

Kinetic Studies on the Reaction of the Heterobimetallic Anion, $(\text{OC})_5\text{CrMn}(\text{CO})_5^- \text{M}^+$ ($\text{M}^+ = \text{Na}^+, \text{PPN}^+$) with Allyl Bromide

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Received October 24, 1994

The heterobimetallic anion, $(\text{OC})_5\text{CrMn}(\text{CO})_5^- \text{M}^+$ ($\text{M}^+ = \text{Na}^+, \text{PPN}^+$), which has a donor-acceptor metal-metal bond,¹ was reacted with allyl bromide to yield $\text{BrCr}(\text{CO})_5^-$ and $\text{Mn}(\text{CO})_5(\text{CH}_2\text{CHCH}_2)$. The reaction mechanism has been proposed in terms of the consecutive reaction pathway in which $\text{Cr}(\text{CO})_5(\text{THF})$ is an important intermediate leading to the corresponding product. Counterion effect on this reaction was also evaluated and the results were compared with those of the corresponding reaction of the mononuclear carbonyl anion, $\text{Mn}(\text{CO})_5^-$.

Introduction

Heterobimetallic complexes have been the subject of numerous recent studies in which chemically inert bonds are activated by two different metal centers in close proximity in the complexes.² The heterobimetallic anion, $(\text{OC})_5\text{CrMn}(\text{CO})_5^- \text{M}^+$ ($\text{M}^+ = \text{Na}^+, \text{PPN}^+$), in which a dative metal-metal bond exists, can be disrupted to give $\text{Mn}(\text{CO})_5^-$ and $\text{Cr}(\text{CO})_5\text{PR}_3$ upon reaction with PR_3 at elevated temperature; however, the feature of the corresponding reaction may be drastically changed by the selection of the ancillary ligand such as PR_3 .^{3,4} Recent interest in heterobimetallic complexes has been mainly focused on the structural investigations: $[\text{MnM}(\text{CO})_{10}]^-$ ($\text{M} = \text{Cr}, \text{W}$)⁵; $[\text{HFeM}(\text{CO})_9]^-$ ($\text{M} = \text{Cr}, \text{W}$)⁶; $[(\mu\text{-H})\text{CrW}(\text{CO})_{10}]^-$ ⁷; $[\text{ReMn}(\text{CO})_{10}]^-$ ⁸; $[(\text{Me}_3\text{P})(\text{OC})_4\text{OsM}(\text{CO})_5]$ ($\text{M} = \text{Cr}, \text{W}$)⁹; $[(\text{Me}_3\text{P})(\text{OC})_4\text{OsRe}(\text{CO})_4(\text{Br})]$ ⁹; $[(\text{OC})_4\text{CoRh}(\text{CO})(\text{PEt}_3)_2]$ ¹⁰ and so on.¹¹

For several years we have been interested in the reactions involving heterobimetallic complexes such as $(\text{OC})_5\text{CrMn}(\text{CO})_5^- \text{M}^+$ ($\text{M}^+ = \text{Na}^+, \text{PPN}^+$ (bis(triphenylphosphoranylidene)ammonium ion)). In this paper, we would like to present the research results on the reaction pathway in which $(\text{OC})_5\text{CrMn}(\text{CO})_5^- \text{M}^+$ ($\text{M}^+ = \text{Na}^+, \text{PPN}^+$) was reacted with allyl bromide and also the counterion effect on this reaction in comparison with that often observed in the corresponding reaction of a mononuclear transition metal carbonylate such as $\text{Mn}(\text{CO})_5^-$.¹²

Experimental Details

General Description. An inert-atmosphere glove box, Schlenk line, and high-vacuum techniques were employed for most of sample transfers and manipulations. Infrared spectra were recorded on a Perkin-Elmer 238B spectrophotometer. ¹H NMR spectra was recorded on a Bruker 200 MHz FTNMR instrument. Temperature was controlled with Haake A81 thermostat. Most of weighing and transfer of compounds were done under an Ar atmosphere in the glove box (Vacuum Atmosphere Co.). Photoreactions were performed using a 450 watt Hg vapor lamp covering a rather broad range of UV-vis wavelengths. Solvents were distilled under N₂ atmosphere from appropriate drying and O₂ scavenging agents: tetrahydrofuran (THF), Na⁰/benzophenone/diglyme;

methylene chloride, P₂O₅; acetonitrile, CaH₂ followed by P₂O₅; methanol, Mg⁰/I₂. All reagents were purchased from ordinary vendors and used as received without further purification.

Preparation of $\text{Cr}(\text{CO})_5\text{THF}$. This compound was prepared according the procedure described in the reference¹⁹ and checked by IR spectroscopy.

