

$(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ 와 PR_3 ($\text{R}=\text{Me}$, OEt , C_6H_5) 리간드와의 반응에 대한 반응속도론적 연구

김상혁 · 유 민 · 박성국 · 이도형 · 윤동신[†] · 김진호 · 박용광*

강원대학교 자연과학대학 화학과

[†]고려대학교 이과대학 화학과

(2008. 9. 12 접수)

Kinetic Studies on the Reaction of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ with PR_3 ($\text{R}=\text{Me}$, OEt , C_6H_5)

Sang Hyuck Kim, Min Yoo, Sung Kuk Park, Do Hyung Lee, Dong Shin Yun[†],
Jin Ho Kim, and Yong Kwang Park*

Department of Chemistry, Kangwon National University, Gangwon-do 200-701, Korea

[†]Department of Chemistry, Korea University, Seoul 136-701, Korea

(Received September 12, 2008)

요 약. 용매가 배워된 카르보닐 착물인 $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ 가 PR_3 ($\text{R}=\text{Me}$, OEt , C_6H_5) 리간드와의 저온(0-20°C) 반응에서 해리적인 치환 반응하는 것으로 밝혀졌다. 이 경우 PR_3 리간드의 농도는 착물의 농도의 10배인 유사 1차반응 조건을 따랐으며 이 리간드 치환반응은 전체적으로 착물의 농도에 대하여 1차 반응이었으며 양의 값의 엔트로피 변화 값을 갖는다(PMe_3 의 경우 $\Delta S^\ddagger = 2.3$ e.u.; $\text{P}(\text{OEt})_3$ 의 경우 $\Delta S^\ddagger = 11.64$ e.u.; $\text{P}(\text{C}_6\text{H}_5)_3$ 의 경우 $\Delta S^\ddagger = 10.52$ e.u.). 또한 엔탈피 변화 값은 다음과 같다(PMe_3 의 경우 $\Delta H^\ddagger = 20.52$ kcal/mol; $\text{P}(\text{OEt})_3$ 의 경우 $\Delta H^\ddagger = 23.49$ kcal/mol; $\text{P}(\text{C}_6\text{H}_5)_3$ 의 경우 $\Delta H^\ddagger = 23.10$ kcal/mol). 위의 두 값(엔트로피 변화 값과 엔탈피 변화 값)과 반응속도가 착물 농도에 관해서 1차로 표현된 사실로부터 반응 중간생성물 $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$ 의 형성을 알 수 있으며 이것과 PR_3 와의 반응을 통하여 $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{PR}_3)$ 가 생성되었다. 그러나 온도가 30°C 이상 되면 반응이 착물 농도에 대하여 1차일 뿐만 아니라 PR_3 의 1차 농도에 관해서도 상당부분 비례한다는 것이 밝혀졌다. 따라서 이럴 경우 반응 메커니즘이 해리적인 치환반응에서 회합적인 치환반응으로 바뀌는 것으로 생각된다.

주제어: 리간드 치환반응, 용매가 배워된 카르보닐 착물, 반응속도론적 연구

ABSTRACT. The solventmetal carbonyl complex, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ was found to undergo a dissociative ligand substitution reaction with PR_3 ($\text{R}=\text{Me}$, OEt , C_6H_5) in THF at rather low temperatures (0°C up to 20°C) under the pseudo-first-order reaction conditions (usually 10-fold excess of PR_3 with respect to the solventmetal carbonyl complex concentrations) where the coordinating solvent, THF is displaced by PR_3 . This substitution reaction follows overall first order dependence on $[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})]$; therefore, the positive entropy change of activation ($\Delta S^\ddagger = 2.3$ e.u. for PMe_3 ; $\Delta S^\ddagger = 11.64$ e.u. for $\text{P}(\text{OEt})_3$; $\Delta S^\ddagger = 10.52$ e.u. for $\text{P}(\text{C}_6\text{H}_5)_3$), together with the similar enthalpy change of activations ($\Delta H^\ddagger = 20.52$ (kcal/mol) for PMe_3 ; $\Delta H^\ddagger = 23.49$ (kcal/mol) for $\text{P}(\text{OEt})_3$; $\Delta H^\ddagger = 23.10$ (kcal/mol) for $\text{P}(\text{C}_6\text{H}_5)_3$) is likely to ensure the possible intermediate, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$, which on reaction with PR_3 , transforms to the product, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{PR}_3)$. However, in case the reaction temperature is raised up to 30°C, this reaction is no longer dependent solely on the solventmetal carbonyl complex concentration. The reaction rate is assumed to be more or less related to the PR_3 concentration. Therefore, in this case, there is some possibility of a mechanistic reaction change from the dissociative character toward the associative one.

