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Kinetic studies of the cleavage of $M^+[M'M''(CO)_9L]^-$ ($M^+ = Na^+, PPN^+$; $M' = Cr, W$; $M'' = Mn, Re$; $L = CO, PR_3$)

Yong K. Park ^{*}, Seon J. Kim, Jin H. Kim, In S. Han, Chang H. Lee

Department of Chemistry, Kangweon National University, Chuncheon 200-701 (Korea)

and Hyung S. Choi

Division of Chemistry, Korea Institute of Science & Technology, Seoul 136-701 (Korea)

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Abstract

Heterobimetallic complexes have a donor–acceptor metal–metal bond in which two electrons from the electron rich metal moiety are donated to the other electron-deficient metal moiety. The heterobimetallic species of interest, $M^+[M'M''(CO)_9L]^-$ ($M^+ = Na^+, PPN^+$; $M' = Cr, W$; $M'' = Mn, Re$; $L = CO, PR_3$) undergoes ligand substitution or metal–metal bond cleavage upon reaction with PR_3 ($R = C_6H_5, C_2H_5$) or CO . Unprecedented reactions by the counter ion were observed. Factors affecting these dimeric disruptions will be discussed on the basis of the kinetic studies.

Introduction

Interest in heterobimetallic complexes is growing because of their usefulness as homogeneous catalysts [1]. These complexes are often a combination of an electron-rich and an electron-deficient metal moiety. The bond of this type in the heterobimetallic complex may be described as a donor–acceptor bond or dative metal–metal bond [2]. The bonding situation, whether it is strong or weak, can be modified by ancillary ligands such as PR_3 or NR_3 . Inter- and intramolecular ligand mobility and $M-M'$ bond cleavage can be affected by the polarity or electron density of the each metal. Recently interest in heterobimetallic complexes has been focused on studying the formation and stability of the mixed metal complexes: $[MnM(CO)_{10}]^-$ ($M = Cr, W$) [3]; $[HFeM(CO)_9]^-$ ($M = Cr, W$) and $[HFe(CO)_3P(OMe)_3W(CO)_5]^-$ [4]; $[(\mu-H)CrW(CO)_{10}]^-$ [5]; $[ReMn(CO)_{10}]$ [3]; $[(Me_3P)(OC)_4OsM(CO)_5]$ ($M = Cr, W$) [6]; $[(Me_3P)(OC)_4OsRe(CO)_4(Br)]$ [7]; $[(OC)_4CoRh(CO)(PEt_3)_2]$ [8].

In anionic complexes such as $[(OC)_5M'M(CO)_5]^-$ ($M' = Mn, Re$; $M = Cr, Mo, W$) [3a] and $[(H)(OC)_4FeM(CO)_5]^-$ ($M = Cr, W$) [9], location of the negative charge on a non group 6 metal atom results in a dative metal–metal bond in the ion; however, a similar charge on a group 6 metal atom leads to a covalent metal–metal

bond [6]. Up to now no systematic investigations of the effects of the ancillary ligands, metals, and counter ions on the formation of dative metal-metal bonds in anionic heterobimetallic complexes had been carried out. Here we report the preparation of a series of anionic heterobimetallic complexes such as $M^+[M'M''(CO)_9L]^-$ ($M^+ = Na^+$, PPN^+ ; $M' = Cr, W$; $M'' = Mn, Re$; $L = CO, PR_3$) and a detailed kinetic study on their reaction with phosphorus ligands.

Experimental

A. Materials. Solvents were distilled under nitrogen from appropriate O_2 scavenging and drying agents. Tetrahydrofuran (THF) and toluene were distilled under nitrogen from sodium/benzophenone ketyl. Hexane was purified by stirring over concentrated H_2SO_4 overnight, then washing with aqueous $NaHCO_3$ and distilling from sodium/benzophenone ketyl. Acetonitrile was purified by distillation twice from calcium hydride and twice from P_2O_5 before being stored over 3-Å molecular sieves. Methylene chloride was distilled from P_2O_5 under N_2 . Ethanol and n-butanol were distilled from calcium hydride. Bis(triphenylphosphine) nitrogen(1^+) chloride (PPN^+Cl^-) was purchased from Aldrich. All other chemicals were purchased from commercial suppliers and used without further purification.

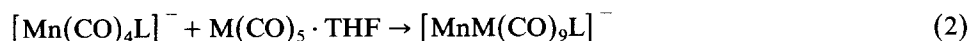
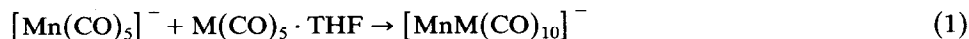
B. Instrumentation. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer with 0.10-mm sealed CaF_2 or $NaCl$ solution cells. ^{13}C NMR spectra were recorded on a Bruker WM-300 spectrometer and all the chemical shifts are referenced in $CDCl_3$. Photoreactions were performed with a 450 watt mercury vapor lamp (Hanovia). Unless stated otherwise, all reactions were carried out under nitrogen, Vacuum Atmospheric Company glovebox, or in an inert atmosphere.

