CHEMISTRY LETTERS, pp. 1787-1790, 1983. © The Chemical Society of Japan 1983

ACETYLENE COORDINATION TO THE POLYMER-BOUND METHYLCYCLOPENTADIENYL MANGANESE COMPLEX

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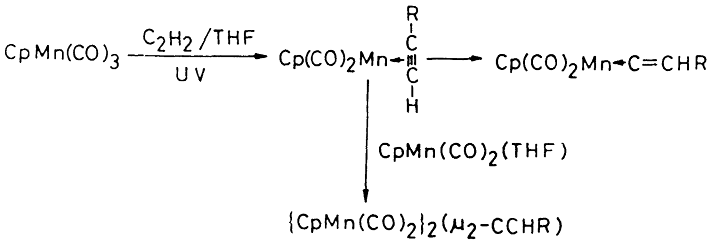
Stable polymer-bound η^2-acetylene complex has been prepared by direct reaction of (η^5- methylvinylcyclopentadienyl)tricarbonylmanganese ($MeVCpMn(CO)_3$)-co-styrene membrane with acetylene on UV irradiation under mild conditions. Reaction of $MeVCpMn(CO)_3$-co-N-vinylpyrrolidone under acetylene has also been investigated.

Wide variety of the chemistry around the coordinatively unsaturated manganese complex, $CpMn(CO)_2$ (Cp = η^5-cyclopentadienyl ring), is currently developing.1) It has been demonstrated1d,2) that the η^2-acetylene complexes of $CpMn(CO)_2(HC\equiv CH)$ and $MeCpMn(CO)_2(HC\equiv CH)$ (MeCp = η^5-methylcyclopentadienyl ring) have particular instability. The detailed investigations on the reactions of $CpMn(CO)_3$ with alkyne confirmed that the η^2-alkyne complexes are the primary products and they isomerize to give vinylidene complexes and/or dimerize to give the μ_2-dimers.1a,1d)

This work represents the first preparations of a stable η^2-acetylene complex of methylcyclopentadienyl manganese by photochemical reaction from the polymer-bound $MeCpMn(CO)_3$ and acetylene at room temperature.



Polymer-bound $MeCpMn(CO)_3$, $MeVCpMn(CO)_3$-co-St(St = styrene) 1 and $MeVCpMn(CO)_3$-co-VPRo(VPRo = N-vinylpyrrolidone) 2, were prepared in the similar manner as reported previously.3,4) Compositions of the copolymers prepared are shown in Table 1. The membranes made of 1 and 2 (abbreviated as PM-1 and PM-2 respectively) were prepared from benzene solutions of the corresponding copolymers: the solutions were spread with a pipet on a quartz plate (9 mm x 20 mm or 20 mm x 40 mm) and dried in vac. at room temperature. Contents of the monomeric units of $MeVCpMn(CO)_3$ in the membranes were 1.7×10^{-7} to 2.2×10^{-7} mol cm^{-2}. The KBr disks for IR measurements were prepared from the powder obtained by grinding the membranes. The quartz plate, coated with the membrane, was placed on the interior side of the photochemical reaction vessel, irradiating with a 100-W high pressure mercury lamp (Richo Kagaku UVL 100P) under normal pressure of acetylene.

The spectral changes in PM-1 on irradiation under acetylene (Fig. 1) show an increase in the absorbance at around 320 and 400 nm. This spectral change is very similar to that in PM-1 on irradiation under nitrogen gas (dinitrogen complex formation) whereas differs from that under argon (coordinatively unsaturated complex formation).$^{4c)}$ From comparison of the IR spectrum of PM-1 and that of the irradiated membrane under the atmosphere of acetylene (Fig. 2), we found the following features in the IR spectra of the latter: 1) the characteristic absoption peak at 1740 cm^{-1}, assigned to $\nu_{C\equiv C}$ of the coordinated acetylene is observed, 2) the decrease in the ν_{Mn-CO} intensities at ca. 660 and 640 cm^{-1} are shown, and 3) the absorption peaks at 1955 and 1890 cm^{-1}, both of which are assigned to ν_{CO} of the MeVCpMn(CO)$_2$(HC≡CH) moieties, are observed. The dependences of the relative intensity$^{5)}$ of the band at 1740 cm^{-1}(I_r(C≡C)) and that of the Mn-CO at ca. 660 cm^{-1}(I_r(Mn-CO)) on the irradiation time(Fig. 3) show that the value of I_r(Mn-CO) decreases with an

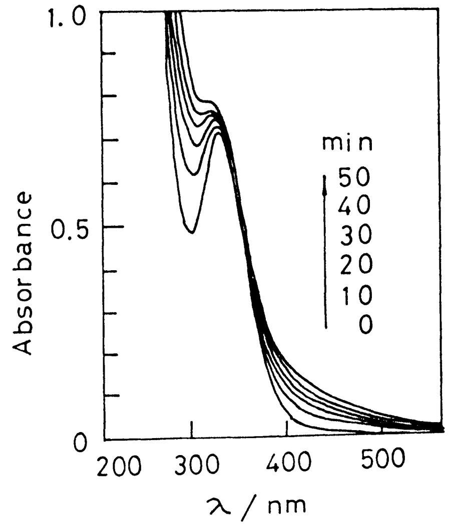


Fig. 1. Spectral change in the PM-1 on irradiation of UV light under normal pressure of acetylene at room temperature.

