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Novel Counter Ion Effect on the Disruption of the Homobimetallic Anion, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5\text{-M}^+$ ($\text{M}^+=\text{Na}^+$, PPN^+) by PR_3 ($\text{R}=\text{C}_6\text{H}_5$, C_2H_5 , OCH_3)

Yong Kwang Park*, Seon Joong Kim, and Chang Hwan Rhee

Department of Chemistry, Kangwon National University, Chuncheon 200-701, Korea

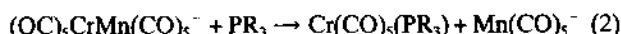
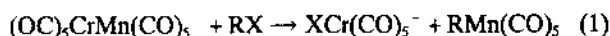
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The homobimetallic anion, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5\text{-M}^+$ ($\text{M}^+=\text{Na}^+$, PPN^+) was disrupted by PR_3 ($\text{R}=\text{C}_6\text{H}_5$, C_2H_5 , OCH_3) in THF at various temperatures (r.t. $\sim 65^\circ\text{C}$) under the pseudo first order reaction conditions where excess of PR_3 was employed under a nitrogen atmosphere. For the reaction involving PPN^+ analog, Mn-Mn heterolytic cleavage occurred, leading to $\text{PPN}^+\text{Mn}(\text{CO})_5\text{-}$ and $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{PR}_3$ as products; however, in case of Na^+ analog, Na^+ seems to play a novel counter ion effect on the disruption reaction 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 $\text{Na}^+\text{Mn}(\text{CO})_4\text{PR}_3\text{-}$ and $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_3$. This reaction is of overall first order with respect to [homobimetallic complex] with the activation parameters ($\Delta H^\ddagger=23.0\pm 0.7$ kcal/mol, $\Delta S^\ddagger=-8.7\pm 0.8$ e.u. for Na^+ analog; $\Delta H^\ddagger=28.8\pm 0.4$ kcal/mol, $\Delta S^\ddagger=15.7\pm 0.6$ e.u. for PPN^+ analog reaction).

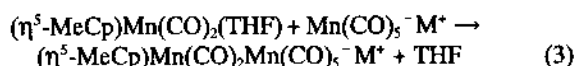
Introduction

Interest in heterobimetallics is growing due to their usefulness as homogeneous catalysts.¹ 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 heterobimetallic complex may be described as a donor-acceptor bond or dative metal-metal bond.²

Recently we have been interested in the reactions involving $(\text{OC})_5\text{CrMn}(\text{CO})_5\text{-M}^+$ ($\text{M}^+=\text{Na}^+$, PPN^+). This heterobimetallic anion reacts either with organic halides or with PR_3 , as shown in the following equations (eq. 1 and eq. 2).³



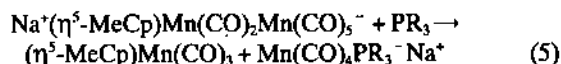
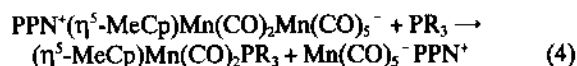
Recently we have prepared $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5\text{-M}^+$ ($\text{M}^+=\text{Na}^+$, PPN^+) from the reaction of $\text{Mn}(\text{CO})_5\text{-M}^+$ ($\text{M}^+=\text{Na}^+$, PPN^+) with $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})_4$ in the same fashion as the above-mentioned heterobimetallics were made (eq. 3).³



Usually it is widely accepted that most of homobimetallics may have rather covalent character in their metal-metal bond; however, this homobimetallic anion is likely to have a donor-acceptor metal-metal bond character as usual het-

erobimetallics would have.

Such a Lewis acid-base relationship in Mn-Mn bond may be in part evidenced by the following disruption reactions (eq. 4 and eq. 5).



For the last two decades much effort has been directed to elucidate the counter ion effects on those reactions involving mononuclear carbonylates such as $\text{HfFe}(\text{CO})_4\text{-}$,⁴ $\text{Mn}(\text{CO})_5\text{-}$,⁶ $\text{Co}(\text{CO})_4\text{-}$,⁷ $\text{CpMo}(\text{CO})_3\text{-}$,⁸ and $\text{CpW}(\text{CO})_3\text{-}$,⁹ however, not much work has been done to understand the counter ion effect on the reactions of anionic bimetallics.