Preparation of $\text{PPN}^+\text{Mn}(\text{CO})_5^-$. A 40 mL THF solution of dimanganese decacarbonyl (2.0 g) was added to a THF solution (5 mL) of 1% Na in Hg. Then the solution was stirred for about 1 hr at room temperature until the infrared spectrum showed only the bands from the $\text{Na}^+\text{Mn}(\text{CO})_5^-$ (IR(THF, cm⁻¹), (CO) 1897 (s), 1862 (s), 1829 (m)). This reaction solution was then passed through a Celite column. A slightly excess equivalent of PPN^+Cl^- dissolved in CH₂Cl₂ (5 mL) was cannulated into the mercury-free solution of $\text{Na}^+\text{Mn}(\text{CO})_5^-$. Followed by 1 hr stirring at room temperature, the solution was passed through a Celite column and the solution volume was reduced to about 15 mL under vacuum. Hexane (30 mL) was added and fine yellow solids were precipitated. The product was washed with hexane several times until the washings were colorless. The yield was 6.92 g (92%). IR (THF, cm⁻¹), ν (CO) 1894 (s), 1860 (s).¹⁴

Preparation of $\text{Na}^+\text{CrMn}(\text{CO})_{10}^-$. To $\text{Na}^+\text{Mn}(\text{CO})_5^-$ (1.5 g; 5.8 mmol) was added the THF solution (70 mL) of $\text{Cr}(\text{CO})_5(\text{THF})$ (5.8 mmol) freshly prepared from the photolytic reaction. This solution was stirred for 3 hrs at room temperature. The solution was then passed through a Celite column and the solution volume was concentrated to about 20 mL under vacuum. Hexane (30 mL) was added and fine yellow solid was precipitated. The product was washed with hexane several times until the washings were colorless. The yield was 1.85 g (77%). IR (THF, cm⁻¹), ν (CO) 2063 (w), 1988 (m), 1950 (s), 1923 (w, sh), 1894 (m), 1862 (m).^{3,4}

Preparation of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$. The following modification to the literature procedures was employed to achieve good yields. To $\text{PPN}^+\text{Mn}(\text{CO})_5^-$ (1.39 g; 2 mmol) was added the THF solution (70 mL) of $\text{Cr}(\text{CO})_5(\text{THF})$ (2 mmol) freshly prepared from the photolytic reaction. This solution was stirred for 3 hrs at room temperature. The reaction solution was then passed through a Celite column and the solution volume was concentrated to about 20 mL under vacuum. Hexane (30 mL) was added and a fine yellow product was precipitated. The product was washed with hexane

several times until the washings were colorless. The yield was 1.5 g (81%). IR (THF, cm^{-1}), ν (CO) 2063 (w), 1988 (m), 1950 (s), 1923 (w, sh), 1894 (m), 1862 (m).³⁴

Reaction of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$ with $\text{CH}_2\text{CHCH}_2\text{Br}$.

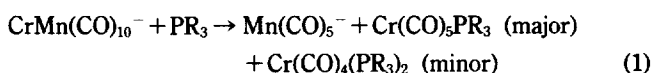
Usually 10 mL of THF was added to the mixture of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$ (0.05 mmol) and a 20-fold excess of $\text{CH}_2\text{CHCH}_2\text{Br}$ in a 10 mL vol. flask *via* cannula at ambient temperature. This THF solution was shaken for a few minutes prior to being kept in a water bath set at a specific temperature. The reaction was monitored by IR ν (CO) spectroscopy. Rates of the reaction were followed by the decrease in absorption of the intense CO band (1894 cm^{-1}) of the reactant which does not overlap with the bands of products. Pseudo first order reaction conditions using at least a 5-fold excess of $\text{CH}_2\text{CHCH}_2\text{Br}$ were employed where appropriate. Rate constants were calculated using a linear least squares program for the first order rate plots of $\ln(A_t - A_\infty)$ vs. time, where A_t is the absorbance at time t and A_∞ is the absorbance at infinity. Usually ten or more IR ν (CO) spectra were obtained for each k_{obs} calculation. Products, $(\text{CH}_2\text{CHCH}_2)\text{Mn}(\text{CO})_5$ and $\text{BrCr}(\text{CO})_5^-$ were identified by their IR ν (CO) spectra as compared with those of the authentic compounds previously isolated and characterized in our laboratory. $(\text{CH}_2\text{CHCH}_2)\text{Mn}(\text{CO})_5$, IR (THF, cm^{-1}), ν (CO) 2063 (m), 1900 (s, sh), 1967 (s), 1945 (s)¹²; $\text{PPN}^+\text{BrCr}(\text{CO})_5^-$, IR (THF, cm^{-1}), ν (CO) 2047 (w), 1913 (s), 1849 (m).^{15,16}