C. Preparations. $[M(CO)_5(THF)]$ ($M = Cr, W$) [9], $[Mn_2(CO)_8(PR_3)_2]$ ($R = C_6H_5, C_2H_5$) [10a], $PPN^+[Mn(CO)_5]^-$ [10b], and $PPN^+[CrMn(CO)_{10}]^-$ [15] were prepared by published procedures. The metal carbonylates were prepared from Na/Hg reduction of the corresponding metal carbonyl dimers [16].

D. Kinetic measurements. The kinetic studies were carried out in dried 10 ml volumetric flasks which were sealed with rubber septum caps. In a typical study, 0.05 mmol of heterobimetallic complex was placed in a 10 ml volumetric flask inside a drybox. The flask was removed from the drybox, a standard solution of the appropriate phosphine in THF was added by syringe, the solution was agitated until it was homogeneous, and then placed in a Haake water bath equipped with a thermostat ($\pm 0.05^\circ C$). Samples for IR spectroscopy were withdrawn periodically by syringe and placed in a sealed 0.1 mm path-length $NaCl$ or CaF_2 infrared cell. The rates of the reaction were monitored by following the disappearance or growth generation in absorbance of the reactant or product, respectively. Under the pseudo first-order reaction conditions, rate constants were calculated by use of 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 absorbance at time infinity, and second-order rate constants were calculated: $k_2 = k_{obsd}/[PR_3]$. Anionic heterobimetallic complexes ($[CrMn(CO)_9PR_3]^-$ derivatives) showed a linear dependence on phosphine concentration indicating an overall second-order reaction. However, the reaction rate of $[CrMn(CO)_{10}]^-$ was independent of $[PR_3]$, and the reaction was found to be first order with respect to $[CrMn(CO)_{10}^-]$ (rate = $k_1[CrMn(CO)_{10}^-]$) [15]. Products were identified from their infrared spectra as compared with previously isolated compounds reported in the literature.

Results and discussion

The heterobimetallic anions were synthesised by the ligand substitution of labile ligand derivatives of group 6 metal carbonyls, $M(\text{CO})_5 \cdot \text{THF}$ ($M = \text{Cr}, \text{W}$) with $[\text{M}'(\text{CO})_5]^-$ ($\text{M}' = \text{Mn}, \text{Re}$) or $[\text{Mn}(\text{CO})_4\text{L}]^-$ ($\text{L} = \text{PPh}_3, \text{PEt}_3$) as depicted in eqs. 1 and 2.



The reactions went to completion during mixing at 25 °C, to give the desired heterobimetallic complexes in high yields (75 to 90%).

Spectroscopic properties. The infrared spectral data for $\text{PPN}^+[\text{CrMn}(\text{CO})_9\text{PPh}_3]^-$ and $\text{Na}^+[\text{CrMn}(\text{CO})_9\text{PPh}_3]^-$ in the $\nu(\text{CO})$ region are listed in Table 1. The spectra of $\text{PPN}^+[\text{CrMn}(\text{CO})_9\text{PPh}_3]^-$ and $\text{Na}^+[\text{CrMn}(\text{CO})_9\text{PPh}_3]^-$ were found to be very similar. However, in the latter a lower energy band at 1836 cm^{-1} was observed, which is ascribed to a $\text{MCO} \cdots \text{Na}^+$ interaction [11]. Surprisingly, this counter-ion effect was not observed in $\text{Na}^+[\text{CrMn}(\text{CO})_{10}]^-$.

Selected ^{13}C NMR data for the complexes are given in Table 2. $\text{PPN}^+[\text{WMn}(\text{CO})_{10}]^-$ shows four singlets, the former two peaks (δ 207.1 ppm (peak ratio 4), δ 206.7 ppm (1)) may correspond to CO's of $\text{Mn}(\text{CO})_5$ moiety. The latter two (δ 205.9 ppm (1), δ 199.5 ppm (4)) may correspond to CO's of $\text{W}(\text{CO})_5$ moiety [13].