Here we report some unusual 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 PR_3 ($\text{R}=\text{C}_6\text{H}_5$, C_2H_5 , OCH_3).

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 Perkin-Elmer 238B spectrophotometer using 0.10 mm sealed CaF_2 , KBr or NaCl solution cells.

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 at-

* PPN^+ =bis(triphenylphosphine)iminium cation.

mosphere from appropriate drying and O₂ scavenging agents. 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 (η^5 -MeCp)Mn(CO)₂(THF).⁴ The preparation procedure of (η^5 -MeCp)Mn(CO)₂(THF) is similar to a method in the literature. A solution of tricarbonyl (η^5 -methylcyclopentadienyl) manganese(I) (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 (ν (CO): 2010 (s), 1924 (s) cm⁻¹) is replaced by those of (η^5 -MeCp)Mn(CO)₂(THF) (ν (CO): 1917 (s), 1840 (s) cm⁻¹). A slow, steady flow of N₂ through the solution during photolysis assists in removal of CO and prevents the reverse reaction.

Preparation of (η^5 -MeCp)Mn(CO)₂Mn(CO)₅⁻M⁺ (M⁺ = Na⁺, PPN⁺). Na⁺Mn(CO)₅⁻ was prepared from Na/Hg reduction of Mn₂(CO)₁₀ at ambient temperature in THF under N₂. PPN⁺Mn(CO)₅⁻ (1.0 mmol) was prepared by adding degassed CH₂Cl₂ solution (10 mL) of PPNCl (1.2 mmol) to THF solution (30 mL) of Na⁺Mn(CO)₅⁻ (1.0 mmol) at ambient temperature under N₂, resulting in the precipitation of Na⁺Cl⁻. To an N₂-filled 200 mL Schlenk flask is added 0.37 g (0.50 mmol) of PPN⁺Mn(CO)₅⁻. Freshly prepared (η^5 -MeCp)Mn(CO)₂(THF) (1.0 mmol, ~100 mL in THF) is added *via* cannula to the flask containing the PPN⁺Mn(CO)₅⁻. 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 (η^5 -MeCp)Mn(CO)₂(THF) and (η^5 -MeCp)Mn(CO)₃ is removed by hexane. This procedure may be repeated to obtain the spectroscopically pure product. (Note: In some instance, (η^5 -MeCp)Mn(CO)₃ 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 PPN⁺ (η^5 -MeCp)Mn(CO)₂Mn(CO)₅⁻ (320 mg, 69% yield) is characterized spectroscopically and by elemental analysis.

The product, PPN⁺ (η^5 -MeCp)Mn(CO)₂Mn(CO)₅⁻ is air sensitive and should be stored under an inert gas atmosphere below 0 °C. The ¹³C NMR spectra of this compound in THF solution exhibit a single sharp resonance at 238.4 ppm downfield from TMS at -50 °C, indicating the rapid carbonyl exchange between the two metals. The ν (CO) in THF show bands at 2005 (m), 1920 (m, sh), 1905 (m, sh), 1890 (s), 1858 (s), 1816 (w). Anal. calcd. for C₄₉H₃₇NP₂Mn₂O₇: C, 63.72, H, 4.04, N, 1.52. Found: C, 63.51, H, 4.23, N, 1.12.

Reaction of (η^5 -MeCp)Mn(CO)₂Mn(CO)₅⁻M⁺ (M⁺ = Na⁺, PPN⁺) with PR₃ (R = C₆H₅, C₂H₅, OCH₃). The kinetic experiments were carried out in a dried 10 mL volumetric flask securely fitted with a rubber septum. In a typical kinetic experiment, 0.05 mmol of the homobimetallic complex was loaded into a 10 mL volumetric flask in a glove box. The respective THF solution of PR₃ of known

concentration was transferred to the complex *via* syringe. This solution was then stirred to be homogeneous and placed in a Haake 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 path-length KBr or CaF₂ IR solution cell. Rates of reaction were observed by following the appearance in absorbances of the respective products (Peak at 1855 cm⁻¹ (η^5 -MeCp)Mn(CO)₂PR₃ from the PPN⁺ analog; peak at 1936 cm⁻¹ for (η^5 -MeCp)Mn(CO)₃ from the corresponding Na⁺ analog).