Results and Discussion

The heterobimetallic anion, $(\text{OC})_5\text{CrMn}(\text{CO})_5^-$, was prepared by the ligand substitution of labile $\text{Cr}(\text{CO})_5(\text{THF})$ with $\text{Mn}(\text{CO})_5^-$ in THF at ambient temperature in high yields (75 to 90%). This synthetic approach appears to be very efficient in comparison with either the procedure utilizing the high temperature thermal displacement of CO from $\text{Cr}(\text{CO})_6$ by $\text{Mn}(\text{CO})_5^-$ ^{5a} or that by the metal exchange reaction $\text{Mn}_2(\text{CO})_{10} + \text{Cr}_2(\text{CO})_{10}^{2-}$.^{5b}

Graham^{5a} and others¹⁸ assumed the negative charge resides on $\text{Cr}(\text{CO})_5$ moiety of $\text{CrMn}(\text{CO})_{10}^-$. However, in analogy with $\text{HFeCr}(\text{CO})_5^-$ anion ($\text{HFe}(\text{CO})_4^- + \text{Cr}(\text{CO})_5(\text{THF})$), it is likely that the anionic fragment $\text{Mn}(\text{CO})_5^-$ may retain much of the negative charge.^{1c} The deconvolution of the IR (THF) ν (CO) spectrum of $\text{CrMn}(\text{CO})_{10}^-$ into six bands does not represent two sets of three bands of intensity patterns that may plausibly be assigned to two non-interacting C_{4v} centers. In fact, considerable coupling of CO vibrations may occur in this heterobimetallic anion.³

The reaction of $\text{M}^+[\text{CrMn}(\text{CO})_{10}]^-$ ($\text{M}^+ = \text{Na}^+, \text{PPN}^+$) with PR_3 (usually 20 fold excess) was carried out in THF (Eq. 1).



The reaction is overall 1st order with respect to $[\text{CrMn}(\text{CO})_{10}^-]$. The activation parameters ($\Delta H^\ddagger = 27.2 \pm 1.5$ kcal/mol and $\Delta S^\ddagger = 57.7 \pm 4.4$ e.u.) suggest a dissociative reaction mechanism in which the Cr-Mn bond cleavage may be involved at the rate-determining step. However, kinetic studies on the reaction of $[(\text{OC})_5\text{CrMn}(\text{CO})_4\text{PR}_3]^-$ with PR_3 show the 2nd order rates, $k_2[(\text{OC})_5\text{CrMn}(\text{CO})_4\text{PR}_3^-][\text{PR}_3]$ (Eq. 2).³

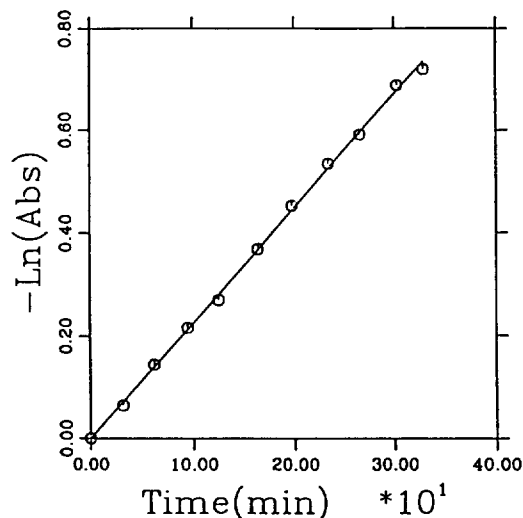
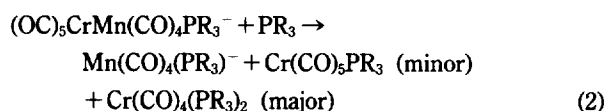
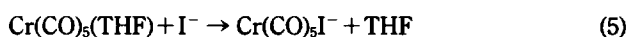
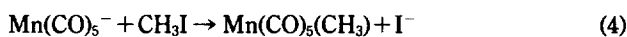


Figure 1. Pseudo 1st order plot of the reaction of $\text{Na}^+\text{CrMn}(\text{CO})_{10}^-$ (5.0 mM) with $\text{CH}_2\text{CHCH}_2\text{Br}$ (100 mM) in THF at 55°C .



Since PR_3 is regarded as a better σ -donor than CO, $\text{Mn}(\text{CO})_4\text{PR}_3^-$ appears to be more basic toward the Lewis acid, $\text{Cr}(\text{CO})_5(\text{THF})$ than $\text{Mn}(\text{CO})_5^-$. This enhanced basicity by PR_3 in $\text{Mn}(\text{CO})_4\text{PR}_3^-$ moiety plausibly creates a stronger Mn-Cr bond than in the all-CO analogue. The greater electron density at the Mn-Cr bond could preferentially cause the initial Cr-CO bond cleavage by the incoming ligand, PR_3 , which may lead to the major product, $\text{Cr}(\text{CO})_4(\text{PR}_3)_2$, eventually. However, once one CO is replaced by PR_3 in $\text{Cr}(\text{CO})_5(\text{THF})$ moiety the Mn-Cr bond may be drastically weakened. Thus this metal-metal bond can be readily cleaved by another PR_3 to yield $\text{Cr}(\text{CO})_4(\text{PR}_3)_2$ and $\text{Mn}(\text{CO})_4\text{PR}_3^-$.

