

동종이핵착물인 $M^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5$ ($M^+=\text{Na}^+$, PPN^+)와 염화알릴간의 반응에 대한 반응속도론적 연구

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(2004. 4. 19 접수)

Kinetic Studies on the Reaction of the Homobimetallic Anion, $M^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5$ ($M^+=\text{Na}^+$, PPN^+) with Allyl Chloride

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(Received April 19, 2004)

요약. 동종이핵착물인 $M^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5$ ($M^+=\text{Na}^+$, PPN^+)과 염화알릴과의 반응을 고순도 질소속에서 염화알릴을 다량 넣어서 유사 1차 반응조건에서 다양한 온도(20 °C~50 °C)에서 반응시켰다. 이 동종이핵착물을 네 개의 원자를 있는 전이 상태를 거치는 단일 단계 반응과 관련되는 것으로 보인다. 이러한 전이 상태 후 CO와 만나서 $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_3$ 와 $(\eta^1\text{-allyl})\text{Mn}(\text{CO})_5$ 로 이어지는 것 같다. 그러나 양이온이 Na^+ 인 경우, 이 양이온은 이 반응에서 동종이핵착물의 $\text{Mn}(\text{CO})_5$ 부분에서 CO하나를 $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$ 쪽으로 이동시켜 결국 $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_3$ 로 만들거나 혹은 양이온(Na^+)과 이탈기인 Cl을 끌어당겨서 반응을 가속화시키는 역할을 하는 것으로 생각되었다. 이 반응은 각각의 반응물질에 관해서 1차, 따라서 전체적으로 2차 반응이며 이 반응에 관련된 활성화 에너지 관련 매개변수들은 다음과 같다(양이온이 Na^+ 인 경우 $\Delta H^\ddagger=17.15\pm 0.17$ kcal/mol, $\Delta S^\ddagger=-9.63\pm 0.10$ e.u.; 양이온이 인 경우 $\Delta H^\ddagger=22.13\pm 0.21$ kcal/mol, $\Delta S^\ddagger=9.74\pm 0.19$ e.u.).

주제어: 동종이핵착물, 염화알릴

ABSTRACT. The homobimetallic anion, $M^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5$ ($M^+=\text{Na}^+$, PPN^+) was disrupted by $\text{CH}_2\text{CHCH}_2\text{Cl}$ in THF at various temperatures (20 °C~50 °C) under the pseudo 1st order reaction conditions where excess of allyl chloride was employed under a nitrogen atmosphere. This homobimetallic anion seems to be involved in a concerted reaction mechanism in which a four-centered transition state is proposed. After undergoing the transition state, this reaction eventually leads to $(\text{MeCp})\text{Mn}(\text{CO})_3$ on addition of CO and $(\eta^1\text{-allyl})\text{Mn}(\text{CO})_5$, respectively. However, in case of Na^+ analog, Na^+ may play a novel counter ion effect on the disruption reaction either by transferring one terminal CO from the $\text{Mn}(\text{CO})_5$ moiety on to the $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$ of the corresponding homobimetallic complex, eventually resulting in $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_3$ or through the interaction between Na^+ and the leaving group (Cl) of allyl chloride. This reaction is of overall second order with respect to homobimetallic complex with the activation parameters ($\Delta H^\ddagger=17.15\pm 0.17$ kcal/mol, $\Delta S^\ddagger=-9.63\pm 0.10$ e.u. for Na^+ analog; $\Delta H^\ddagger=22.13\pm 0.21$ kcal/mol, $\Delta S^\ddagger=9.74\pm 0.19$ e.u. for PPN^+ analog reaction).

Keywords: Homobimetallic Complex, Allyl Chloride

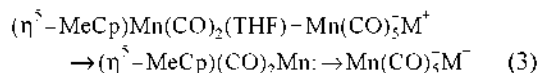
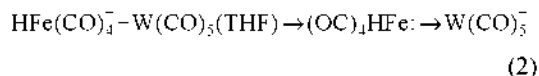
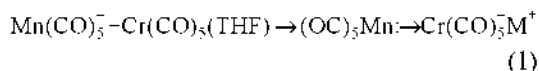
INTRODUCTION

Organometallic chemistry has enjoyed tremendous growth in the last about 30 years. The use of organometallic complexes to model heterogeneous catalyst systems and as homogeneous catalysts themselves gave a practical reason for studying fascinating complexes that have very different properties than Werner-type complexes.¹

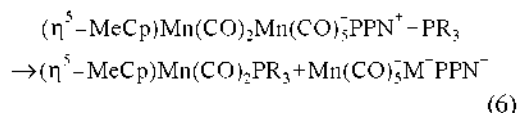
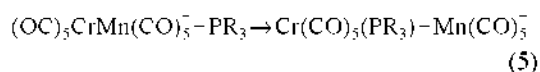
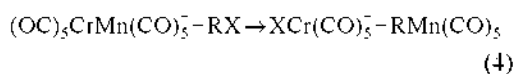
Interest in bimetallic organometallic compounds is based on the expectation that their chemical behavior both in stoichiometric synthesis and in catalysis may differ significantly from that of the analogous mononuclear complexes.²

It has been proposed that organometallic reactions occur through a sequence of 16 and 18 electron intermediates. Although there are exceptions to this rule, it is quite valuable in discussing organometallic reactions.³