Table 1

IR spectral data (THF) for the various heterobimetallic complexes, $\text{M}^+[\text{M}'\text{M}''(\text{CO})_9\text{L}]^-$ ($\text{M}^+ = \text{Na}^+, \text{PPN}^+$; $\text{M}' = \text{Cr}, \text{W}$; $\text{M}'' = \text{Mn}, \text{Re}$; $\text{L} = \text{CO}, \text{PR}_3$)

Heterobimetallics	$\nu(\text{CO}), \text{cm}^{-1}$
$\text{PPN}^+[\text{CrMn}(\text{CO})_9\text{PPh}_3]^-$	2015(w), 1950(w), 1915(s), 1849(m)
$\text{Na}^+[\text{CrMn}(\text{CO})_9\text{PPh}_3]^-$	2015(w), 1950(m), 1915(s), 1845 (m), 1810(w)
$\text{PPN}^+[\text{CrMn}(\text{CO})_9\text{PEt}_3]^-$	2037(w), 1971(w), 1915(s), 1850(s)
$\text{PPN}^+[\text{WMn}(\text{CO})_9\text{PEt}_3]^-$	2048(w), 1960(w), 1905(s), 1837(s)
$\text{PPN}^+[\text{WMn}(\text{CO})_9\text{PPh}_3]^-$	2025(w), 1950(m), 1910(s), 1840(m)
$\text{Na}^+[\text{CrMn}(\text{CO})_{10}]^-$	2063(w), 1988(m), 1950(s), 1923(m), 1894(s), 1862(m)
$\text{PPN}^+[\text{CrMn}(\text{CO})_{10}]^-^a$	2063(w), 1988(m), 1950(s), 1923(m), 1894(s), 1862(m)
$\text{PPN}^+[\text{WMn}(\text{CO})_{10}]^-^a$	2066(m), 2007(m), 1948(s), 1926(m), 1898(s), 1861(m)
$\text{PPN}^+[\text{CrRe}(\text{CO})_{10}]^-^a$	2078(w), 1985(s), 1961(vs), 1928(m), 1888(s), 1858(m)

^a Ref. 4.

Table 2

^{13}C NMR data for the heterobimetallic complexes, $\text{PPN}^+[\text{MMn}(\text{CO})_9\text{L}]^-$ ($\text{M} = \text{Cr}, \text{W}$; $\text{L} = \text{CO}, \text{PPh}_3$)^a

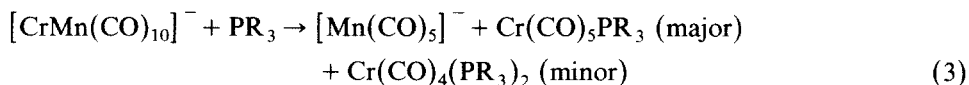
Heterobimetallics	$\delta(\text{CO}), \text{ppm}$		
	Mn	W	Cr
$\text{PPN}^+[\text{WMn}(\text{CO})_{10}]^-$	207.1(4) ^b , 206.7(1)	205.9(1), 199.5(4)	
$\text{PPN}^+[\text{CrMn}(\text{CO})_9\text{PPh}_3]^-$	203.1(4)	202.5(1), 199.3(4)	
$\text{Na}^+[\text{CrMn}(\text{CO})_9\text{PPh}_3]^-$	216.4(4)		235.3(1), 220.5(5)
$[\text{Cr}(\text{CO})_6]^-^c$			212.5

^a CDCl_3 solution at 20 °C. ^b Peak ratio in parenthesis. ^c Ref. 6.

However, $\text{PPN}^+[\text{MMn}(\text{CO})_9\text{PPh}_3]^-$ ($\text{M} = \text{Cr}, \text{W}$) has three singlets. Only one resonance is associated with the carbonyl carbons of $[\text{Mn}(\text{CO})_4\text{PPh}_3]^-$. As expected, two peaks for the $\text{W}(\text{CO})_5$ moiety are found at higher field for $[\text{WMn}(\text{CO})_9\text{PPh}_3]^-$; thus PPh_3 is probably *trans* to M ($\text{M} = \text{Cr}, \text{W}$) in $[\text{MMn}(\text{CO})_9\text{PR}_3]^-$.

A measure of the donor-acceptor properties of L' has been reported by Bodner and co-workers [13b] in which a correlation was obtained between the donor-acceptor ratio and the chemical shift difference ($\Delta\delta$) of the *cis* carbonyls between $\text{Cr}(\text{CO})_5(\text{L}')$ and $\text{Cr}(\text{CO})_6$. The $\Delta\delta$ values for the derivatives with $\text{L}' = \text{PCl}_3, \text{PPh}_3$, and PEt_3 are 0.18, 5.25, and 5.96, respectively [6]. A $\Delta\delta$ value of 8.0 was obtained for $\text{PPN}^+[\text{CrMn}(\text{CO})_9\text{PPh}_3]^-$ (see Table 2) which indicates that $[\text{Mn}(\text{CO})_4\text{PPh}_3]^-$ has a larger donor-acceptor ratio than common phosphorus-donor ligands. This donor ability of $[\text{Mn}(\text{CO})_4\text{PR}_3]^-$ may have a great influence on the reaction kinetics and this will be discussed in more detail later.