The reaction of $\text{CrMn}(\text{CO})_{10}^-$ with CH_3I was proven to be overall 1st order with respect to $[\text{CrMn}(\text{CO})_{10}^-]$.¹⁹ The reaction can be described in terms of the consecutive reaction pathway (Eq. 3, 4, 5) in which $\text{Cr}(\text{CO})_5(\text{THF})$ is an important intermediate, leading to the products, $\text{Mn}(\text{CO})_5(\text{CH}_3)$ and $\text{Cr}(\text{CO})_5\text{I}^-$ (Eq. 3-5).



Reactions of $\text{CrMn}(\text{CO})_{10}^- \text{M}^+$ ($\text{M}^+ = \text{Na}^+, \text{PPN}^+$) with $\text{CH}_2\text{CHCH}_2\text{Br}$. Reactions of $(\text{OC})_5\text{CrMn}(\text{CO})_5^-$ with a 20-fold excess of allyl bromide in THF were monitored by the IR carbonyl peak change. This reaction follows the 1st order dependence on $[(\text{OC})_5\text{CrMn}(\text{CO})_5^-]$ and the rate is represented by Eq. 6, as is evidenced in Figure 1, 2 and Table 1, 2.

$$\text{rate} = k_1[(\text{OC})_5\text{CrMn}(\text{CO})_5^-] \quad (6)$$

Determination of the Activation Parameters. The

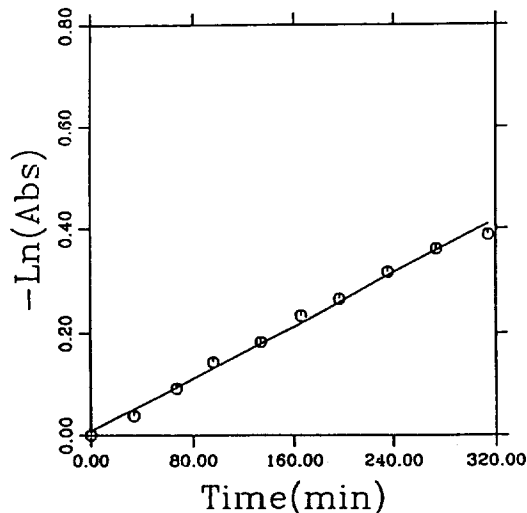


Figure 2. Pseudo 1st order plot of the reaction of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$ (5.0 mM) with $\text{CH}_2\text{CHCH}_2\text{Br}$ (100 mM) in THF at 55 °C.

Table 1. The relationship between $\text{CH}_2\text{CHCH}_2\text{Br}$ concentrations and the rates (k_{obs}) of the reaction of $\text{Na}^+\text{CrMn}(\text{CO})_{10}^-$ in THF at 55 °C

Conc. [$\text{CrMn}(\text{CO})_{10}^-$] M ($\times 10^3$)	Conc. [$\text{CH}_2\text{CHCH}_2\text{Br}$] M ($\times 10^3$)	$k_{\text{obs}} \times 10^6, \text{s}^{-1}$
5.0	25	35.8 ± 0.5
5.0	50	35.6 ± 0.7
5.0	100	35.6 ± 0.5
5.0	200	37.1 ± 0.9

Table 2. The relationship between $\text{CH}_2\text{CHCH}_2\text{Br}$ concentrations and the rates (k_{obs}) of the reaction of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$ in THF at 55 °C

Conc. [$\text{CrMn}(\text{CO})_{10}^-$] M ($\times 10^3$)	Conc. [$\text{CH}_2\text{CHCH}_2\text{Br}$] M ($\times 10^3$)	$k_{\text{obs}} \times 10^6, \text{s}^{-1}$
5.0	25	17.9 ± 0.4
5.0	50	19.4 ± 0.7
5.0	100	18.7 ± 0.8
5.0	200	20.2 ± 0.8

first order rate constants, k_1 , were also obtained for the reaction in THF at various temperatures (Table 3 and 4) in which the rates are linearly dependent upon the temperature. The activation parameters were calculated from the Eyring plots (Figure 3, 4). The activation parameters ($\Delta H^\ddagger = 31.6 \pm 2.0$ kcal/mol and $\Delta S^\ddagger = 15.6 \pm 6.3$ e.u. for $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$; $\Delta H^\ddagger = 29.4 \pm 2.0$ kcal/mol and $\Delta S^\ddagger = 10.3 \pm 6.1$ e.u. for $\text{Na}^+\text{CrMn}(\text{CO})_{10}^-$) together with the rate being the first order on $[\text{CrMn}(\text{CO})_{10}^-]$ strongly suggest a dissociative character at the rate-determining step, which may involve the initial cleavage of Cr-Mn bond leading to the intermediates, $\text{Cr}(\text{CO})_5(\text{THF})$ and $\text{Mn}(\text{CO})_5^-$. Polar coordinating solvent may stabilize the possible intermediates, $\text{Cr}(\text{CO})_5(\text{solvent})$ and Mn