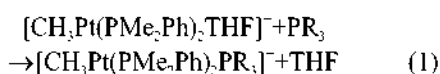
Keywords: Ligand Substitution, Solventmetal Carbonyl Complex, Kinetic Study

INTRODUCTION

Solvent-metal carbonyl complexes seem to have their possible role in homogeneous catalysis.^{1,3} Metal carbonyls of 18-electrons with η⁵-C₅H₅ react by an associative process via a pair of electrons localized on the ligand (Cp ring slip-page) in the ligand substitution reaction.⁴

However, in our substitution reaction of (η⁵-MeCp)Mn(CO)₂(THF) with PR₃, the Mn-O bond (of Mn-THF) is relatively weak compared with other metal-ligand bond so that which process (Mn-O bond cleavage vs MeCp(η⁵→η³) ring slip-page) is more facile one, will determine the reaction pathway whether it is involved in associative ligand substitution or dissociative ligand substitution.

The displacement of coordinated THF from square planar platinum(II) complex shows that the enthalpies of the reaction are -26.4 kcal/mol for P(OEt)₃ and -26.2 kcal/mol for PMe₃⁵ (Eq. 1).



Another mechanistic study on the substitution reaction of M(CO)₃(THF) (M=Cr, Mo, W) with PR₃ (at least 10-fold excess of PR₃) shows an associative process indicating the overall 2nd order kinetics and the activation parameters (ΔH[‡]=40~80 kJ/mol and ΔS[‡]=8~122 e.u.); however, there seems to be a gradual mechanistic changeover from a dissociative character toward an associative one along the series of Cr, Mo, and W.³

EXPERIMENTAL

All operations were carried out under a nitrogen atmosphere by using standard Schlenk techniques or an Ar-filled glove box. Rigorous exclusion of trace moisture and oxygen degassed as described below. Infrared spectra were recorded on a Jasco FT-IR 460 spectrophotometer using 0.10-mm sealed CaF₂ or KBr solution cells. ¹H NMR spectra were previously obtained from Varian Gemini-200FT spectro meter in solutions of CDCl₃, DMSO-d₆, and CD₃OD.⁷ The GC-MASS

spectral data were previously collected from the GC-MASS (Hewlett Packard Model GC 5890).⁷ Photochemical reactions were performed by using a 450 watt Hg vapor lamp (Hanovia). THF were distilled under nitrogen from purple sodium/benzophenone ketyl. Hexane was stirred over concentrated H₂SO₄ overnight, washed with aqueous NaHCO₃ and distilled from Na⁰/benzophenone ketyl. All other reagents purchased were reagent grade and used without further purification.

Preparation of (η⁵-MeCp)Mn(CO)₂(THF).⁶ The preparation procedure of (η⁵-MeCp)Mn(CO)₂(THF) is similar to the method in the literature. A solution of (η⁵-MeCp)Mn(CO)₂ (0.05 g, 0.2 mmol) in freshly distilled THF (50 ml) is photolyzed for 10 min with nitrogen purge. A slow, steady flow of N₂ through the solution during photolysis assists in removing CO and prevents the reverse reaction.

(η⁵-MeCp)Mn(CO)₂(THF). υ(CO)IR(THF): 1923(s), 1847(s) cm⁻¹

Identification of (η⁵-MeCp)Mn(CO)₂(PR₃) (R=Me, OEt, C₆H₅). After each kinetic experiment was over, the respective reaction mixture solution was dried under vacuum to have the oily product. This reaction mixture was then on column chromatograph using hexane/THF mixed solvent system. Products such as (η⁵-MeCp)Mn(CO)₂PR₃ (R=Me, OEt, C₆H₅) were identified by the respective (CO) spectra as compared with those of the authentic compounds previously isolated and characterized in our laboratory (Table 1).⁷

Kinetic Measurements. The kinetic experiments were carried out in a dried 10 ml vial securely fitted with a rubber septum. In a typical kinetic experiment, 0.05 mmol of (η⁵-MeCp)Mn(CO)₂(THF) freshly prepared from the photochemical reaction of (η⁵-MeCp)Mn(CO)₃ in THF at ambient temper-