Reactions of $\text{M}^+[\text{CrMn}(\text{CO})_{10}]^-$ ($\text{M}^+ = \text{Na}^+, \text{PPN}^+$) with PR_3 ($\text{R} = \text{C}_6\text{H}_5, \text{OCH}_3, \text{C}_2\text{H}_5$). Kinetic studies of the cleavage of $\text{M}^+[\text{CrMn}(\text{CO})_{10}]^-$ ($\text{M}^+ = \text{Na}^+, \text{PPN}^+$) [14] in the presence of PPh_3 were carried out in THF solution. The reaction products obtained were $[\text{Mn}(\text{CO})_5]^-$ and the mono- and di-substituted chromium carbonyls (eq. 3).

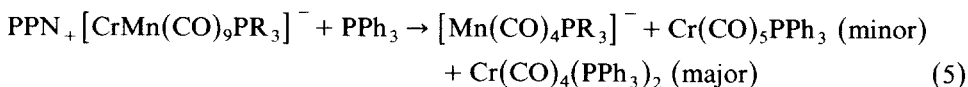


Reaction of $[\text{CrMn}(\text{CO})_{10}]^-$ with a 20-fold excess of PR_3 were typically performed in THF and monitored against time by $\nu(\text{CO})$ IR. The reaction rate was first order for $[\text{CrMn}(\text{CO})_{10}]^-$ (0.005 M) and zero order for $[\text{PR}_3]$ (0.025–0.30 M) [15].

$$\text{rate} = k_1 [\text{CrMn}(\text{CO})_{10}]^- \quad (4)$$

The first order rate constants, k_1 , were also measured for the reaction of $[\text{CrMn}(\text{CO})_{10}]^-$ with PPh_3 in THF as a function of temperature (Table 3) and the activation parameters were calculated from the Eyring plots (Fig. 1 and Table 4). The activation parameters of $\Delta H^\ddagger = 27.24 \pm 1.5$ kcal/mol and $\Delta S^\ddagger = 58.7 \pm 4.4$ e.u. suggest a dissociative mechanism in which cleavage of either the metal-metal bond or the metal-carbonyl bond is the rate-determining step [15].

Reactions of $\text{M}^+[\text{CrMn}(\text{CO})_9\text{PR}_3]^-$ ($\text{M}^+ = \text{Na}^+, \text{PPN}^+$) with PR_3 ($\text{R} = \text{C}_6\text{H}_5, \text{OCH}_3, \text{C}_2\text{H}_5$). Kinetic studies of the reactions of $\text{PPN}^+[\text{CrMn}(\text{CO})_9\text{PPh}_3]^-$ and $\text{PPN}^+[\text{CrMn}(\text{CO})_9\text{PEt}_3]^-$ with PR_3 were performed in THF under the pseudo first-order condition. All the reactions gave $\text{PPN}^+[\text{Mn}(\text{CO})_4\text{PR}_3]^-$ and $\text{Cr}(\text{CO})_4(\text{PR}_3)_2$ as major products, which is sharp contrast to the products $\text{PPN}^+[\text{Mn}(\text{CO})_5]^-$ and $\text{Cr}(\text{CO})_5(\text{PR}_3)$, obtained in case of $\text{PPN}^+[\text{CrMn}(\text{CO})_{10}]^-$. $\text{Cr}(\text{CO})_5\text{PR}_3$ was not obtained at reaction temperatures below 60°C. The reaction described in eq. 5 follows second-order kinetics, being first order in both $[\text{CrMn}(\text{CO})_9\text{PR}_3]^-$ and $[\text{PPh}_3]$, respectively.



$$\text{rate} = k_2 [\text{CrMn}(\text{CO})_9\text{PR}_3]^- [\text{PPh}_3] \quad (6)$$

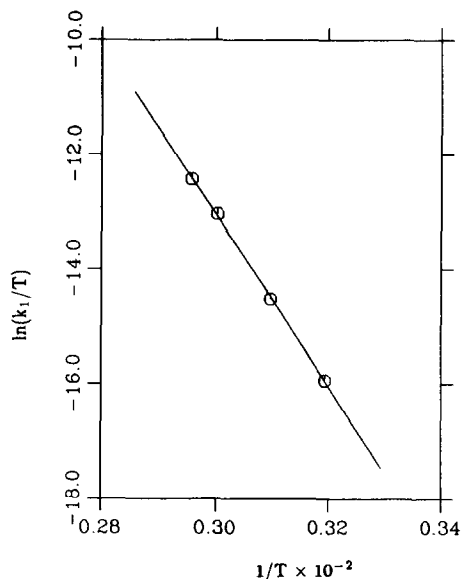


Fig. 1. Eyring plot for the reaction of $\text{Na}^+[\text{CrMn}(\text{CO})_{10}]^-$ with $\text{P}(\text{C}_6\text{H}_5)_3$ (20-fold excess) in THF.