Table 3. Temperature dependence on the reaction of $\text{Na}^+\text{CrMn}(\text{CO})_{10}^-$ with $\text{CH}_2\text{CHCH}_2\text{Br}$ in THF^a

Complex	Temp. (°C)	$k_{\text{obs}} \times 10^6, \text{s}^{-1}$
$\text{Na}^+\text{CrMn}(\text{CO})_{10}^-$	45	7.7 ± 0.6
	50	14.3 ± 0.3
	55	35.6 ± 0.6
	60	61.4 ± 1.1

^a $[\text{CrMn}(\text{CO})_{10}^-] = 5.0$ mM; $[\text{CH}_2\text{CHCH}_2\text{Br}] = 100$ mM.

Table 4. Temperature dependence on the reaction of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$ with $\text{CH}_2\text{CHCH}_2\text{Br}$ in THF^a

Complex	Temp. (°C)	$k_{\text{obs}} \times 10^6, \text{s}^{-1}$
$\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$	45	3.4 ± 0.2
	50	7.9 ± 0.4
	55	18.7 ± 0.8
	60	32.1 ± 1.0

^a $[\text{CrMn}(\text{CO})_{10}^-] = 5.0$ mM; $[\text{CH}_2\text{CHCH}_2\text{Br}] = 100$ mM.

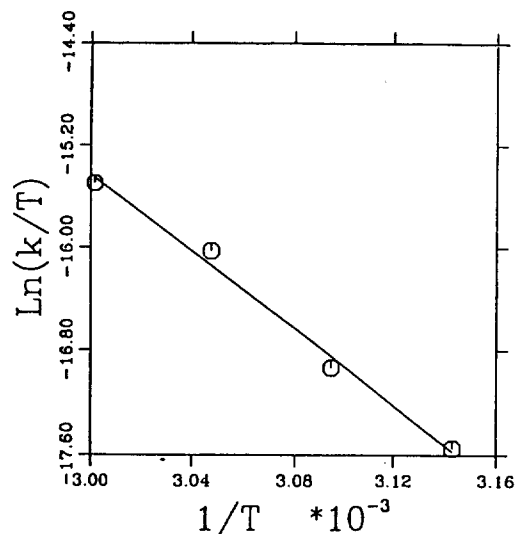


Figure 3. Eyring plot for the reaction of $\text{Na}^+\text{CrMn}(\text{CO})_{10}^-$ (5.0 mM) with $\text{CH}_2\text{CHCH}_2\text{Br}$ (100 mM) in THF.

$(\text{CO})_5^-$; however, in case of $\text{Mn}(\text{CO})_5^-$ the small protic polar solvent (CH_3OH) may be the best choice for the stabilization of the metal carbonylate through intermolecular hydrogen bonding interactions while CH_3CN may not be so effective in this respect (Table 5, 6).

For the reaction of $(\text{OC})_5\text{CrMn}(\text{CO})_5^-$ with CH_3I , the reaction rate of $\text{Mn}(\text{CO})_5^-$ with CH_3I is extremely faster (Eq. 4) than that of the first reaction step involved (Eq. 3); however, the situation does not apply to the corresponding reaction involving $\text{CH}_2\text{CHCH}_2\text{Br}$ because $\text{Mn}(\text{CO})_5^-$ reacts with $\text{CH}_2\text{CHCH}_2\text{Br}$ slowly but slightly faster than the dissociation reaction of $(\text{OC})_5\text{CrMn}(\text{CO})_5^-$ in the presence of allyl bromide; therefore, the difference in the enthalpy of activation ($\Delta H^\ddagger = 31.6 \pm 2.0$ kcal/mol vs 19.4 ± 0.3 kcal/mol) may represent an extra energy barrier for the reaction of $\text{Mn}(\text{CO})_5^-$ with $\text{CH}_2\text{CHCH}_2\text{Br}$ in addition to the enthalpy of activation

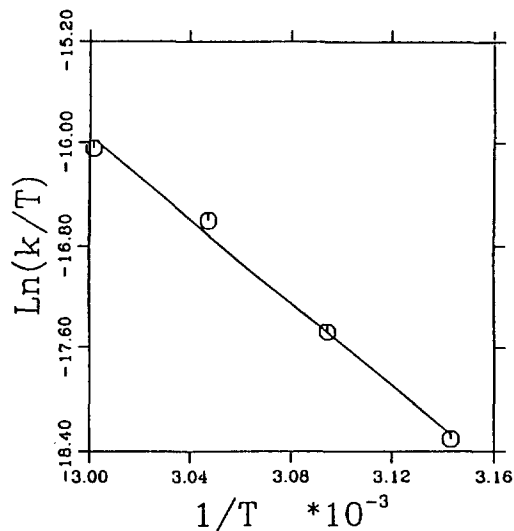


Figure 4. Eyring plot for the reaction of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$ (5.0 mM) with $\text{CH}_2\text{CHCH}_2\text{Br}$ (100 mM) in THF.