Interest in heterobimetallics is growing due to their usefulness as homogeneous catalysts.⁴ These complexes are often a combination of an electron-rich and an electron-deficient metal moiety. The metal-metal bond of this type in the hetero- or homobimetallic complex may be described as a donor-acceptor bond or dative metal-metal bond (eq. 1, eq. 2 and eq. 3).^{5,6,7}

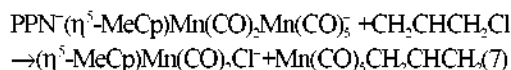


Recently We have been interested in the reactions involving $(\text{OC})_5\text{CrMn}(\text{CO})_5\text{M}^-$ and $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5\text{M}^+$ ($\text{M}^+ = \text{Na}^+$, PPN^+). This bimetallic anion reacts either with organic halides or with PR_3 as shown in the following equations (eq. 4, 5, 6).⁷



It is widely accepted that most of homobimetallics may have rather covalent character in their metal-metal bond; however, this homobimetallics anion is likely to have a donor-acceptor metal-metal bond character as usual heterobimetallics would have.

Such a Lewis acid-base relationship in Mn-Mn bond may be in part evidenced by the following disruption reactions (eq. 7).



For the last two decades much effort has been directed to elucidate the counter ion effects on those reactions involving mononuclear carbonylates such as $\text{HFe}(\text{CO})_4^-$,⁸ $\text{Mn}(\text{CO})_5^-$,⁹ $\text{Co}(\text{CO})_4^-$,¹⁰ $\text{CpMo}(\text{CO})_3^-$,¹¹ and $\text{CpW}(\text{CO})_3^-$,¹²; however, not much work has been done to understand the counter ion effect on the reactions of anionic bimetallics.

Here we report some novel kinetic results from the $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5\text{M}^+$ ($\text{M}^+ = \text{Na}^+$, PPN^+) disrupted by allyl chloride.

EXPERIMENTAL

An inert-atmosphere glove box, Schlenk wares and high vacuum line were employed for most of sample transfers and manipulations. Infrared spectra were recorded on a Bruker IFS-48 spectrophotometer using 0.10 mm sealed CaF_2 , KBr or NaCl solution cells. Temperature was controlled with Haake A81 thermostat.

Photoreactions were performed using a 550 watt Hg vapor lamp covering a rather broad range of UV-VIS wavelengths. Solvents were distilled and degassed under a N_2 atmosphere from appropriate drying and O_2 scavenging agents: tetrahydrofuran (THF), Na/benzophenone; hexane, Na/benzophe-

none: methylene chloride, P_2O_5 ; acetonitrile, CaH_2 followed P_2O_5 ; methanol, Mg/I_2 . All other liquid substrates were degassed by the freeze-pump-thaw cycles before being used in the dry-box or under Ar. All other reagents were purchased from ordinary vendors and used as received without further purification.

Preparation of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$.⁶ The preparation procedure of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ is similar to a method in the literature. A solution of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$ (0.654 g, 3.0 mmol) in freshly distilled THF (90 ml) is photolyzed for 24 min. with nitrogen purge, or until >80% of the IR bands of the tricarbonyl complex ($\nu(\text{CO})$ IR(THF): 2017(s), 1929(s) cm^{-1}) is replaced by those of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$. ($\nu(\text{CO})$ IR(THF): 1923(s), 1847(s) cm^{-1}). A slow, steady flow of N_2 through the solution during photolysis assists in removal of CO and prevents the reverse reaction.

Preparation of $\text{Mn}(\text{CO})_5^- \text{M}^+$ ($M^+=\text{Na}^+$, PPN^+). A 40 ml THF solution of dimanganese decacarbonyl (2.0 g) was added to 5 g of 1% sodium (Na) in mercury (Hg). Then the solution was stirred for about 1 hr at room temperature until the infrared spectrum showed only the bands from the $\text{Mn}(\text{CO})_5^- \text{Na}^+$ ($\nu(\text{CO})$ IR(THF): 1897(s), 1863(s), 1831(s) cm^{-1}). The yield was 93%.

$\text{Mn}(\text{CO})_5^- \text{PPN}^+$ (1.0 mmol) was prepared by adding degassed CH_2Cl_2 solution (10 ml) of PPNCl (1.2 mmol) to THF solution (30 ml) of $\text{Mn}(\text{CO})_5^- \text{Na}^+$ (1.0 mmol) at ambient temperature under N_2 . Followed by 1 hr stirred at room temperature, this solution resulted in the precipitation of Na^+Cl^- . The yield was 80%. $\nu(\text{CO})$ IR(THF) 1895(s), 1861(s) cm^{-1} .¹³

Preparation of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^- \text{M}^+$ ($M^+=\text{Na}^+$, PPN^+).⁷ To an N_2 -filled 200 ml Schlenk flask is added 0.37 g (0.50 mmol) of $\text{Mn}(\text{CO})_5^- \text{Na}^+$. Freshly prepared $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ (1.0 mmol, in ~100 ml of THF) is added via cannula to the flask containing the $\text{Mn}(\text{CO})_5^- \text{M}^+$. The mixture is stirred for 5 min after which the solution is concentrated to 5 ml under vacuum. n-Hexane is slowly added to precipitate out a red-brown solid. The mother liquid is removed via cannula and solid washed