Table 3

Temperature dependence of the reaction of $\text{PPN}^+[\text{CrMn}(\text{CO})_9\text{L}]^-$ ($\text{L} = \text{CO}, \text{PR}_3$) with a 20-fold excess of $\text{P}(\text{C}_6\text{H}_5)_3$ in THF ^{a,b}

Heterobimetallic complex	Temp. ($^{\circ}\text{C}$)	$k_{\text{obs}} \times 10^6, \text{M}^{-1} \text{s}^{-1}$ ^c
$\text{PPN}^+[\text{CrMn}(\text{CO})_9\text{PPh}_3]^-$	30	1.47 ± 0.17
	40	4.58 ± 0.23
	50	13.8 ± 0.73
	60	40.1 ± 2.58
$\text{PPN}^+[\text{CrMn}(\text{CO})_9\text{PEt}_3]^-$	30	0.75 ± 0.19
	40	1.71 ± 0.34
	50	8.36 ± 0.57
	60	25.5 ± 3.1
$\text{PPN}^+[\text{CrMn}(\text{CO})_{10}]^-$	40	3.28 ± 0.29
	50	9.03 ± 0.49
	60	44.5 ± 7.6
	70	76.7 ± 9.8

^a [Dimer]; 5.0 mmol. ^b $[\text{P}(\text{C}_6\text{H}_5)_3]$; 100 mmol. ^c Confidence limits at 90%.

Table 4

The reaction rate of $\text{M}^+[\text{CrMn}(\text{CO})_9\text{L}]^-$ ($\text{M}^+ = \text{Na}^+, \text{PPN}^+$; $\text{L} = \text{CO}, \text{PPh}_3, \text{PEt}_3$) with a 20-fold excess of $\text{P}(\text{C}_6\text{H}_5)_3$ in THF at 40°C

Heterobimetallic complex	Temp. ($^{\circ}\text{C}$)	$k_{\text{obs}} \times 10^6, \text{M}^{-1} \text{s}^{-1}$
$\text{PPN}^+[\text{CrMn}(\text{CO})_{10}]^-$	40	3.28 ± 0.29
$\text{Na}^+[\text{CrMn}(\text{CO})_{10}]^-$	40	3.74 ± 0.28
$\text{PPN}^+[\text{CrMn}(\text{CO})_9\text{PPh}_3]^-$	40	4.58 ± 0.23
$\text{Na}^+[\text{CrMn}(\text{CO})_9\text{PPh}_3]^-$	40	39.3 ± 3.2
$\text{PPN}^+[\text{CrMn}(\text{CO})_9\text{PEt}_3]^-$	40	1.71 ± 0.34

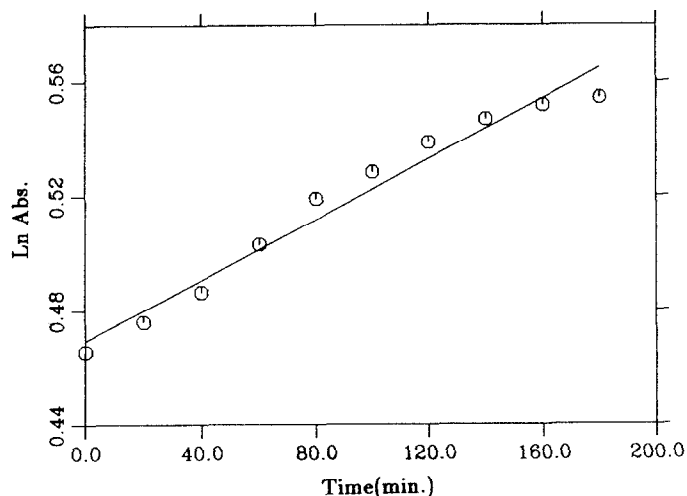


Fig. 2. Pseudo-first-order plot of the reaction of $\text{PPN}^+[\text{CrMn}(\text{CO})_9\text{PEt}_3]^-$ with $\text{P}(\text{C}_6\text{H}_5)_3$ (20-fold excess) in THF at 50.0°C .

The measured second order rate constants, k_2 , for the reactions of $\text{PPN}^+[\text{CrMn}(\text{CO})_9\text{L}]^-$ ($\text{L} = \text{PPh}_3, \text{PEt}_3$) with PPh_3 are shown Fig. 2. The calculated activation parameters from Fig. 3 are shown in Table 5. The activation parameters determined for $[\text{CrMn}(\text{CO})_9\text{PPh}_3]^-$, were $\Delta H^\ddagger = 21.3 \pm 0.5$ kcal/mol and $\Delta S^\ddagger = -10.6 \pm 1.6$ e.u., while $\Delta H^\ddagger = 23.7 \pm 0.5$ kcal/mol, $\Delta S^\ddagger = -4.14 \pm 3.1$ e.u. for $[\text{CrMn}(\text{CO})_9\text{PEt}_3]^-$. The negative changes in the entropy of activation suggest that an associative character is probably involved in the rate-determining step, which