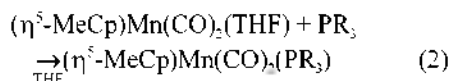
Table 1. Solution IR spectral data for (η⁵-MeCp)Mn(CO)₂PR₃ (R=Me, OEt, C₆H₅) in THF

Complexes	υ(CO), cm ⁻¹
(η ⁵ -MeCp)Mn(CO) ₃	2010(s), 1924(s)
(η ⁵ -MeCp)Mn(CO) ₂ (THF)	1920(s), 1845(s)
(η ⁵ -MeCp)Mn(CO) ₂ (PMe ₃)	1915(s), 1856(s)
(η ⁵ -MeCp)Mn(CO) ₂ (P(OEt) ₃)	1935(s), 1870(s)
(η ⁵ -MeCp)Mn(CO) ₂ (P(C ₆ H ₅) ₃)	1927(s), 1863(s)

ature under N_2 , was loaded into a 10ml vial. The respective THF solution of triethylphosphite, triphenylphosphine, or trimethylphosphine of known concentration was added by a syringe. This solution was then stirred and placed in a water bath equipped with a constant-temperature controller (± 0.1 °C). Samples for IR spectral analysis were withdrawn periodically with a syringe and placed in a sealed 0.1 mm pathlength KBr or CaF₂ infrared solution cell. Rates of reaction were observed by following the disappearance in absorbance of the reactant's $\nu(\text{CO})\text{IR}$ which does not overlap with the other carbonyl bands: $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ at 1845 cm^{-1} . Under the pseudo-first-order reaction conditions, rate constants were calculated using a linear least-squares program for the first order rate plots of $[\text{A}_t - \text{A}_\infty]$ vs time, where A_t is the absorbance at time t and A_∞ is the absorbance at time infinity.

RESULTS AND DISCUSSION

The solvent-metal carbonyl complex, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$, which was prepared from the photochemical reaction of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_3$ in THF at UV irradiation,⁶ on reaction with PR_3 ($\text{R}=\text{Me}, \text{OEt}, \text{C}_6\text{H}_5$) yielded the corresponding $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{PR}_3)$ (Eq. 2).



It is widely accepted that the neutral metal carbonyl complex with Cp ligand is likely to undergo an associative ligand substitution with PR_3 in case this complex is electronically saturated due to the $\text{Cp}(\eta^5 \rightarrow \eta^3)$ ring slippage.^{1,8} In the substitution reaction of $\text{M}(\text{CO})_3(\text{THF})$ ($\text{M}=\text{Cr}, \text{Mo}, \text{W}$) with PR_3 shows mainly an associative ligand substitution process.⁵ However, in this case, as compared with the variations of metal and the PR_3 ligand, there appeared a wide range of ΔS^\ddagger ($-122\text{ e.u.} \sim +8\text{ e.u.}$), which may demonstrate some mechanistic change from associative character to a dissociative one to some degree. Here, the substitution reaction of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ with PR_3 shows the over-

Table 2. The relationship between PR_3 ($\text{R}=\text{Me}, \text{OEt}, \text{C}_6\text{H}_5$) concentrations and the rates (k_{obs}) of the reaction of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ with PR_3 in THF at 10 °C

Ligand	$[\text{PR}_3]\text{ M}(\times 10^3)$	$k_{\text{obs}}(\times 10^4), \text{ s}^{-1}$
PMe_3	5.0	0.62 ± 0.01
	25	1.51 ± 0.02
	50	2.87 ± 0.06
$\text{P}(\text{OEt})_3$	5.0	2.57 ± 0.07
	25	1.47 ± 0.07
	50	1.73 ± 0.09
$\text{P}(\text{C}_6\text{H}_5)_3$	5.0	1.33 ± 0.03
	25	1.81 ± 0.02
	50	2.22 ± 0.02

$[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})]=5.0\text{ mM}$

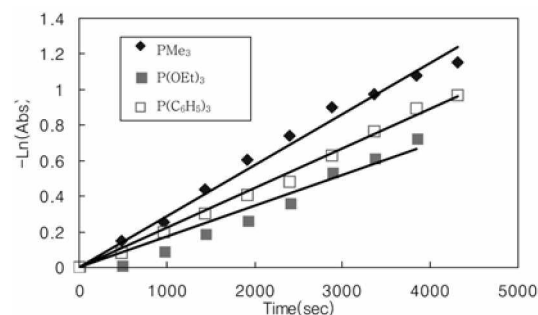


Fig. 1. Pseudo-first-order plot for the reaction of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ with PR_3 ($\text{R}=\text{Me}, \text{OEt}, \text{C}_6\text{H}_5$) (10-fold excess) in THF at 10 °C.

all first order dependence with respect to the concentration of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$. The reaction rate was observed to have no linear relationship with the PR_3 concentration (Table 2).