Under the pseudo-first-order reaction conditions where at least more than a 5-fold excess of PR₃ 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_∞] vs time, where A_t is the absorbance at time A_t and A_∞ is the one at time infinity. Products such as (η^5 -MeCp)Mn(CO)₂PR₃, (η^5 -MeCp)Mn(CO)₃, Mn(CO)₄PR₃⁻, and Mn(CO)₅⁻ were identified by their IR ν (CO) spectra as compared with those of the authentic compounds previously isolated and characterized in our laboratory.^{3,10}

Results and Discussion

The synthesis of the anionic homobimetallic complex, (η^5 -MeCp)Mn(CO)₂⁻Mn(CO)₅⁻M⁺ (M⁺ = Na⁺, PPN⁺) was achieved by the simple addition of Mn(CO)₅⁻M⁺ to (η^5 -MeCp)Mn(CO)₂(THF) freshly prepared from the photo-chemical reaction of (η^5 -MeCp)Mn(CO)₃ in THF at ambient temperature under N₂ as depicted in equation (3).

Here this homobimetallic anion has a Mn-Mn bond resembling donor-acceptor metal-metal bond where Mn(CO)₅⁻ is considered as a Lewis base and (η^5 -MeCp)Mn(CO)₂ a Lewis acid. This relationship seems to hold good, based on the shift of the IR carbonyl spectra of (η^5 -MeCp)Mn(CO)₂ moiety of the homobimetallic complex to the lower frequencies (1890, 1816 cm⁻¹) compared with those of (η^5 -MeCp)Mn(CO)₂(THF) (1917, 1840 cm⁻¹) (Table 1).

The electron density built up on Mn of (η^5 -MeCp)Mn(CO)₂ moiety due to the donor (Mn(CO)₅⁻) may be in part back-donated through d_π-p_π^{*} orbital interaction to terminal

Table 1. Infrared data for relevant complexes

Complex	ν (CO)IR
PPN ⁺ [(η^5 -MeCp)Mn(CO) ₂ Mn(CO) ₅] ⁻	2005 (m), 1920 (m, sh), 1905 (m, sh), 1890 (s), 1858 (s), 1816 (s)
Na ⁺ [(η^5 -MeCp)Mn(CO) ₂ Mn(CO) ₅] ⁻	2005 (m), 1914 (m, sh), 1905 (m, sh), 1885 (s), 1852 (s), 1822 (m)
(η^5 -MeCp)Mn(CO) ₂ (THF)	1917 (s), 1840 (s)
PPN ⁺ [(η^5 -MeCp)Mn(CO) ₂ Cl] ⁻	1893 (s), 1816 (s)
(η^5 -MeCp)Mn(CO) ₂ PPh ₃	1920 (s), 1855 (s)
(η^5 -MeCp)Mn(CO) ₃	2010 (s), 1924 (s)
PPN ⁺ [Mn(CO) ₅] ⁻	1897 (s), 1858 (s)
PPN ⁺ [Mn(CO) ₄ PPh ₃] ⁻	1941 (m), 1846 (w), 1809 (s)
PPN ⁺ [Mn(CO) ₄ P(OMe) ₃] ⁻	1954 (m), 1858 (w), 1820 (s)
PPN ⁺ [Mn(CO) ₄ PEt ₃] ⁻	1958 (m), 1823 (w), 1790 (s)