twice with n-hexane. During this time the excess of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ and $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$ is removed by hexane. This procedure may be repeated to obtain the spectroscopically pure product. (Note: In some instance, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$ could not be completely removed and the product may slowly decompose in solution.) The solid is redissolved in THF (~50 ml) and filtered in a 50 ml Schlenk flask with a Celite containing glass filter to remove the decomposed compound. The solvent is removed under reduced pressure and the product is rinsed with 15 ml of cold n-hexane. The resulting $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^- \text{M}^+$ (Na^+ =320 mg, 69% yield $\nu(\text{CO})$ IR(THF) 2005(m), 1920(m, sh), 1905(m, sh), 1885(s), 1852(s), 1822(m); PPN^+ 320 mg, 69% yield $\nu(\text{CO})$ IR(THF) 2005(m), 1920(m, sh), 1905(m, sh), 1890(s), 1858(s), 1816(w, sh) Anal. calcd. for $\text{C}_{19}\text{H}_{17}\text{Mn}_2\text{O}_7$: C, 63.72, H, 4.04, N, 1.52 Found: C, 63.51, H, 4.23, N, 1.12) is characterized spectroscopically and by elemental analysis.

The product, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^- \text{M}^+$ is air sensitive and should be stored under an inert gas atmosphere below -20°C ($(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^- \text{PPN}^+$ is air sensitive and should be stored under an inert gas atmosphere below 0°C).

Reaction of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^- \text{M}^+$ ($M^+=\text{PPN}^+$, Na^+) with Allyl chloride ($\text{CH}_2\text{CHCH}_2\text{Cl}$). The kinetic experiments were carried out in dried 10 ml volumetric flasks which were securely fitted with rubber septa. Usually 10 ml of THF was added to mixture of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^- \text{M}^+$ ($M^+=\text{PPN}^+$, Na^+) (0.05 mmol) and 20-fold excess of allyl chloride in a 10 ml vol. flask via cannula at ambient temperature. This THF solution was shaken for a few minutes prior to being kept in a water bath (note: water bath equipped with a constant-temperature control of 0.1°C) set at a specific temperature. Samples for IR spectral analysis were withdrawn periodically with a syringe and placed in a sealed 0.1 mm path-length KBr or CaF_2 infrared cell. Rates of reaction were observed by following the disappearance in absorption of the reactant's $\nu(\text{CO})$ IR which did not overlap with the other carbonyl bands: $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^- \text{PPN}^+$ = 1861 cm^{-1} ; Na^+ =1859 cm^{-1}).

Table 1. Infrared data for relevant complexes

Complex	$\nu(\text{CO})/\text{IR}$
$\text{PPN}^-(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-$	2016 (w), 1927 (m, sh), 1893 (s), 1861 (s), 1825 (w, sh)
$\text{Na}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-$	2005 (w), 1914 (m, sh), 1905 (m, sh), 1885 (s), 1852 (s), 1822 (m)
$(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$	1923 (s), 18470 (s)
$\text{PPN}^-(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Cl}^-$	1893 (s), 1816 (s)
$(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{PPh}_3$	1920 (s), 1855 (s)
$(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_3$	2017 (s), 1930 (s)
$\text{PPN}^-[Mn(\text{CO})_5]^-$	1894 (s), 1861 (s)
$\text{Na}^+[Mn(\text{CO})_5]^+$	2063 (m), 1980(s), 1974(s), 1960(s)
$Mn(\text{CO})_5(\text{CH}_2\text{CHCH}_2)$	1987 (m), 1974 (s), 1951 (s)
$\text{PPN}^-[Mn(\text{CO})_5\text{PPh}_3]^-$	1941 (m), 1846 (w), 1809 (s)
$\text{PPN}^-[Mn(\text{CO})_5\text{P}(\text{OMe})_3]^-$	1954 (m), 1858 (w), 1820 (s)
$\text{PPN}^-[Mn(\text{CO})_5\text{PEt}_3]^-$	1958 (m), 1823 (w), 1790 (s)

Under the pseudo-first-order reaction conditions where at least more than a 20-fold excess of allyl chloride with respect to that of the homobimetallic compound was employed, the rate constants were calculated using a linear least squares program for the first-order rate plots of $[A_t - A_\infty]$ vs time, where A_t is the absorbance at time t and A_∞ is the one at time infinity. Products such as $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{-}(\text{CH}_2\text{CHCH}_2)$, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_3$, $Mn(\text{CO})_5(\text{CH}_2\text{CHCH}_2)$ and $Mn(\text{CO})_5$ were identified by their IR $\nu(\text{CO})$ spectra as compared with those of the authentic compounds previously isolated and characterized in our laboratory.

RESULTS AND DISCUSSION

The synthesis of the anionic homobimetallic complex, $M^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-$ ($M^+ = \text{PPN}^+$, Na^+) was achieved by the simple addition of $M^+\text{Mn}(\text{CO})_5$ to $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ freshly prepared from the photochemical reaction of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_3$ in THF at ambient temperature under N_2 as depicted in Eq. (3).

Here this homobimetallic anion has a Mn-Mn bond resembling donor-acceptor metal-metal bond where $Mn(\text{CO})_5$ is considered as a Lewis base and $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$, a Lewis acid. This relationship seems to hold good, based on the shift of the IR carbonyl spectra of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$ moiety of the homobimetallic complex to the lower frequencies (1890 , 1816 cm^{-1}) compared with those of $(\eta^5\text{-$

$\text{MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ (1923 , 1847 cm^{-1}) (Table 1).