However, in case of PMe_3 , there may be a minor associative process to some degree in competition with the major dissociative one (Table 2).

The activation parameters were calculated from the Eyring Plot (Fig. 2).

During the reaction, as $\nu(\text{CO})\text{IR}(\text{THF})(1920, 1845\text{ cm}^{-1})$ of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ shrinks, the corresponding $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{PR}_3)$ ($\text{R}=\text{Me}, 1915, 1856$; $\text{R}=\text{OEt}, 1935, 1870$; $\text{R}=\text{C}_6\text{H}_5, 1927, 1863$) gradually grows; therefore, the absorbance change vs time of the $(\text{CO})\text{IR}$ of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ at 1845 cm^{-1} was monitored for the kinetic purpose (Fig. 3). The reaction rate was also observed to be enhanced with temperature rise (0 °C-20 °C)

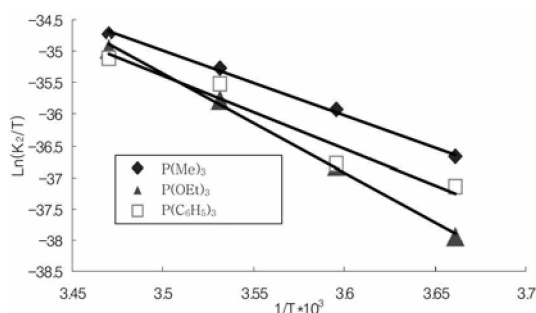


Fig. 2. Eyring plot for the reaction of (η^5 -MeCp)Mn(CO)₂(THF) with PR₃ (R=Me, OEt, C₆H₅) (10-fold excess) in THF.

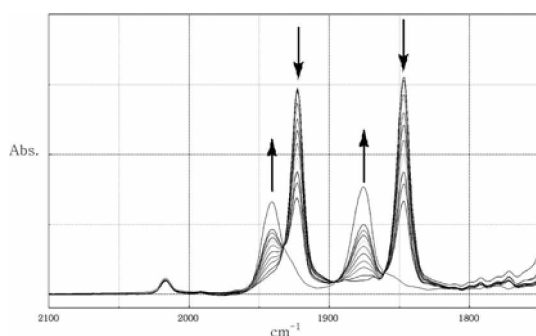


Fig. 3. The (CO)IR spectral variations during the reaction of (η^5 -MeCp)Mn(CO)₂(THF) with P(OEt)₃ (10-fold excess) in THF at 10 °C.

Table 3. Temperature dependence on the rate of the reaction of (η^5 -MeCp)Mn(CO)₂(THF) with PR₃ (R=Me, OEt, C₆H₅) in THF

Ligand	Temp.(°C)	k _{obs} (×10 ⁴), s ⁻¹
PMe ₃	0	0.67±0.03
	5	1.45±0.03
	10	2.87±0.06
	15	5.03±0.05
P(OEt) ₃	0	0.19±0.01
	5	0.60±0.02
	10	1.73±0.09
	15	4.01±0.08
P(C ₆ H ₅) ₃	0	0.42±0.02
	5	0.61±0.02
	10	2.22±0.02
	15	3.40±0.03

[(η^5 -MeCp)Mn(CO)₂(THF)]=5.0 mM; [PR₃]=50 mM

(Table 3).

The activation parameters ($\Delta H^\ddagger=20.52$ kcal/mol, $\Delta S^\ddagger=2.3$ e.u. for PMe₃; $\Delta H^\ddagger=23.49$ kcal/mol, $\Delta S^\ddagger=$

Table 4. Activation parameters from the reaction of (η^5 -MeCp)Mn(CO)₂(THF) with PR₃ (R=Me, OEt, C₆H₅) in THF

Ligand	Activation Parameters
PMe ₃	$\Delta H^\ddagger = 20.52$ (kcal/mol)
	$\Delta S^\ddagger = 2.3$ (e.u.)
P(OEt) ₃	$\Delta H^\ddagger = 23.49$ (kcal/mol)
	$\Delta S^\ddagger = 11.64$ (e.u.)
P(C ₆ H ₅) ₃	$\Delta H^\ddagger = 23.10$ (kcal/mol)
	$\Delta S^\ddagger = 10.52$ (e.u.)