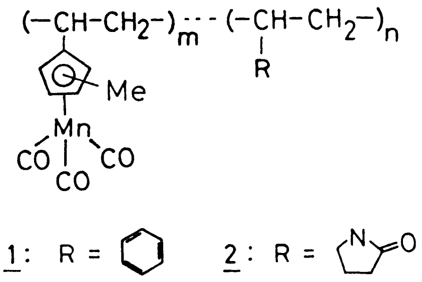


Table 1. Compositions of the Copolymers

Copolymer	Mole fraction in the copolymer$^{a)}$ m	n
MeVCpMn(CO)$_3$-co-St	0.21	0.79
MeVCpMn(CO)$_3$-co-VPRo	0.18	0.82

a) m and n denote the mole fractions of MeVCpMn(CO)$_3$ and St or VPRo respectively.

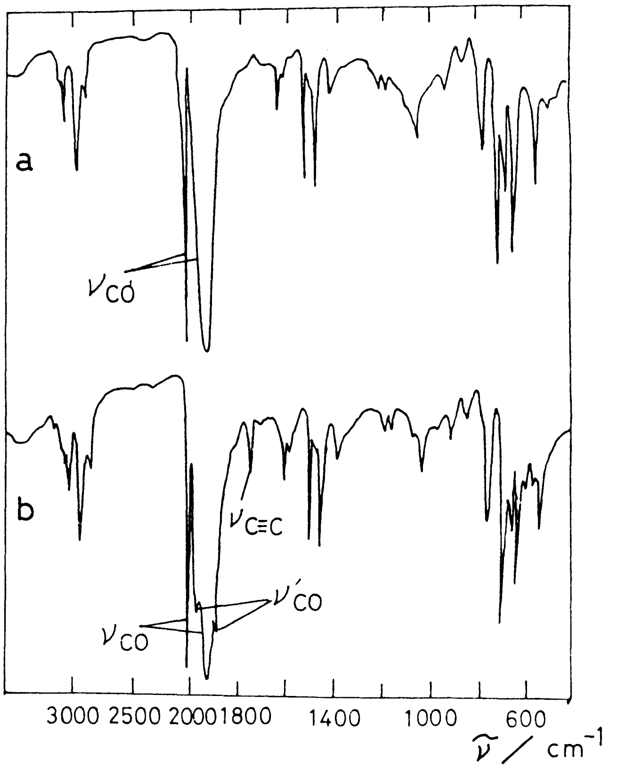


Fig. 2. IR spectra of PM-1 (a) and the irradiated PM-1 for 1 h under normal pressure of acetylene at room temperature (b).

increase in the I_r(C≡C) value. It is known that relatively strong $\nu_{C\equiv C}$ bands are observed in the IR spectra of the η^2-alkyne complexes: $\nu_{C\equiv C}$(ν_{CO}) peaks(cm^{-1}), 1840 (1981, 1921) for CpMn(CO)$_2$(HC≡CPh)$^{2)}$; (1983, 1922) for CpMn(CO)$_2$(PhC≡CPh)$^{6)}$; 1919 (2033, 1969) for CpMn(CO)$_2$(F$_3$C-C≡C-CF$_3$)$^{7)}$; 1689 for Cp(C$_6$H$_6$)Mo(HC≡CH).$^{8)}$ While the $\nu_{C=C}$ peaks of the coordinated vinylidene complexes, e.g., {CpMn(CO)$_2$}$_2$(C=CH$_2$), appears at lower frequency(1542 cm^{-1}).$^{1b)}$ When the acetylene complex of PM-1 was allowed to stand under argon at 60°C for about 20 h, the IR peak at 1740 cm^{-1} disappeared due to release of the acetylene molecules. The acetylene complex of PM-1(0.275g) in a 20 ml of test tube with a rubber cap was kept at 60°C for 25 h under Ar and, then, the evolved acetylene was determined to be 6.38 x 10^{-5} moles by means of gas chromatography. From this result, the degree of the acetylene coordination was estimated to be at least ca. 15% of the total manganese.