The electron density built up on Mn of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$ moiety due to the donor $(Mn(\text{CO})_5^-)$ may be in part back-donated through $d_\pi\text{-}p_\pi^*$ orbital interaction to terminal CO of $(\eta^5\text{-MeCp})\text{Mn}$ moiety of the homobimetallic compound.

Similar situation was also observed at $\text{PPN}^-(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Cl}^-$ (1893 , 1816 cm^{-1}).¹⁴ This interpretation is further supported elsewhere from the relative ligating ability comparison of anionic transition metal complexes, transition metal hydrides, and traditional ligands to $Mn(\text{CO})_5$.¹⁶

Reaction of $M^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-$ ($M^+ = \text{Na}^+$, PPN^+). Reactions of $M^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-$ ($M^+ = \text{Na}^+$, PPN^+) with a 20 fold excess of allyl chloride in THF were monitored by the IR carbonyl peak change. This reaction follows overall second order dependence on the reactants: first order with respect to $[M^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{-}Mn(\text{CO})_5^-]$ and another first order with respect to [allyl chloride].

The rate is represented by Eq. 8⁷ as is evidenced in Fig. 1, 2, 3, 4 and Table 2.

$$\begin{aligned} \text{rate} &= k_{\text{obs}}[M^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-] \\ k_2 &= K_{\text{obs}}/[\text{CH}_2\text{CHCH}_2\text{Cl}] \\ \text{rate} &= k_2[M^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-] \\ &\quad [\text{CH}_2\text{CHCH}_2\text{Cl}] \end{aligned} \quad (8)$$

Determination of the Activation Parameters. The second order rate constants, k_2 , was also obtained for the reaction in THF at various temperatures

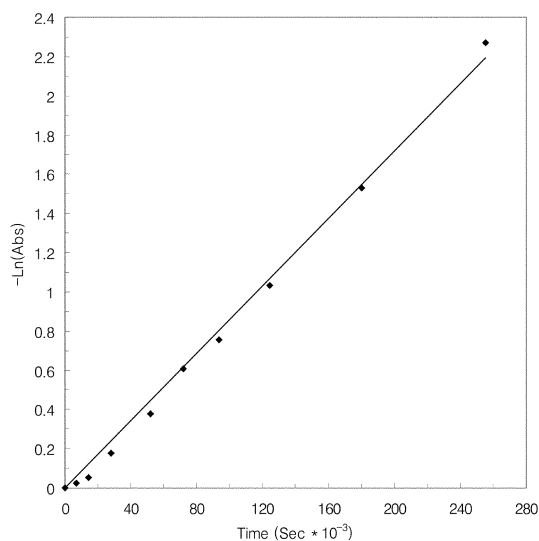


Fig. 1. Pseudo 1st order plot reaction of $\text{PPN}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_2$] (5.0 mM) with $\text{CH}_2\text{CHCH}_2\text{Cl}$ (25 mM) in THF at 40 °C.

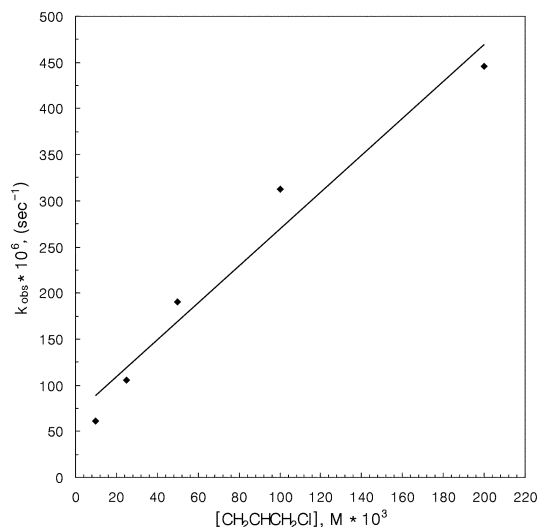


Fig. 3. Plot of k_{obs} vs. $[\text{CH}_2\text{CHCH}_2\text{Cl}]$ for the reaction of $\text{PPN}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_2$] in THF at 40 °C.

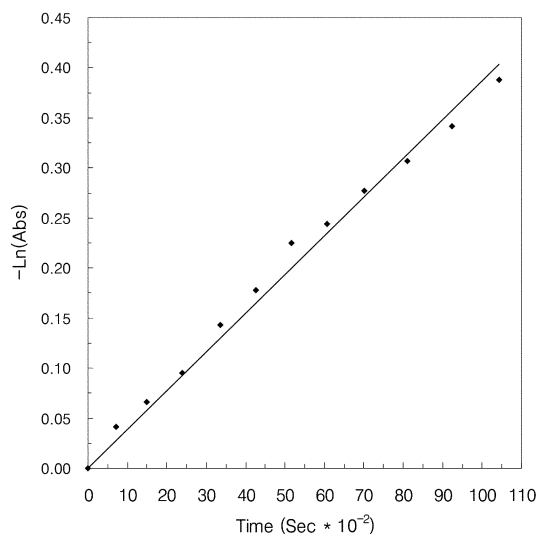


Fig. 2. Pseudo 1st order plot of reaction of $\text{Na}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_2$] (5.0 mM) with (100 mM) in THF at 20 °C.