[(η^5 -MeCp)Mn(CO)₂(THF)]=5.0 mM; [PR₃]=50 mM

=11.64 e.u. for P(OEt)₃; $\Delta H^\ddagger=23.10$ kcal/mol, $\Delta S^\ddagger=10.52$ e.u. for P(C₆H₅)₃) together with the reaction rate being of overall the first order with respect to [(η^5 -MeCp)Mn(CO)₂(THF)] strongly suggest a dissociative character at the rate-determining step, which may involve the initial cleavage of Mn-THF bond, followed by the attack of PR₃, leading to the corresponding product, (η^5 -MeCp)Mn(CO)₂(PR₃) (Table 4).

Mechanistic Considerations. The respective $\nu(\text{CO})$ IR for the (η^5 -MeCp)Mn(CO)₂(PR₃) (R=Me, 1915, 1849; R=OEt, 1935, 1870; R=C₆H₅, 1927, 1863) (Table 1) suggests that the relative σ -donation ability of ligand, PR₃ is as follows:⁹



At the elevated temperature (30 °C), it looks rather surprising that the k_{obs} is more or less dependent upon the PR₃ concentrations.

The relative σ -donating ability of PR₃ seems to work definitely on the reaction rate at the elevated reaction temperature (30 °C) toward the associative process. Table 4 shows that the reaction with the most nucleophilic PMe₃ proceeds much faster than the one with less nucleophilic P(C₆H₅)₃, followed by the one with least nucleophile, P(OEt)₃ of the three. This change in reaction mechanism

Table 5. The relationship between steric factor of PR₃ and the reaction rates in THF

Ligand	Temp.(°C)	Ligand Cone Angle(°)	k _{obs} (×10 ⁴), s ⁻¹
PMe ₃	30	118	17.01±0.17
P(OEt) ₃	30	106	6.95±0.07
P(C ₆ H ₅) ₃	30	142	9.45±0.38

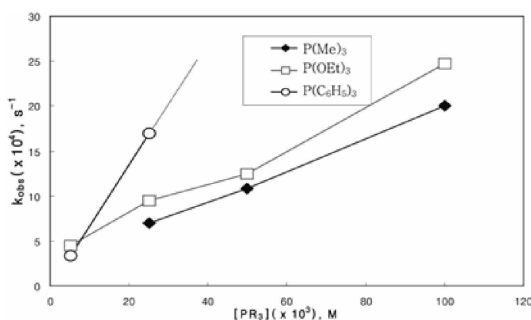
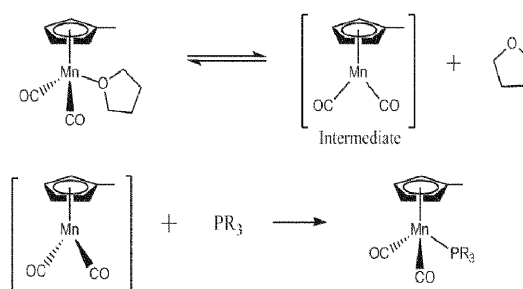


Fig. 4. The relationship between k_{obs} and $[PR_3]$ in THF at 30 °C.

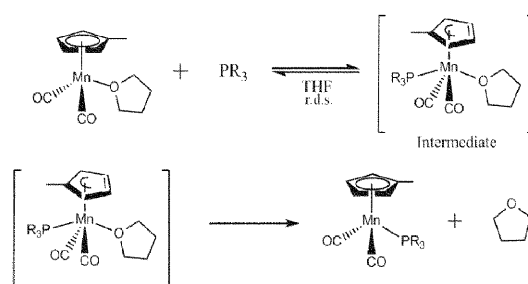
from the dissociative character toward associative one is assumed to be even clearer with far excess of $[PR_3]$ at the elevated temperature. Similar mechanistic changes in ligand substitution are observed elsewhere in the literatures.^{3,19} It seems reasonable that more nucleophilic PMe_3 , with high kinetic energy (at elevated temp.) is more likely to directly attack the Mn metal center without waiting for the THF to depart from the Mn metal complex. However, the steric hindrance (ligand cone angle) of PR_3 (106° for $P(OEt)_3$; 118° for PMe_3 ; 142° for $P(C_6H_5)_3$) does not seem to be inversely proportional to the rate (Fig. 4 and Table 5).