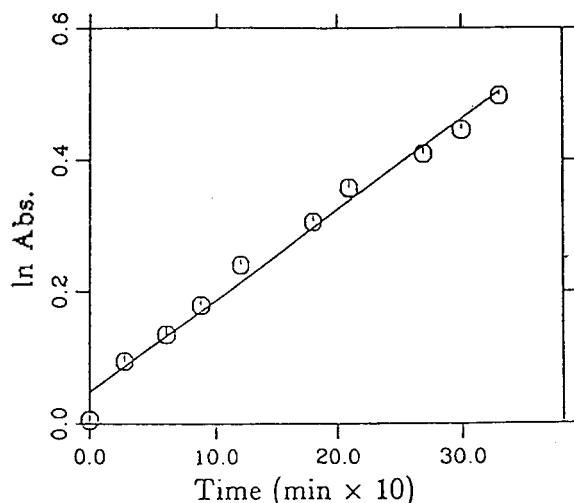


Figure 1. Pseudo-first-order plot of the reaction of $\text{Na}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-$ with $\text{P}(\text{C}_6\text{H}_5)_3$ (40-fold excess) in THF at $50.0\text{ }^\circ\text{C}$.

CO of $(\eta^5\text{-MeCp})\text{Mn}$ moiety of the homobimetallic compound.

Similar situation was also observed at $\text{PPN}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Cl}^-$ ($1893, 1816\text{ cm}^{-1}$).¹⁰ This interpretation is further supported elsewhere from the relative ligating ability comparison of anionic transition metal complexes, transition metal hydrides, and traditional ligands to $\text{M}(\text{CO})_5^0$ ($\text{M}=\text{Cr}, \text{W}$).¹¹

Reaction of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^- \text{M}^+$ ($\text{M}^+=\text{Na}^+, \text{PPN}^+$). Reactions of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^- \text{M}^+$ ($\text{M}^+=\text{Na}^+, \text{PPN}^+$) with a 20 fold excess of PR_3 ($\text{R}=\text{C}_6\text{H}_5, \text{C}_2\text{H}_5, \text{OCH}_3$) in THF were monitored by the IR carbonyl peak change. This reaction follows overall first order dependence on $[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^- \text{M}^+]$ and the rate is represented by Eq. 6, as is evidenced in Figure 1 and Table 2.

$$\text{rate} = k_1 [(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^- \text{M}^+] \quad (6)$$

Determination of the Activation Parameters.

The first order rate constants, k_1 , was also obtained for the reaction in THF at various temperatures (Table 3), in which the rates are linearly dependent upon temperature.

The activation parameters were calculated from the Eyring plot (Figure 2). The activation parameters ($\Delta H^\ddagger=28.8\pm$

Table 2. The relationship between $\text{P}(\text{C}_6\text{H}_5)_3$ concentrations and the rate (k_{obs}) of $\text{M}^+[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-]$ ($\text{M}^+=\text{Na}^+, \text{PPN}^+$) in THF at $40\text{ }^\circ\text{C}$

Homobimetallics	Conc., M^a (fold) ^b	$k_{\text{obs}} \times 10^6$
$\text{Na}^+[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-]$	0.10 (20) ^c	6.38 ± 0.42
	0.20 (40)	7.93 ± 0.32
$\text{PPN}^+[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-]$	0.025 (5)	126 ± 17
	0.200 (40)	117 ± 11

^a Molar concentration of $\text{P}(\text{C}_6\text{H}_5)_3$. ^b Figures in parenthesis indicates the number of fold in excess with respect to the concentrations of homobimetallics. ^c The concentration of $\text{P}(\text{C}_6\text{H}_5)_3$ is 0.10 M , which is 20 fold in excess with respect to the concentration of the corresponding homobimetallic.

Table 3. Temperature dependence on the reaction of $\text{M}^+[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-]$ ($\text{M}^+=\text{Na}^+, \text{PPN}^+$) with 40 fold excess of $\text{P}(\text{C}_6\text{H}_5)_3$ in THF^{a,b}

Homobimetallics	Temp. ($^\circ\text{C}$)	$k_{\text{obs}} \times 10^5, \text{M}^{-1}\text{s}^{-1c}$
$\text{PPN}^+[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-]$	30	2.60 ± 0.31
	40	11.8 ± 1.05
	45	27.8 ± 1.21
	50	51.4 ± 3.57
$\text{Na}^+[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-]$	40	0.79 ± 0.04
	50	2.30 ± 0.13
	60	6.61 ± 0.32
	65	14.0 ± 1.0

^a $[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-]=5.0\text{ mM}$. ^b $[\text{P}(\text{C}_6\text{H}_5)_3]=100\text{ mM}$. ^c Confidence limit at 90%.

