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Kinetics and Mechanism of Substitution Reaction of $PPN^+(\eta^5\text{-}MeCp)Mn(CO)_2Cl^-$ with PR_3 (R=Me, Et, OEt, C_6H_5)

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The transition metal carbonylate, $PPN^+(\eta^5\text{-}MeCp)Mn(CO)_2Cl^-$ undergoes a novel ligand substitution reaction with PR_3 (R=Me, Et, OEt, C_6H_5) in THF at elevated temperatures (40 ℃ up to 60 ℃) under the pseudo-first-order reaction conditions (usually 20-fold excess of PR_3 with respect to metal carbonylate concentrations) where chloride is displaced by PR_3. The reaction follows overall first order dependence on $[(\eta^5\text{-}MeCp)Mn(CO)_2Cl^-]$; however, the negative entropy changes of activation ($\Delta S^{\neq} = -19.3$ e.u. for $P(OEt)_3$; $\Delta S^{\neq} = -16.4$ e.u. for PPh_3) suggest the existence of the intermediate, $(\eta^3\text{-}MeCp)Mn(CO)_2(THF)Cl^-$, which eventually transforms to the product $(\eta^5\text{-}MeCp)Mn(CO)_2(PR_3)$.

Introduction

For the last decades, many chemists observed the nucleophilicity of the transition metal carbonylates toward organic halides and also studied the counterion effect on the reaction.[1] The displacement of X^- from RX (X^-=halides) by metal carbonylates usually follows an overall second order rate law, rate$=k_2[M(CO)_x^-][RX]$ for the reaction (1).

$$M(CO)_x^- + RX \rightarrow RM(CO)_x + X^- \qquad (1)$$

The metal carbonylate, however, does not undergo a ligand substitution reaction with PR_3 at elevated temperatures probably due to the strong *dπ-pπ** back-bonding between the metal and the carbonyl carbon. Several years ago we reported on the reaction of $M^+[M'M''(CO)_9L]^-$ ($M^+=Na^+$, PPN^+; M'=Cr, W; M''=Mn, Re; L=CO, PR_3) with PR_3, where the heterobimetallic complex contains a donor-acceptor metal-metal bond.[2]

In this case, however, ligand substitution reaction could be accomplished by relieving the high electron density on Mn onto the Lewis acid moiety, $M(CO)_5$ (M=Cr, W), as shown in equation (2).

$$(OC)_5CrMn(CO)_5^- + PR_3 \rightarrow Mn(CO)_5^- + Cr(CO)_5PR_3 \text{ (major)} + Cr(CO)_4(PR_3)_2 \text{ (minor)} \qquad (2)$$

Tremendous amount of research on the ligand substitution reaction of the neutral metal carbonyl with PR_3 has been performed in the last twenty years including the following reaction as shown in equation (3).[3]

$$Mn(CO)_5Br + PR_3 \rightarrow cis\text{-}Mn(CO)_4(PR_3)Br + CO \qquad (3)$$

Here we report a rare ligand substitution reaction in which the metal carbonylate $(\eta^5\text{-}MeCp)Mn(CO)_2Cl^-$ shows Cl^-/PR_3 exchange leading to the product, $(\eta^5\text{-}MeCp)Mn(CO)_2(PR_3)$. From the ligand substitution kinetics, the reaction mechanism will be discussed in detail.

Experimental

All operations were carried out under a nitrogen atmosphere by using standard Schlenk techniques or an Ar-filled glovebox. Rigorous exclusion of trace moisture and oxygen was standard procedure. Solvents were dried and degassed as described below. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer using 0.10-mm sealed CaF_2 or KBr solution cells. ^1H NMR spectra were obtained from Varian Gemini-200 FT spectrometer in solutions of $CDCl_3$, DMSO-d_6, and CD_3OD. The GC-MASS spectral data were collected from the GC-MASS (Hewlett Packard model GC 5890), Department of Chemistry Yonsei University (Wonju, Kangwondo). Photoreactions were performed by using a 450 watt Hg vapor lamp (Hanovia).

Tetrahydrofuran (THF) was distilled under nitrogen from purple sodium/benzophenone ketyl. Hexane was stirred over concentrated H_2SO_4 overnight, washed with aqueous $NaHCO_3$ and distilled from Na^0/benzophenone ketyl. Methylene chloride was refluxed over calcium hydride and distilled under N_2. Ethanol and methanol were distilled from calcium hydride. Bis(triphenylphosphine)iminium chloride (PPN^+Cl^-) was purchased from Aldrich. All other reagents purchased were reagent grade and used without further purification.