This reaction situation (associative ligand substitution) is assumed to be very similar to S_N2 reaction where strong nucleophile readily attacks $C^{\delta-}-X$ prior to $C-X$ bond cleavage, particularly at high concentration of the nucleophile and high reaction temperature as well. The entropy change of activation for PMe_3 ($\Delta S^\ddagger = 2.3$ e.u.) being rather smaller than those of the other ligand ($\Delta S^\ddagger = 11.64$ e.u. for $P(OEt)_3$; $\Delta S^\ddagger = 10.52$ e.u. for $P(C_6H_5)_3$) may also support the possibility of the reaction pathway change (major dissociative process in competition with minor associative one for reaction involving PMe_3). In this case, Scheme 1 is the major possible process, concurrently with Scheme 2 (minor one).

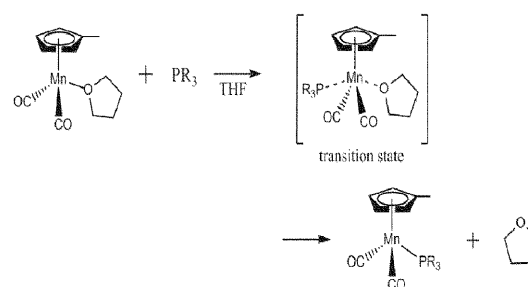
At reasonably low reaction temperature (0 °C ~ 20 °C), this ligand substitution on the whole follows the dissociative process (Scheme 1), which is evidenced by the activation parameters and the overall first order kinetic data; however, at ele-



Scheme 1.



Scheme 2A.



Scheme 2B.

ated temperatures (≥ 30 °C) where the kinetic energy is merely enough for the reactive PR_3 ($R = Me, OEt, C_6H_5$), chances are high for the associative ligand substitution to occur (Scheme 2A, or 2B). However, during the above-mentioned reaction no intermediate $(\eta^5-MeCp)Mn(CO)_2$, or $(\eta^5-MeCp)Mn(CO)_2(THF)PR_3$, could be observed, based on the $\nu(CO)$ IR spectral changes vs reaction time (Fig. 3). Therefore, at elevated reaction temperature, the associative interchange (I_a) involving the plausible transition state (Scheme 2B) can also be proposed. More in-depth kinetic study on this reaction at elevated temperature should be done in near future.

Acknowledgement. This research was supported by the Research Grant from Kangwon National University in 2006. The Author (Y. K. Park) greatly appreciates those generous donations (metal carbonyls, ligand and so on) from Professor J. J. Ko, Department of Chemistry, Korea University.

REFERENCES

1. Awad, H. H.; Dobson, G. R.; Van Eldik, R. J. *Chem. Soc., Chem. Commun.* **1987**, 1839.
2. Zhang, S.; Dobson, G. R.; H. C.; Zang, V.; Van Eldik, R. *Inorg. Chem.* **1990**, *29*, 3477.
3. Wieland, S.; Van Eldik, R. *Organometallics* **1991**, *10*, 3110.
4. O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.
5. Nolan, S. P.; Hoff, C. D. *J. Organomet. Chem.* **1985**, *290*, 365.
6. (a) Butler, I. S.; Coville, N. J.; Cozak, D. *Inorg. Synth.* **1978**, *19*, 188. (b) Nyholm, R. S.; Sabdhu, S. S.; Stiddard, M. H. B. *J. Chem. Soc.* **1963**, *92*, 5916.
7. Park, Y. K.; Lee, Y. G.; Kim, G. S. *Bull. Kor. Chem. Soc.* **1996**, *17*, 138.
8. Rerek, M. E.; Basolo, F. *Organometallics*. **1983**, *2*, 372.
9. PMe₃ > P(C₆H₅)₃ > P(OEt)₃. The σ -donation by PR₃ may enhance the electron density on the Mn, which promotes $d\pi \rightarrow d\pi^*$ back-donation. This back-donation eventually lowers the corresponding carbonyl bond order which will be represented in the $\nu(\text{CO})\text{IR}$ (Table 1).
10. Natalya, N. T.; Huggins, J. M.; Lebioda, L. *Inorg. Chem.* **1988**, *27*, 424.