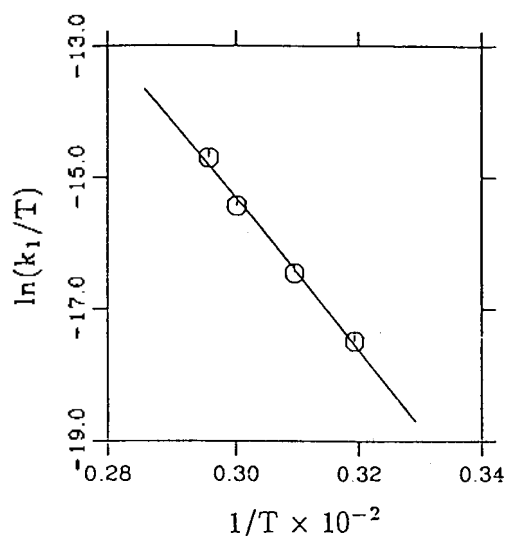


Figure 2. Eyring plot for the reaction of $\text{Na}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-$ with $\text{P}(\text{C}_6\text{H}_5)_3$ (40-fold excess) in THF.

0.4 kcal/mol , $\Delta S^\ddagger=15.7\pm 0.6\text{ e.u.}$ for PPN^+ analogue) together with the rate being overall the first order with respect to $[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^- \text{PPN}^+]$ strongly suggest a dissociative character at the rate-determining step, which may involve the initial cleavage of Mn-Mn bond leading to the intermediates, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ and $\text{Mn}(\text{CO})_5^- \text{PPN}^+$.

Here $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$ moiety from the anionic homobimetallic complex may be stabilized by THF, eventually leading to $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{PR}_3)$ upon reaction with PR_3 (Scheme 1).

We previously observed the rapid formation of $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{PR}_3)$ where $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ is allowed to react with PR_3 in THF at ambient temperature under a nitrogen atmosphere.

Mechanistic Consideration. It looks rather surprising that in case of Na^+ analogue's reaction, we observed $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_3$ and $\text{Mn}(\text{CO})_4(\text{PR}_3)$ Na^+ as major products while for the reaction involving PPN^+ analogue, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{PR}_3)$ and $\text{Mn}(\text{CO})_5^- \text{PPN}^+$ were obtained as major ones. This drastic change in the product distribution may be enough evidence for us to believe that counter ion may alt-

er its reaction pathway, which was repeatedly shown previously in the disruption reaction of $L(\text{OC})_2\text{Cr}-\text{Mn}(\text{CO})_4L^-$ M^+ ($L=\text{CO}, \text{PR}_3$; $M^+=\text{Na}^+, \text{PPN}^+$) with PR_3 .^{3d}

Na^+ is well known to promote bridging carbonyl in the bimetallic complex as well as Lewis acid does.¹² In that circumstance, 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; $\mu^2\text{-CO}$ is transformed into a terminal CO producing $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_3$ moiety. At this moment, $\text{Mn}(\text{CO})_5$ moiety of this bimetallic complex may lose one carbonyl ligand, creating an open coordination site which can accommodate one THF solvent molecule.

This intermediate in Scheme 2 may then have a $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_3$ moiety attached to $\text{Mn}(\text{CO})_4(\text{THF})$ adduct, eventually leading to $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_3$ and $\text{Na}^+\text{Mn}(\text{CO})_4(\text{PR}_3)$ on reaction with PR_3 .

The negative entropy change of activation ($\Delta S^\ddagger = -8.7$ e.u.) may suggest the possibility of THF molecule adduct intermediate formation prior to PR_3 attack. As the $\text{Mn}(\text{CO})_4(\text{THF})$ moiety of the intermediate may need more electron density, an electron-donating ligand such as $\text{P}(\text{C}_2\text{H}_5)_3$ can be a good candidate for stabilization one of the corresponding products, $\text{Mn}(\text{CO})_4\text{P}(\text{C}_2\text{H}_5)_3$ (Table 4 and Scheme 2)

However, for the reaction involving PPN^+ analogue the rate-determining step may involve the Mn-Mn heterolytic cleavage, leading to $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2^-$ (THF) and $\text{PPN}^+\text{Mn}(\text{CO})_5$. This THF adduct intermediate on reaction with PR_3 may rapidly go to $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{PR}_3)$ eventually (Scheme 1).