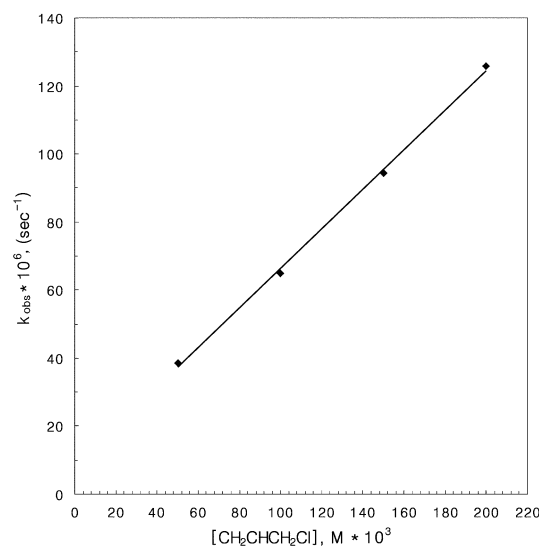


Fig. 4. Plot of k_{obs} vs. $[\text{CH}_2\text{CHCH}_2\text{Cl}]$ for the reaction of $\text{Na}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_2$] in THF at 20 °C.

(Table 3), in which the rates are linearly dependent upon temperature.

The activation parameters were calculated from the Eyring plot (Fig. 5, 6). The activation parameters ($\Delta H^\ddagger=22.34\pm 0.45$ kcal/mol, $\Delta S^\ddagger=9.74\pm 0.19$ e.u. for PPN^+ analogue; $\Delta H^\ddagger=17.15\pm 0.17$ kcal/mol, ΔS^\ddagger

$=-9.63\pm 0.10$ e.u. for Na^+ analogue, Table 4.) together with the rate being overall the second order: first order with respect to $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_2$ (M^+) and another first order with respect to [allyl chloride] strongly suggest a associative character at the rate-determining step, which may involve the initial cleavages of Mn-Mn bond and C-Cl bond followed by the formations of Mn-C bond and Mn-

Table 2. The relationship between $\text{CH}_2\text{CHCH}_2\text{Cl}$ concentrations and the rates of the reaction of $\text{M}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_2\text{J}^-$ ($\text{M}^+=\text{Na}^+$ at 20 °C, PPN^+ at 40 °C) in THF

Homobimetallics	Conc., M^a (fold) ^b	$k_{\text{obs}} \times 10^6$
$\text{PPN}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_2\text{J}^-$	0.010 (2)	61.00 ± 0.60
	0.025 (5)	85.90 ± 0.40
	0.050 (10)	190.40 ± 5.70
	0.100 (20)	312.70 ± 0.66
	0.200 (40)	445.90 ± 0.75
$\text{Na}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_2\text{J}^-$	0.050 (10)	38.66 ± 0.43
	0.100 (20)	64.83 ± 0.71
	0.150 (30)	94.48 ± 0.47
	0.200 (40)	125.70 ± 1.88

^aMolar concentration of $\text{CH}_2\text{CHCH}_2\text{Cl}$; ^bFigures in parenthesis indicate the number of fold in excess with respect to the concentrations of homobimetallics.

Table 3. Temperature dependence on the reaction of $\text{M}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_2\text{J}^-$ ($\text{M}^+=\text{Na}^+$, PPN^+) with $\text{CH}_2\text{CHCH}_2\text{Cl}$ in THF^a

Homobimetallics	Temp. (°C)	$k_{\text{obs}} \times 10^6$ (s ⁻¹)
$\text{PPN}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_2\text{J}^-$	25	47.2 ± 0.15
	30	79.9 ± 2.49
	35	135.0 ± 1.55
	40	312.7 ± 0.66
$\text{Na}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_2\text{J}^-$	20	64.82 ± 2.48
	25	111.83 ± 1.86
	30	180.44 ± 1.12
	35	310.29 ± 2.43
	40	422.29 ± 4.15

^a $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_2\text{M}^+=5.0$ mM, $\text{CH}_2\text{CHCH}_2\text{Cl}=100$ mM

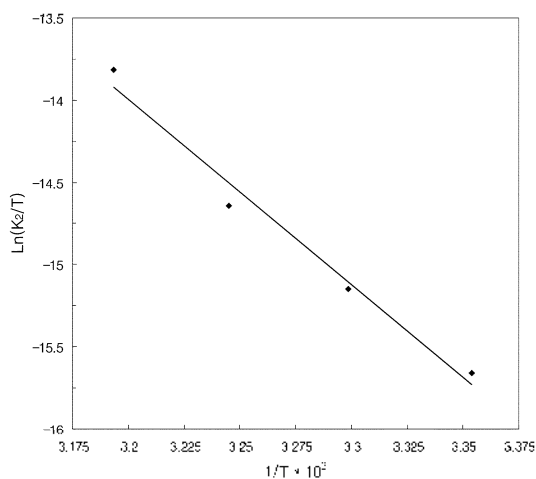


Fig. 5. Eyring plot for the reaction of $\text{PPN}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_2\text{J}^-$ (5.0 mM) with $\text{CH}_2\text{CHCH}_2\text{Cl}$ (100 mM) in THF.