Table 5. Solvent dependence on the reaction of $\text{Na}^+\text{CrMn}(\text{CO})_{10}^-$ with $\text{CH}_2\text{CHCH}_2\text{Br}$ at 55 °C^a

Complex	Solvent (ϵ) ^b	$k_{\text{obs}} \times 10^6, \text{s}^{-1}$
$\text{Na}^+\text{CrMn}(\text{CO})_{10}^-$	THF (7.3)	35.6 ± 0.5
	MeOH (32.7)	97.3 ± 5.1
	CH_3CN (36.2)	52.5 ± 2.8

^a $[\text{CrMn}(\text{CO})_{10}^-] = 5.0 \text{ mM}$; $[\text{CH}_2\text{CHCH}_2\text{Br}] = 100 \text{ mM}$. ^bmeasured at 25 °C.

Table 6. Solvent dependence on the reaction of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$ with $\text{CH}_2\text{CHCH}_2\text{Br}$ at 55 °C^a

Complex	Solvent (ϵ) ^b	$k_{\text{obs}} \times 10^6, \text{s}^{-1}$
$\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$	THF (7.3)	18.7 ± 0.8
	MeOH (32.7)	95.5 ± 6.5
	CH_3CN (36.2)	51.5 ± 2.4

^a $[\text{CrMn}(\text{CO})_{10}^-] = 5.0 \text{ mM}$; $[\text{CH}_2\text{CHCH}_2\text{Br}] = 100 \text{ mM}$. ^bmeasured at 25 °C.

for the Cr-Mn bond cleavage.

Mechanistic Considerations. To account for the kinetic data obtained, three reaction pathways were proposed.

Single Electron Transfer (Radical Process)

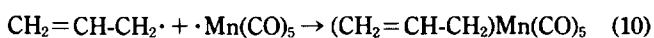
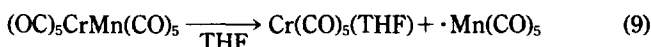
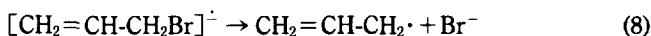
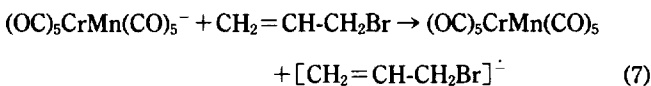
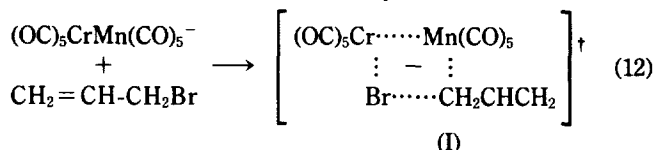
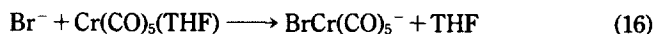
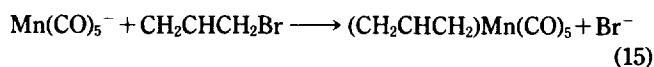
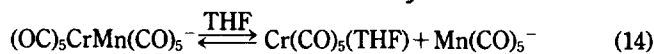


Figure 5. ESR spectrum of the reaction mixture of $(\text{OC})_5\text{CrMn}(\text{CO})_5^- \text{PPN}^+$ with $\text{CH}_2\text{CHCH}_2\text{Br}$ in THF in the presence of DMPO at ambient temperature.

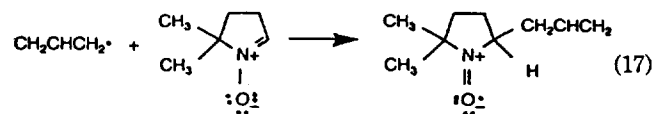
Concerted Reaction Pathway



Consecutive Reaction Pathway



The first proposed reaction mechanism, SET, was supported by the allyl radical formation; To see if any radical was formed or not, the reaction of $(\text{OC})_5\text{CrMn}(\text{CO})_5^- \text{PPN}^+$ with allyl bromide was performed in THF at ambient temperature with (or without) DMPO (5,5-dimethyl-1-pyrroline N-oxide), the radical trapping agent (Eq. 17).