Here, the enthalpy change of activation ($\Delta H^\ddagger = 28.8 \pm 0.4$ kcal/mol) may be the heterolytic Mn-Mn bond dissociation energy, which may be further supported by the positive entropy change of activation ($\Delta S^\ddagger = 15.7 \pm 0.6$ e.u.).

The intermediate, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ can accommodate one PR_3 almost without any steric congestion; therefore,

Table 4. Activation parameters for the reaction of $M^+[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5]^-$ ($M^+=\text{Na}^+, \text{PPN}^+$) with 40 fold excess of $\text{P}(\text{C}_2\text{H}_5)_3$ in THF

Homobimetallics	ΔH^\ddagger (kcal/mol)	ΔS^\ddagger (e.u.)
$\text{Na}^+[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5]^-$	23.0 ± 0.7	-8.7 ± 0.8
$\text{PPN}^+[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5]^-$	28.8 ± 0.4	15.7 ± 0.6

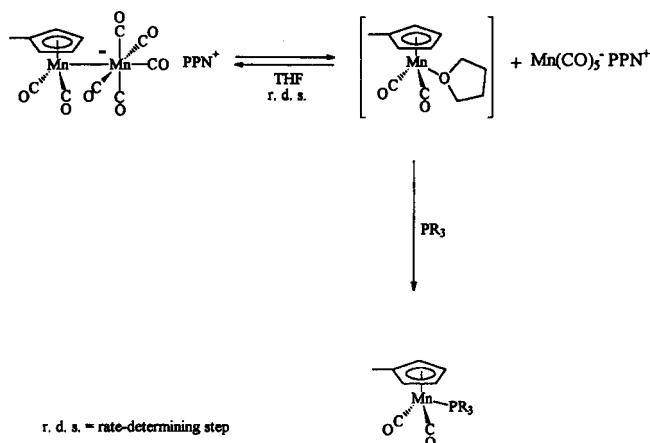
Table 5. Incoming ligand dependence on the reaction rate of $M^+[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5]^-$ ($M^+=\text{Na}^+, \text{PPN}^+$) with 40 fold excess of PR_3 in THF

Homobimetallics	Temp. (°C)	Ligand	$k_{\text{obs}} \times 10^5$	Cone angle (°)
$\text{PPN}^+[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5]^-$	45	$\text{P}(\text{C}_2\text{H}_5)_3$	27.8 ± 1.1	145
		$\text{P}(\text{C}_2\text{H}_5)_3$	25.7 ± 1.6	132
		$\text{P}(\text{OCH}_3)_3$	28.1 ± 1.1	107
$\text{Na}^+[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5]^-$	40	$\text{P}(\text{C}_2\text{H}_5)_3$	2.30 ± 0.13	145
		$\text{P}(\text{C}_2\text{H}_5)_3$	8.24 ± 0.52	132
		$\text{P}(\text{OCH}_3)_3$	4.45 ± 0.35	107

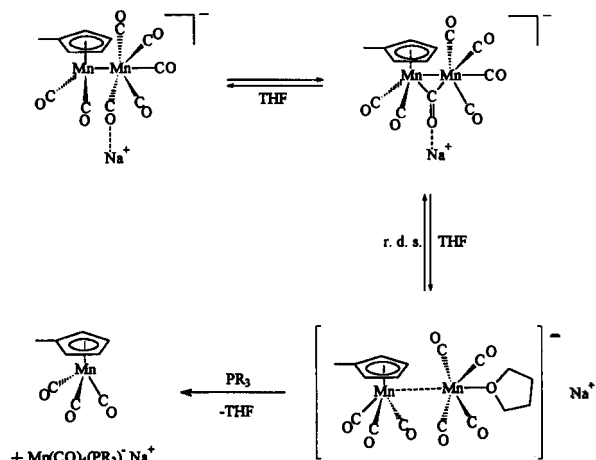
^aRef. 13. C. A. Tolman, *J. Am. Chem. Soc.* 1970, 92, 2925.