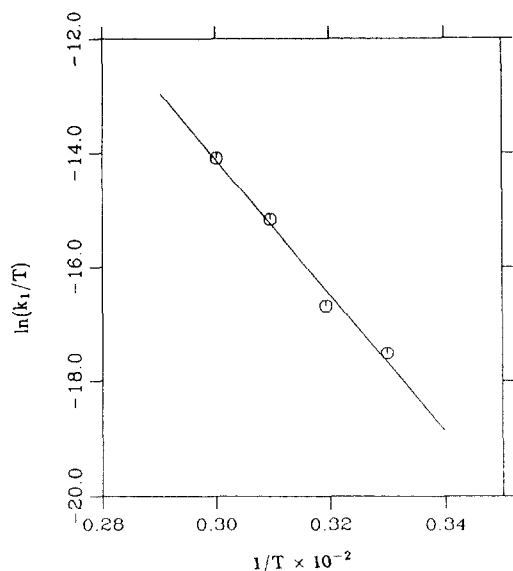


Fig. 3. Eyring plot for the reaction of $\text{PPN}^+[\text{CrMn}(\text{CO})_9\text{PEt}_3]^-$ with $\text{P}(\text{C}_6\text{H}_5)_3$ (20-fold excess) in THF.

Table 5

Activation parameters for the reaction of $M^+ [CrMn(CO)_9L]^-$ ($M^+ = Na^+, PPN^+$; $L = CO, PPh_3, PEt_3$) with a 20-fold excess of $P(C_6H_5)_3$ ^a

Heterobimetallic complex	ΔH^\ddagger (kcal/mol)	ΔS^\ddagger (e.u.)
$PPN^+ [CrMn(CO)_{10}]^-$	27.2 ± 1.5	58.7 ± 4.4
$Na^+ [CrMn(CO)_{10}]^-$	29.2 ± 0.5	16.0 ± 1.5
$PPN^+ [CrMn(CO)_9PPh_3]^-$	21.3 ± 0.5	-10.6 ± 1.6
$Na^+ [CrMn(CO)_9PPh_3]^-$	14.9 ± 0.6	-26.6 ± 1.9
$PPN^+ [CrMn(CO)_9PEt_3]^-$	23.7 ± 0.5	-4.14 ± 3.1

^a Errors are given at 95% confidence limits.

Table 6

Product distributions for the reaction of the heterobimetallic complexes with PPh_3

Heterobimetallic complex	Products (yield (%))
$PPN^+ [CrMn(CO)_{10}]^-$	$[Mn(CO)_5]^- + Cr(CO)_5PPh_3$ (95) + $Cr(CO)_4(PPh_3)_2$ (5)
$Na^+ [CrMn(CO)_{10}]^-$	$[Mn(CO)_5]^- + Cr(CO)_5PPh_3$ (90) + $Cr(CO)_4(PPh_3)_2$ (10)
$PPN^+ [CrMn(CO)_9PPh_3]^-$	$[Mn(CO)_4PPh_3]^- + Cr(CO)_5PPh_3$ (2) + $Cr(CO)_4(PPh_3)_2$ (98)
$Na^+ [CrMn(CO)_9PPh_3]^-$	$[Mn(CO)_4PPh_3]^- + Cr(CO)_5PPh_3$ (67) + $Cr(CO)_4(PPh_3)_2$ (33)
$PPN^+ [CrMn(CO)_9PEt_3]^-$	$[Mn(CO)_4PEt_3]^- + Cr(CO)_5PPh_3$ (2) + $Cr(CO)_4(PPh_3)_2$ (98)

involves the initial PR_3 attack on Cr moiety followed by cleavage of Cr–CO bond cleavage. Accordingly the resulting disubstituted Cr product was observed as a major product.