The results may be accounted by the following reaction mechanism.

$$\text{Ⓟ-MeCpMn(CO)}_3 \xrightarrow[\text{-CO}]{\text{UV light}} \text{Ⓟ-MeCpMn(CO)}_2 \xrightarrow{C_2H_2} \text{Ⓟ-MeCpMn(CO)}_2(C_2H_2)$$

Ⓟ = polymer back-bone

Upon irradiation of PM-2 under acetylene, the color of the membrane turned from yellow to wine-red and the absorption spectrum of the irradiated membrane is similar to that of MeCpMn(CO)$_2$(THF) which have the isosbestic points at 325 and 350 nm.$^{4c)}$ The IR frequencies of the non-irradiated and irradiated PM-2 are listed in Table 2. Upon irradiation of PM-2 under argon, the IR frequency at 1836 cm^{-1} was also observed. The results seem to suggest that the pendant pyrrolidone rings coordinate to the MeCpMn(CO)$_2$ fragments which are formed by the UV irradiation. The results account for the reaction mechanism represented in the Scheme.

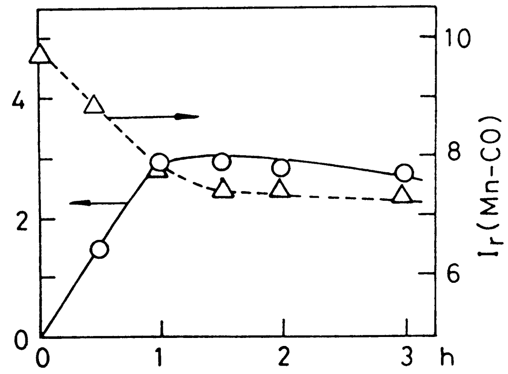


Fig. 3. Dependences of the relative intensities of $\nu_{C\equiv C}$ and ν_{Mn-CO} of PM-1 on the irradiation time.

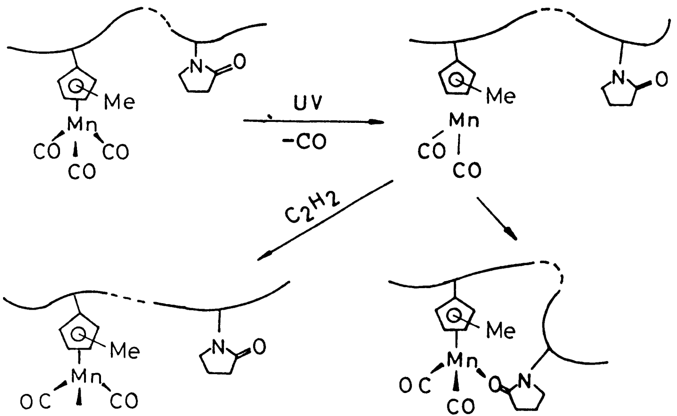
High stability of the η^2-acetylene

Table 2. IR Frequencies(cm^{-1})$^{a)}$ of MeVCpMn(CO)$_3$-co-VPRo(PM-2).

	ν_{CO}(carbonyl)			$\nu_{C=O}$(pyrrolidone)$^{b)}$	$\nu_{C\equiv C}$
Nonirradiated	2009(vs)	1920(vs)			
Irradiated under Ar$^{d)}$	2008(vs)	1920(vs)	1834(s)$^{c)}$	1655(vs)	
Irradiated under C$_2$H$_2$$^{e)}$	2009(vs)	1920(vs)	1836(s)$^{c)}$	1655(vs)	1740(w)

a) vs = very strong, s = strong, w = weak. b) $\nu_{C=O}$ of the uncoordinated pyrrolidone ring. c) Assigned to ν_{CO} of the carbonyl group which coordinates to the manganese having a pyrrolidone ring as the ligand.$^{9)}$ d) Irradiated for 1 h under normal pressure of Ar at room temperature. e) Irradiated for 1 h under normal pressure of acetylene at room temperature.

complex of PM-1 may be ascribed to that the MeCpMn-$(CO)_2(HC{\equiv}CH)$ moieties in the membrane are tightly bound to the polymer back-bone, therefore, their transrational and rotational motions are greatly suppressed. It may be suggested that, even at higher temperature, the polymer complex in the membranes would exhibit similar behavior to that of the corresponding monomeric complex in such matrices as argon and dinitrogen prepared at low temperature.[1d)] Consequently, the polymer-bound acetylene complex prepared from PM-1 was found to very stable: no appreciable change in the IR and absoption spectra of the irradiated PM-1 was observed for several days under atmospheric air at room temperature.



Scheme

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No 58550598).

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9) The carbonyl stretching frequencies of $CpMn(CO)_2(THF)$ are 1930 and 1845 cm^{-1}.[1d)]

(Received September 1, 1983)