Table 6. Product distributions for the reaction of $[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5]^- M^+$ ($M^+=\text{Na}^+, \text{PPN}^+$) with $\text{P}(\text{C}_2\text{H}_5)_3$ in THF

Homobimetallics	Products
$\text{PPN}^+[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5]^-$	$(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{P}(\text{C}_2\text{H}_5)_3$, $\text{Mn}(\text{CO})_5^-$ (90%), $\text{Mn}(\text{CO})_4\text{P}(\text{C}_2\text{H}_5)_3$ (10%)
$\text{Na}^+[(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5]^-$	$\text{Mn}(\text{CO})_4\text{P}(\text{C}_2\text{H}_5)_3^-$, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_3$ (95%), $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{P}(\text{C}_2\text{H}_5)_3$ (5%)
$[\text{Na}^+(18\text{-crown-6})][(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5]^-$	$(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{P}(\text{C}_2\text{H}_5)_3$, $\text{Mn}(\text{CO})_5^-$



Scheme 1.



Scheme 2.

neither steric nor electronic effect caused by the incoming ligand, PR_3 is observed on the reaction (Table 5).

The Minor product, $\text{Mn}(\text{CO})_4\text{PR}_3^-$, from the reaction involving PPN^+ analog may be formed due to the prior CO displacement by PR_3 , followed by Mn-Mn bond cleavage. Similar results were observed in the minor reaction involving Na^+ analog yielding $\text{Mn}(\text{CO})_4\text{PR}_3^-$ and $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{PR}_3$ as minor products (Table 6).

An excess of 18-crown-6 was introduced to the $\text{Na}^+(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5^-$. As expected, 18-crown-6 encircles Na^+ , keeping Na^+ from interacting with the coordinated CO ligand; therefore, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{PR}_3)$ and $\text{Mn}(\text{CO})_5^-$

were observed as products. These products are exactly what can be expected from the reaction involving PPN⁺ analogue (Table 6).

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The CO₂ Hydrogenation toward the Mixture of Methanol and Dimethyl Ether: Investigation of Hybrid Catalysts

Ki-Won Jun, K.S. Rama Rao[†], Mi-Hee Jung, and Kyu-Wan Lee

*Chemical Technology Lab I, Korea Research Institute of Chemical Technology,
P.O. Box 107, Yusong, Taejeon 305-600, Korea*

[†]*Catalysis Section, Indian Institute of Chemical Technology, Hyderabad 500 007, India*

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Catalytic hydrogenation of carbon dioxide for the simultaneous synthesis of methanol and dimethyl ether (together called oxygenates) over a combination of methanol synthesis and methanol dehydration catalysts has been studied. Various methanol synthesis and methanol dehydration catalysts were examined for this reaction. The addition of promoters like Ga₂O₃ and Cr₂O₃ to Cu/ZnO catalyst gave much more enhanced yield on the formation of oxygenates. From the results, the promotional effect of Cr₂O₃ has been explained in terms of increase in the intrinsic activity of Cu while that of Ga₂O₃ being increase in the dispersion of Cu. Among the methanol dehydration catalysts examined, the solid acids bearing high population of intermediate-strength acid sites were found to be very effective for the production of oxygenates. HY zeolite which contains strong acid sites produce small amount of hydrocarbons as by-products. However, CuNaY zeolite in which the presence of strong acid sites are minimum gives very high oxygenates yield without the formation of hydrocarbons.

Introduction

The subject on the utilization of CO₂ has attained great importance in recent years from the view point of the global warming nature of CO₂. Among the methods of converting CO₂ directly into value added products, hydrogenation of CO₂ is perhaps the most simple route.¹ Cu/ZnO bas-

ed catalysts were found to be effective towards methanol synthesis either from CO or CO₂ hydrogenation.²⁻⁴ Several reports have been cited on the simultaneous production of methanol (MeOH), and dimethyl ether (DME) from CO₂ or CO hydrogenation over hybrid catalysts, *i.e.*, combination of methanol synthesis (MS) and methanol dehydration (MD) catalysts.⁵⁻⁷ The improvement of oxygenate yield over hy-