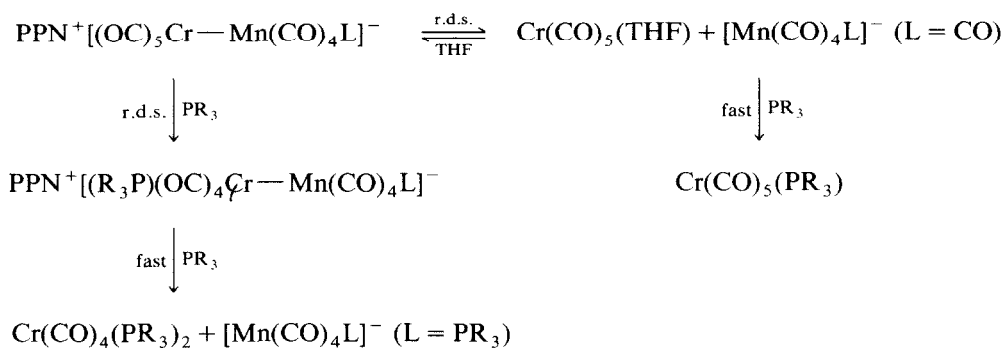
The electronic nature of the incoming ligand (PR_3) seems to be a dominant factor in determining the reaction rate of $PPN^+[CrMn(CO)_9PPh_3]^-$. However, neither electronic nor steric factors are likely to be involved in the reaction of $PPN^+[CrMn(CO)_{10}]^-$ as shown in Table 7. This striking difference in the effects of the ligand on the reactions can be well explained if the reaction orders of the various reactions are considered. Since PPh_3 is regarded as a better σ -donor in $PPN^+[Mn(CO)_4PPh_3]^-$ than CO is in $PPN^-[Mn(CO)_5]^-$, the former anion appears to be more basic toward Lewis acid than the latter [18]. This enhanced basicity by PPh_3 probably produces a stronger Mn–Cr bond than in the all-CO analogue. The

Table 7

Dependence of the rate of the reaction of $PPN^+[CrMn(CO)_9L]^-$ ($L = CO, PPh_3$) with a 20-fold excess of PR_3 at 60 °C on incoming ligand

Heterobimetallic complex	Ligand	$k_{obs} \times 10^6$	Cone angle (°) ^a
$PPN^+ [CrMn(CO)_9PPh_3]^-$	$P(C_6H_5)_3$	38.9 ± 2.6	145
	$P(OCH_3)_3$	59.3 ± 3.2	107
	$P(C_2H_5)_3$	152 ± 14	132
$PPN^+ [CrMn(CO)_{10}]^-$	$P(C_6H_5)_3$	38.8 ± 4.0	145
	$P(OCH_3)_3$	45.7 ± 6.9	107
	$P(C_2H_5)_3$	44.0 ± 3.6	132

^a Ref. 20.



Scheme 1. r.d.s. = rate determining step.

greater electron density at the Mn–Cr bond could preferentially cause the initial Cr–CO bond cleavage by the incoming ligand, PR_3 . In contrast, the Cr–Mn bond is broken first in case of $\text{PPN}^+[\text{CrMn}(\text{CO})_{10}]^-$ [17]. These observations are further supported by the shift of the major $\nu(\text{CO})$ IR band for the C_{4v} $\text{Cr}(\text{CO})_5$ fragment bound to the ligand $[\text{Mn}(\text{CO})_4\text{L}]^-$ ($\text{L} = \text{CO}$, 1950 cm^{-1} ; PPh_3 , 1915 cm^{-1} ; PEt_3 , 1912 cm^{-1}) [12, 19].

The ligand substitution effect in the cleavage reactions is shown in Scheme 1. Heterobimetallic complexes such as $[\text{CrMn}(\text{CO})_9\text{L}]^-$ ($\text{L} = \text{CO}$, PR_3), probably have different rate-determining steps for cleavage by PPh_3 for different ligands (L). The reaction of $[\text{CrMn}(\text{CO})_{10}]^-$ with PPh_3 is first order in $[\text{CrMn}(\text{CO})_{10}]^-$ and the entropy of activation ($\Delta S^\ddagger = 58.7 \pm 4.4 \text{ e.u.}$) suggests a dissociative process. Nevertheless, if Cr–CO cleavage is applicable here, one would expect to obtain predominantly neutral disubstituted products ($\text{Cr}(\text{CO})_4(\text{PR}_3)_2$). In fact only 20% of the product obtained at 65°C was disubstituted. These results indicate that metal–metal bond cleavage is the rate-determining step.

Two competing reaction pathways as shown in Scheme 1 may account for reaction product distribution obtained in these reaction (Table 7). In the dominant reaction pathway, attack by the PR_3 ligand on the Cr metal center is followed by ligand substitution. However, once the electron-donating ligand is bonded to Cr, the Cr–Mn bond may be drastically weakened [9], thus this bond can be readily cleaved by the incoming PR_3 ligand. This reaction pathway accounts for the overall second order kinetics and the formation of the disubstituted Cr product, $\text{Cr}(\text{CO})_4(\text{PR}_3)_2$ as the major species.

The third-row transition metal heterobimetallic complexes, $\text{PPN}^+[\text{WMn}(\text{CO})_{10}]^-$ and $\text{PPN}^+[\text{CrRe}(\text{CO})_{10}]^-$ did not react with PR_3 ($\text{R} = \text{C}_6\text{H}_5$) even in the presence of a 20-fold excess of phosphine at elevated temperature (70°C). The robust nature of these complexes is not clearly understood.