Without DMPO no appreciable ESR hyperfine splitting patterns due to allyl radical were observed; however, in the presence of DMPO, the spectrum exhibits two groups of triplet arising from one ^{14}N ($I=1$) and one ^1H ($I=1/2$) nuclei (Figure 5). The large proton coupling constant ($a_H = 20.03\text{G}$) and the small nitrogen coupling constant ($a_N = 14.20\text{G}$) were obtained, which are similar to those ($a_H = 20.02\text{G}$; $a_N = 14.01\text{G}$) of the propyl radical formation from the reaction of the manganese hydride with propyl iodide in the presence of DMPO in THF at ambient temperature²⁰ as well as those of the methyl radical formation ($a_H = 23.00\text{G}$; $a_N = 16.25\text{G}$).²¹ The g value ($g = 2.0093$) of the possible allyl substituted DMPO radical is very close to the free electron value ($g = 2.0023$).²⁶

This ESR spectrum partly supports the SET mechanism; however, the fact that no ESR peak were observed without DMPO in the reaction mixture and the kinetic data (overall first order dependence of the metal complex concentration, etc) may disapprove this SET reaction pathway. To confirm this hypothesis, several back-to-back kinetic reactions were performed with and without radical scavengers such as DMPO, benzoquinone, or benzophenone. The kinetic run without DMPO at 60 °C gave the observed rate constant

of $32.3(1.5) \times 10^{-6} \text{ s}^{-1}$, and the run with DMPO gave $33.6(0.6) \times 10^{-6} \text{ s}^{-1}$, both values are within an experimental error range. The reactions employing other radical scavengers gave similar results.

The sharp contrast between these data sets could lead us to draw the conclusion that this reaction may involve the SET reaction pathway; however, this may not be the major reaction pathway, but, a minor one, if any, instead.

The proposed concerted reaction pathway appears to be possible; However, the overall first order rate dependency on $[(\text{OC})_5\text{CrMn}(\text{CO})_5]^-$ may rule out this possibility. The dependence of solvent polarity on the rate may also be related to the stabilization of the possible polar intermediates, which also disfavor the concerted reaction mechanism. The proposed intermediate (I in Eq. 12) may involve a considerable steric hindrance due to the bulky allyl bromide approaching to the coordinatively saturated $(\text{OC})_5\text{CrMn}(\text{CO})_5^-$ complex.

The kinetic data together with the results from the ligating ability comparison studies¹⁷ could lead us to propose the consecutive reaction pathway. First of all, the overall first order rate dependence upon $[(\text{OC})_5\text{CrMn}(\text{CO})_5]^-$ supports this mechanism. The polar solvent stabilizes the polar intermediates, $\text{Cr}(\text{CO})_5$ (solvent) and $\text{Mn}(\text{CO})_5^-$; moreover, the polar protic solvent such as CH_3OH seems to be very effective in stabilizing $\text{Mn}(\text{CO})_5^-$ through the intermolecular hydrogen bonding interactions. This polar solvent participation in the polar intermediate stabilization further supports this reaction pathway. The moderately positive entropy change of activation ($\Delta S^\ddagger = 15.6 \pm 6.3 \text{ e.u.}$ for PPN⁺ salt; $10.3 \pm 6.1 \text{ e.u.}$ for Na⁺ salt) may suggest the initial Cr-Mn bond cleavage (Eq. 14) is an energetic step. In these reactions Br⁻ reacts rapidly with $\text{Cr}(\text{CO})_5(\text{THF})$ in THF even at ambient temperature to yield $\text{Cr}(\text{CO})_5\text{Br}^-$ (eq. 16).

The reaction product was confirmed to be $(\eta^1\text{-CH}_2\text{CHCH}_2)\text{Mn}(\text{CO})_5$ which was evidenced by the ¹H NMR spectrum (¹H NMR in CDCl_3 ; δ 4.86-4.66 (m, 1H), 2.76 (d, $J=7.13 \text{ Hz}$, 2H), 1.79 (d, $J=12.20 \text{ Hz}$, 2H)). The reaction of $\text{Mn}(\text{CO})_5^-$ with $\text{CH}_2\text{CHCH}_2\text{Br}$ did not produce any detectable amount of $(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Mn}(\text{CO})_4$ with the concomitant evolution of CO from $(\eta^1\text{-CH}_2\text{CHCH}_2)\text{Mn}(\text{CO})_5$ even at the elevated temperature (30-60 °C).

The control reaction of $\text{Mn}(\text{CO})_5^-$ with the photochemically prepared $\text{Cr}(\text{CO})_5(\text{THF})$ produced $(\text{OC})_5\text{CrMn}(\text{CO})_5^-$ very fast and almost in quantitative yield because $\text{Mn}(\text{CO})_5^-$ is assumed to be a very reactive Lewis base towards the Lewis acid, $\text{Cr}(\text{CO})_5(\text{THF})$, at ambient temperature in THF.