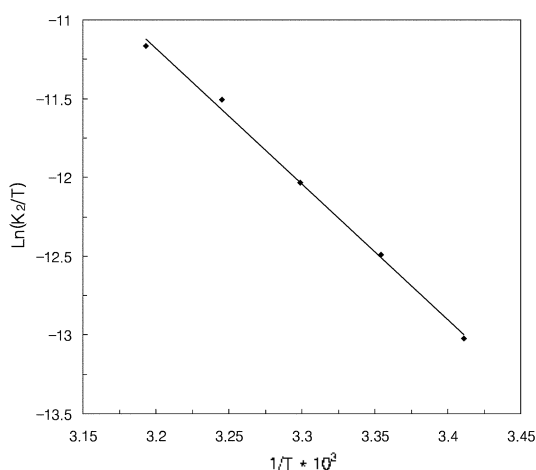
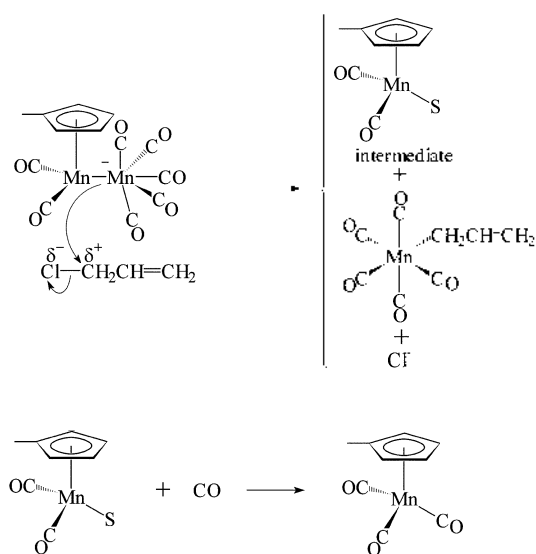


Fig. 6. Eyring plot for the reaction of $\text{Na}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_2\text{J}^-$ (5.0 mM) with $\text{CH}_2\text{CHCH}_2\text{Cl}$ (100 mM) in THF.

Table 4. Activation parameters from the reaction of $M^-(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5$ ($M^+=\text{Na}^+$, PPN⁺) with $\text{CH}_2\text{CHCH}_2\text{Cl}$ in THF

Homobimetallics	Activation parameters
PPN ⁺ ($\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5$]	$\Delta H^\ddagger = 22.13 \pm 0.21$ (kcal/mol) $\Delta S^\ddagger = 9.74 \pm 0.19$ (e.u.)
$\text{Na}^-(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5$]	$\Delta H^\ddagger = 17.15 \pm 0.17$ (kcal/mol) $\Delta S^\ddagger = -9.63 \pm 0.10$ (e.u.)



Cl bond, leading to $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{MnCl}$ and $\text{Mn}(\text{CO})_5(\text{CH}_2\text{CH}=\text{CH}_2)$, respectively (Scheme 1).

In this reaction, Na⁺ is assumed to play as a Lewis acid to pull electron density from the $\text{Mn}(\text{CO})_5$ moiety of this homobimetallic anion, which will definitely reduce its nucleophilicity; however, this small-sized cation may have another

function to interact with the leaving group (Cl⁻).

The former interaction may decrease the reaction rate (minor negative effect) while the latter one may increase the reaction rate (major positive effect).

Therefore, the so-called inverse counter ion effect is observed here in this anionic homobimetallic reaction with allyl chloride. As a result of this inverse counter ion effect on the reaction, a tremendous increase in the reaction rate was observed, when compared with that of PPN⁺ analog reaction (Table 3).

Polar coordinating solvent may stabilize the possible intermediates, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{solvent})$ and $\text{Mn}(\text{CO})_5$; however, in case of $\text{Mn}(\text{CO})_5$, the small protic polar solvent (CH_3OH) may be best choice for the stabilization of the metal carbonylate through intermolecular hydrogen bonding interactions while CH_3CN may be so effective in this respect (Table 5; Scheme 1). We previously observed the rapid formation of $\text{Mn}(\text{CO})_5(\text{CH}_2\text{CH}=\text{CH}_2)$ where PPN⁺ $\text{Mn}(\text{CO})_5$ is allowed to react with $\text{CH}_2\text{CHCH}_2\text{Cl}$ in THF at ambient temperature under nitrogen atmosphere.

Mechanistic Considerations. It looks rather surprising that we observed $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$ and $\text{Mn}(\text{CO})_5(\text{CH}_2\text{CH}=\text{CH}_2)$ as major products; however, no experimental evidence in favor of either the possible intermediate such as $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$, or the plausible product, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Cl}$ was found.

The $\nu(\text{CO})$ IR spectral variations during the reaction did not indicate those species existence.

This anionic homobimetallic, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5$ on reaction with allyl chloride in the coordination solvent such as THF, MeOH, and CH_3CN may lead to either $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{solvent})$ or $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Cl}$ at first in addition to

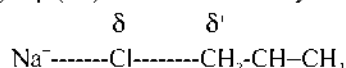
Table 5. Solvent dependence on the reaction of $M^-(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5$ ($M^+=\text{Na}^+$, PPN⁺) with $\text{CH}_2\text{CHCH}_2\text{Cl}$ at 25 °C

Homobimetallics	Solvent (ϵ)	$k_{\text{obs}} \times 10^6$ (s ⁻¹)
$\text{Na}^-(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5$]	THF (7.3)	111.83 ± 1.86
	MeOH (32.7)	634.47 ± 6.31
	CH_3CN (36.2)	109.81 ± 6.59
PPN ⁺ ($\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5$]	THF (7.3)	47.2 ± 0.15
	MeOH (32.7)	661.40 ± 6.31
	CH_3CN (36.2)	96.47 ± 6.59

$\text{Mn}(\text{CO})_5(\text{CH}_2\text{CHCH}_2)$.