Counter ion effect. In a similar reaction rate study as described above, $\text{Na}^+[\text{CrMn}(\text{CO})_9\text{PPh}_3]^-$ was treated with PPh_3 to produce $[\text{Mn}(\text{CO})_4\text{PPh}_3]^-$, $\text{Cr}(\text{CO})_4(\text{PPh}_3)_2$ (67%) and $\text{Cr}(\text{CO})_5\text{PPh}_3$ (33%). The rate law was found to be first order for both $[\text{Na}^+\text{CrMn}(\text{CO})_9\text{PPh}_3]^-$ and $[\text{PPh}_3]$, respectively, but the overall reaction was second order (equation 7).

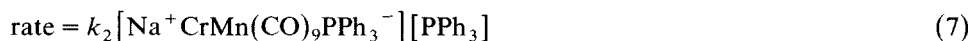


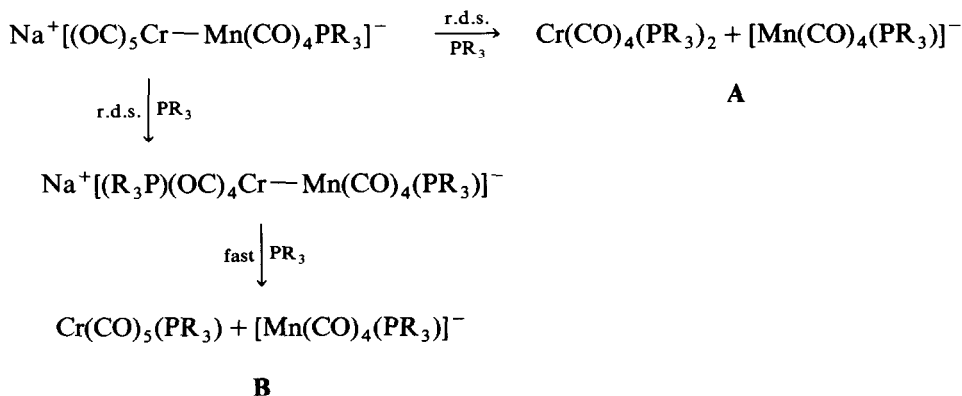
Table 8

The relationship between $P(C_6H_5)_3$ concentrations and the rate (k_{obs}) of the reaction of $PPN^+ [CrMn(CO)_9L]^-$ ($L = PPh_3, PEt_3$) with in THF at $60^\circ C$

Heterobimetallic complex	Concentration, M (fold)	$k_{obs} \times 10^6$
$PPN^+ [CrMn(CO)_9PPh_3]^-$	0.025(5-)	8.93 ± 1.1
	0.05(10-)	17.6 ± 1.9
	0.10(20-)	38.9 ± 2.6
	0.20(40-)	72.8 ± 3.7
	0.30(60-)	113 ± 8.5
$PPN^+ [CrMn(CO)_9PEt_3]^-$	0.025(5-)	5.15 ± 1.9
	0.10(20-)	25.5 ± 3.2
	0.15(30-)	38.2 ± 4.5

Activation parameters for the reaction were determined $\Delta H^\ddagger = 14.9 \pm 0.6$ kcal/mol and $\Delta S^\ddagger = -26.6 \pm 1.9$ e.u. (Table 5). The rate constant for $Na^+ [CrMn(CO)_9PPh_3]^-$ at $40^\circ C$ was $(39.3 \pm 3.2) \times 10^{-6} M^{-1} s^{-1}$ which is approximately 9 times greater than that of the PPN^+ analogue. This counter ion effect may be related to the previous studies on the ion pairing of the anionic metal carbonyls [11]. Therefore, it is possible that the cationic interactions can alter the electron density either on the Cr-CO (at the rate determining step) or Cr-Mn bond (at fast step) resulting in a reaction rate higher than for the PPN^+ analogue.

The products obtained from the reaction of $Na^+ [CrMn(CO)_9PR_3]^-$ with PR_3 are $Cr(CO)_5PPh_3$ (major) and $Cr(CO)_4(PR_3)_2$ (minor). The negative entropy of activation indicates an associative character at the rate-determining step. As is observed in Scheme 2, $Na^+ [CrMn(CO)_9]^-$ may have two possible pathways for disruption. In path A, the PPh_3 attacks the Cr-Mn bond prior to the substitution of CO on Cr resulting mono-substituted $Cr(CO)_5PPh_3$. Path B is similar to the mechanism involving $PPN^+ [CrMn(CO)_9PPh_3]^-$. The proposed disruption pathways of $Na^+ [CrMn(CO)_9PR_3]^-$ may indicate the Na^+ ion assist in the disruption through the $Cr \cdots Na$ or $Cr-CO \cdots Na$ interactions. Thus, the entering ligand, PPh_3 , could attack the Cr metal site dominantly over Cr-CO substitution due to the



Scheme 2. r.d.s. = rate determining step.

interaction between Na^+ and Cr metal even though one expects there is some electron density build up caused by the electron donating ligand, PR_3 .

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