitution lability of the pendant pyrrolidone.

The reaction mechanism for the coordination of acetylene with PR-2 resin is essentially represented by the following scheme:

$$\begin{tikzcd}
\text{P-MeCpMn(CO)}_3 \arrow[r, shift left, "h\nu"] & \text{P-MeCpMn(CO)}_2 \arrow[l, shift left, "\text{CO}"] \arrow[r, shift left, "\text{C}_2\text{H}_2"] \arrow[d, shift left, "\text{PRo}"] & \text{P-MeCpMn(CO)}_2(\text{C}_2\text{H}_2) \arrow[l, shift left] \\
 & \text{P-MeCpMn(CO)}_2(\text{PRo}). \arrow[u, shift left] &
\end{tikzcd}$$

In this scheme, PRo represents the pendant pyrrolidone ring which coordinates to the manganese through the oxygen atom.

ACKNOWLEDGMENT

This work was partially supported by a Grant-in-Aid for Science Research from the Ministry of Education, Science, and Culture (No 44033).

REFERENCES

[1] K. G. Kaulton, *Coord. Chem. Rev.*, *38*, 1 (1981).
[2] K. Folting, J. C. Hufman, L. N. Lewis, and K. G. Kaulton, *Inorg. Chem.*, *18*, 3483 (1979).
[3] J. W. Hershberger and J. K. Kochi, *Polyhedron*, *2*, 929 (1983).
[4] N. G. Connely and M. D. Kitchen, *J. Chem. Soc., Dalton Trans.*, p. 931 (1977).
[5] D. Sellmann and W. Weiss, *J. Organomet. Chem.*, *160*, 183 (1978).
[6] C. P. Casey and S. M. Neumann, *J. Am. Chem. Soc.*, *100*, 2544 (1978).
[7] D. Sellman and D. Weiss, *Angew. Chem., Int. Ed. Engl.*, *16*, 880 (1977).
[8] Y. Kurimura, F. Ohta, J. Gohda, H. Nishide, and E. Tsuchida, *Makromol. Chem.*, *183*, 2889 (1982).
[9] Y. Kurimura, F. Ohta, N. Ohtsuka, and E. Tsuchida, *Chem. Lett.*, p. 1787 (1983).
[10] A. N. Nesmeyanov, G. Aleksandrov, A. B. Antonova, K. N. Anisimov,

N. Kolobava, and Y. T. Struchkov, *J. Organomet. Chem., 110,* C36 (1976).

[11] C. U. Pittman Jr., G. V. Marlin, and T. D. Rounsefell, *Macromolecules, 6,* 1 (1973).

[12] Y. Kurimura, Y. Takagi, M. Suka, C. Mizukoshi, and E. Tsuchida, *Nippon Kagaku Kaishi, 3,* 373 (1985).

[13] A. B. Antonova, N. E. Kolbova, P. V. Petrovsky, B. V. Lokshin, and N. S. Obezyuk, *J. Organomet. Chem., 137,* 55 (1977).

[14] M. L. Green, J. Knight, and J. A. Seagel, *J. Chem. Soc., Dalton Trans.,* p. 2189 (1977).