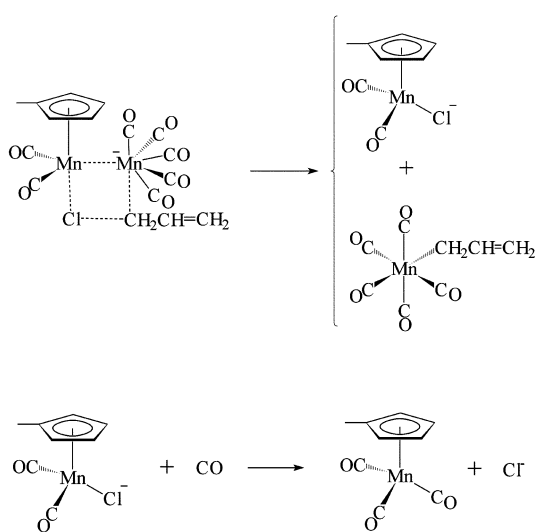
Either $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_5(\text{solvent})$ or $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_4\text{Cl}$ on reaction with the CO dissolved in solvent due to the decomposition of the metal carbonyl species during the reaction may easily yield $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_5$.

Here, Na^+ pulls electron density on the anionic metal (Mn) center so that the nucleophilicity of this homobimetallic anion may be decreased to some degree; however, this small-sized cation may induce increase in the reaction rate by the interaction with the leaving group (Cl⁻) on reaction with allyl chloride.



In case Na^+ pulls electron density from the Cl moiety of allyl chloride, the $\text{CH}_2(\text{sp}^3)$ moiety attached directly to Cl should be similar to the $\text{CH}_2(\text{sp}^2)$; therefore, this CH_2 group may become so partially positive as to accept the nucleophile's attack, which may lead to increase in reaction rate compared with that of PPN⁺ analog reaction. This is so-called inverse counter ion effect especially when the small-sized cation is involved in interaction with some activated organic halides such as benzyl halides or allyl halides (Scheme 2).

Also, Na^+ is well known to promote bridging car-

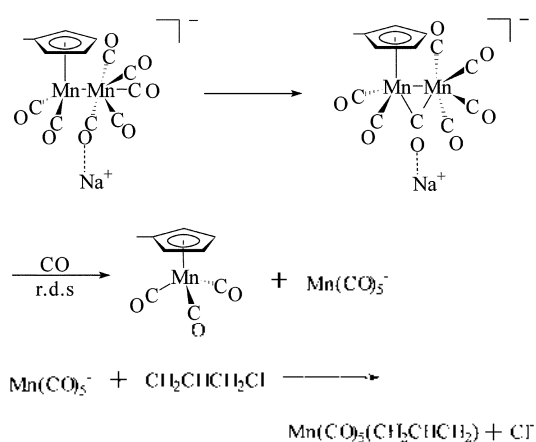


Scheme 2. Concerted reaction mechanism.

bonyl in the bimetallic complex as well as Lewis acid does.¹⁵ In this circumstance of the homobimetallic anion with allyl chloride, Na^+ pulls electron density from the bridging carbonyl oxygen, leading to more stable sp_2 hybridized carbonyl carbon from that terminal sp hybridized carbonyl carbon. This carbonyl-bridged bimetallic intermediate may undergo a structural reorganization; The $\mu^2\text{-CO}$ is transformed into a terminal CO producing $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_5$ moiety. At this moment of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_5$ formation, the other moiety of this homobimetallic anion, $\text{Mn}(\text{CO})_4^-$ may pick CO dissolved in the solvent, leading to $\text{Mn}(\text{CO})_5^-$, which can rapidly react with $\text{CH}_2\text{CHCH}_2\text{Cl}$, ending up with $\text{Mn}(\text{CO})_5(\text{CH}_2\text{CHCH}_2)$ eventually. However, $\text{Mn}(\text{CO})_4$ or $\text{Mn}(\text{CO})_4(\text{THF})$ is not likely to survive for further reactions due to the thermal instability (Scheme 3).

Scheme 3 (consecutive reaction pathway), however, may have some drawbacks in describing this reaction pathway.

First, the kinetic experimental is of overall second order; first order with respect to [homobimetallic anion] and another first order with respect to [allyl chloride]. However, the rate-determining step of this consecutive reaction is involved in the Mn-Mn bond cleavage, which indicates that this reaction is of first order with respect to [homobimetallic anion] only. Moreover, $\text{Mn}(\text{CO})_5^-$, in this case, is assumed to be an intermediate which is likely to rapidly



Scheme 3. Concerted reaction pathway.

react with allyl chloride to yield $\text{Mn}(\text{CO})_5(\text{CH}_2\text{CHCH}_2)$. When Na^+ is involved, we also should overcome the extremely unstable $\text{Mn}(\text{CO})_4$ species as a result of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_3$ with the aid of Na^+ as shown Scheme 3.

$\text{Mn}(\text{CO})_4$ species on reaction with CO will get into a far more stable $\text{Mn}(\text{CO})_5^-$. However, $\text{Mn}(\text{CO})_4^-$ (solvent) $^-$ will definitely undergo decomposition.