Counterion Effect on Reaction Rates. It seems obvious that bulky cation such as PPN⁺ can hardly penetrate the coordination sphere of $(\text{OC})_5\text{CrMn}(\text{CO})_5^-$ so as to interact with either coordinated CO ligands or metal centers involved. There is some electron density build-up on Cr-Mn bond though much of it may be drained into the carbonyl bonds through back donation. Similar situation may be expected from the corresponding reaction involving Na⁺ salt in the presence of excess 18-crown-6.

For the reactions of the mononuclear transition metal carbonylates ($\text{Mn}(\text{CO})_5^-$,¹² $\text{CpMo}(\text{CO})_3^-$,²² $\text{Co}(\text{CO})_4^-$,²³ $\text{CpW}(\text{CO})_3^-$ ²⁴) with alkyl halides, a "normal" counterion effect was observed; the less associated the anion is with its cation, the greater is its nucleophilicity. However, the "inverse" counterion

Table 7. Activation parameters from the reaction of $\text{M}^+\text{CrMn}(\text{CO})_{10}^-$ ($\text{M}^+ = \text{Na}^+$, PPN⁺) with $\text{CH}_2\text{CHCH}_2\text{Br}$ in THF^a

Complex	Activation Parameters ^b
$\text{Na}^+\text{CrMn}(\text{CO})_{10}^-$	$\Delta H^\ddagger = 29.4 \pm 2.0 \text{ kcal/mol}$ $\Delta S^\ddagger = 10.3 \pm 6.1 \text{ e.u.}$
$\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$	$\Delta H^\ddagger = 31.6 \pm 2.0 \text{ kcal/mol}$ $\Delta S^\ddagger = 15.6 \pm 6.3 \text{ e.u.}$

^a $[\text{CrMn}(\text{CO})_{10}^-] = 5.0 \text{ mM}$; $[\text{CH}_2\text{CHCH}_2\text{Br}] = 100 \text{ mM}$. ^b Error limits represent 99.5% confidence limits.

Table 8. Counterion dependence of kinetic data for the reaction of $\text{CrMn}(\text{CO})_{10}^-$ with $\text{CH}_2\text{CHCH}_2\text{Br}$ in THF at 55 °C^a

Counterion	$k_{\text{obs}} \times 10^6, \text{ s}^{-1}$
Na^+	35.6 ± 0.5
PPN ⁺	18.7 ± 0.8
$\text{Na}^+ + [18\text{-C-6}]^b$	20.0 ± 0.7

^a $[\text{CrMn}(\text{CO})_{10}^-] = 5.0 \text{ mM}$; $[\text{CH}_2\text{CHCH}_2\text{Br}] = 100 \text{ mM}$. ^b $[18\text{-C-6}]$; 10.0 mM.

effect was observed in the similar reaction involving the activated organic halides such as benzyl halides^{22b} or allyl halides.²⁵ In such cases, the contact ion pairs were to enhance the corresponding reaction rates *via* the leaving group assistance by the less bulky cation which is the dominant factor determining the rate, though the tight ion pairing deteriorates its nucleophilicity to some extent.

With this in mind, we tried to evaluate the specific role the counterion may play in this heterobimetallic complex; however, the drastic difference in the reaction pathway of the reactions between the mononuclear species and the heterobimetallic ones has made the direct comparison impossible. It seems, however, not surprising that Na⁺ must interact with Cr-Mn bond in which high electron density resides, which may show the faster reaction rate than that of the PPN⁺ salt (Table 7). The leaving group (Br⁻) assisted by Na⁺, namely "inverse" counterion effect^{22b,25} may be presumed to be possible in the case of the second reaction step of $\text{Mn}(\text{CO})_5^-$ with $\text{CH}_2\text{CHCH}_2\text{Br}$ (Eq. 15), which may also help enhance the rate.

It is of importance and of interest to see whether $\text{Mn}(\text{CO})_5^-$ attacks the γ -carbon or α -carbon of the $\text{CH}_2\text{CHCH}_2\text{Br}$; however, the previously studied reaction of $\text{CpMo}(\text{CO})_3^-$ with allyl halide showed ¹H NMR evidence which confirms the α -carbon attack.²⁵ Any appreciable interaction between Na⁺ and the coordinated carbonyl ligands in $(\text{OC})_5\text{CrMn}(\text{CO})_5^-$ could not be detected, which may not lead to the $(\eta^3\text{-allyl})\text{Mn}(\text{CO})_4$.

Acknowledgment. Research supports both from the Korea Research Foundation (1993) and Korea Science and Engineering Foundation (92-25-00-04) are greatly appreciated.

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