A more plausible description as to the reaction pathway can be made in Scheme 2 (concerted reaction mechanism), where we may propose 4-centered transition state through which $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Cl}^-$ and $\text{Mn}(\text{CO})_4(\text{CH}_2\text{CHCH}_2)$ may be formed simultaneously. Here, Na^+ can function as a binder ($\Delta S^\ddagger = -9.63$ e.u.) and may be involved in leaving group assistance on interaction with Cl^- of allyl chloride. However, polar solvent contribution to the stability of the possible intermediate may be somewhat limited, which may suspect the polar solvent effect on the reaction rate (Table 4).

Scheme 1(polar S_N2 type reaction pathway) is likely to be another candidate for describing the reaction mechanism. However, this homobimetallic anion is rather a weaker nucleophile than $\text{Mn}(\text{CO})_5^-$ because $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$ moiety is considered a Lewis acid moiety which pulls electron density from $\text{Mn}(\text{CO})_5^-$ in this homobimetallic anion. As a result of weak nucleophile, this homobimetallic anion may attack allyl chloride to yield $\text{Mn}(\text{CO})_5(\text{CH}_2\text{CHCH}_2)$ and $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$ species. However, here at this moment of homobimetallic anion's attack at allyl chloride, the Mn-Mn bond should be broken and the new Mn-C bond formation may occur at the same time.

However, the leaving group, Cl^- either goes to PPN^+ , or cling to $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$ species to form $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Cl}^-$. These two possibilities seem to be open for discussion. We should also notice that $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$ moiety can pick up CO dissolved in the solvent without the formation of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Cl}^-$, leading to the product, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_3$, both in Scheme 1 and Scheme 2.

Acknowledgement. The author(Y. K. Park) appreciates the supports from both the Korea Science and

Engineering Foundation(016042-1-2) and Kangwon National University.

REFERENCES

- (a) R. G. Wilkins, *The study of Kinetics and Mechanism of Reactions of Transition Metal Complexes* (Boston: Allyn and Bacon, 1974).
- Review articles include: (a) Muetterties, E. L.; Krause, M. *J. Angew. Chem. Int. Ed. Engl.* 1983, 22, 147. (b) Roberts, D. A.; Geoffroy, G. L. *In Comprehensive Organometallic Chemistry* Wilkinson, E. Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, UK, 1982; Vol. 6, Chapter 40, pp 763-877. (c) Gladfeldter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* 1980, 18, 207. (d) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* 1993, 32, 923. (e) Barlow, S.; O'Hare, D. *Chem. Rev.* 1997, 97, 637. (f) Dirk Tews and Petra Escarpa Gaede, *Organometallics* 2001, 20, 3869-3875.
- C. A. Tolman, *Chem. Soc. Rev.* 1972, 1, 337.
- (a) Roberts, D. A.; Geoffroy, G. L. in *Comprehensive Organometallic Chemistry*, Wilkinson, G. Ed.; Pergamon Press: Oxford, 1982, 763. (b) Casey, C. P.; Bullock, R. M. *Organometallics* 1984, 3, 1100. (c) Amdt, L. W.; Darensbourg, M. Y.; Delord, T.; Bancroft, B. T. *J. Am. Chem. Soc.* 1986, 108, 2617. (d) Rosenberg, S.; Mahoney, W. S.; Hayes, J. M.; Geoffroy, G. L. *Organometallics* 1986, 5, 1065. (e) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* 1987, 20, 167.
- Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *J. Chem. Soc. Chem. Commun.* 1983, 854.
- Butler, I. S.; Coville, N. J.; Cozak, D. *Inorg. Synth.* 1978, 19, 188.
- (a) Park, Y. K.; Han, I. S.; Huh, T. S. *Bull. Korean Chem. Soc.* 1990, 11, 221. (b) Park, Y. K.; Kim, G. S.; Song, G. O. *Bull. Korean Chem. Soc.* 1995, 16, 310. (c) Park, Y. K.; Han, I. S.; Kim, J. H.; Lee, C. J.; Baek, Y. O.; Song, G. O. *Bull. Korean Chem. Soc.* 1994, 15, 537. (d) Park, Y. K.; Kim, S. J.; Kim, I. H.; Han, I. S.; Lee, C. H. *J. Organomet. Chem.* 1991, 408, 193. (e) Yong Kwang Park, Seon Joong Kim, Chang Hwan Rhee. *Bull. Korean Chem. Soc.* 1998, 19, 462.
- Collman, J. P. *Acc. Chem. Res.* 1975, 8, 342.
- Darensbourg, M. Y.; Darensbourg, D. J.; Drew, D. A.; Burns, D. *J. Am. Chem. Soc.* 1976, 98, 3127.
- Moro, A.; Foa, M.; Cassar, L. *J. Organomet. Chem.* 1980, 212, C68.
- (a) Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R.; Hankel, J. M.; Kump, R. L. *J. Am. Chem. Soc.* 1982, 104, 1521. (b) Darensbourg, M. Y.; Jimenez, P.; Sack-

- ett, J. R. *J. Organomet. Chem.* **1980**, *202*, C68.
12. Winston, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 2055.
13. K. Y. Lee; D. J. Kuchynka and J. K. Kochi. *Organometallis.* **1987**, *6*, 1886.
14. Butts, S. B.; Sttauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093.
15. Park, Y. K.; Lee, Y. G.; Kim, G. S. *Bull. Korean Chem. Soc.* **1996**, *17*, 138.
16. Park, Y. K.; Lee, *Bull. Korean Chem. Soc.* **1994**, *15*, 436.
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