Preparation of $(\eta^5\text{-}MeCp)Mn(CO)_2(THF)$. The preparation procedure of $(\eta^5\text{-}MeCp)Mn(CO)_2(THF)$ is similar to a method in the literature.[4]

Preparation of $PPN^+(\eta^5\text{-}MeCp)Mn(CO)_2Cl^-$. To a N_2-filled 100 mL Schlenk flask PPN^+Cl^- (1.20 mmol) was loaded. The system was evacuated for 1 hr and then back-filled with N_2. A 10 mL portion of degassed dichloromethane was added *via* a syringe and the solution stirred for several minutes. To the PPN^+Cl^- (1.20 mmol) solution was added a THF solution (30 mL) of $(\eta^5\text{-}MeCp)Mn(CO)_2(THF)$ (1.0 mmol) freshly prepared from the photolytic reaction. This solution was stirred for 1 hr at room temperature and then the solution was concentrated to 20 mL under vacuum. Hexane (50 mL) was slowly added to precipitate the product and the mother liquid was removed via cannula. The solid was washed with hexane until the washings were colorless. After removal of the hexane, the solid product was redissolved in THF (20 mL) and passed through Celite-containing glass filter. Hexane was slowly added to the solution as the precipitation began. The fine red brown solid was separated and dried in vacuo to give 0.5 mmol of the product (50% yield).

$PPN^+(\eta^5\text{-}MeCp)Mn(CO)_2Cl^-$. ν(CO)IR (THF) in cm^{-1}, 1893 (s), 1816 (s). Anal. Calcd for $C_{44}H_{37}NO_2P_2Cl$: C, 69.16; H, 4.88; N, 1.83. Found: C, 69.42; H, 5.72; N, 1.82. ^1H NMR (DMSO-d_6) in δ (ppm): 4.10 and 3.93 (4H, 2s), 1.60 (3H, s) along with the peaks from PPN^+ cation.

Identification of $(\eta^5\text{-}MeCp)Mn(CO)_2(PR_3)$ (R=Me, Et, OEt, C_6H_5). To a N_2-filled 100 mL Schlenk flask was loaded $PPN^+(\eta^5\text{-}MeCp)Mn(CO)_2Cl^-$ (1.0 mmol), followed by the addition of a 40 mL portion of degassed THF *via* syringe. PR_3 was added to the dark-red solution, and the reaction mixture was heated in a water bath at 60 ℃. The progress of the reaction was monitored by the ν(CO)IR bands of the product, $(\eta^5\text{-}MeCp)Mn(CO)_2(PR_3)$ (R=OEt, C_6H_5) (10-12 hr). The other reaction products $(\eta^5\text{-}MeCp)Mn(CO)_2(PR_3)$ (R=Me, Et) were quickly obtained on mixing the reactants, which confirmed by the IR spectroscopy. The vacuum-dried reaction mixtures were extracted into hexane and passed through a Celite-containing glass filter to isolate the PPN^+Cl^-. The hexane was removed under vacuum from the yellow filtrate at about 60 ℃ yielding a yellow oily mixture. Thin layer chromatography under nitrogen of a drop of this oil on a silica gel plate (Whatman #4420-222) in a 4 : 1 hexane-THF mixture shows the presence of $(\eta^5\text{-}MeCp)Mn(CO)_3$ (Rf=0.88), $(\eta^5\text{-}MeCp)Mn(CO)_2[P(C_6H_5)_3]$ (Rf=0.71), $[P(C_6H_5)_3]$ (Rf=0.03). The orange-colored product extracted from the yellow oil by the column chromatography under nitrogen turned out to be $(\eta^5\text{-}MeCp)Mn(CO)_2[P(C_6H_5)_3]$. The eluent used was a 4 : 1 hexane-THF mixture. The other products $(\eta^5\text{-}MeCp)Mn(CO)_2(PR_3)$ (R=Et, Me, OEt) were obtained as pure compounds under vacuum. The spectroscopic data are as follows: **$(\eta^5\text{-}MeCp)Mn(CO)_2(PEt_3)$**: ν(CO)IR (THF) in cm^{-1}: 1918 (s), 1852 (s). ^1H NMR (CD_3OD) in δ (ppm): 4.35 (4H, d), 1.99 (3H, s), 1.71 (6H, m), 1.12 (9H, m). Mass, m/e [relative intensity, assignment]: 308 [14, $(\eta^5\text{-}MeCp)Mn(CO)_2(PEt_3)$], 252 [100, $(\eta^5\text{-}MeCp)Mn(PEt_3)$], 134 [32, $(\eta^5\text{-}MeCp)Mn$]. **$(\eta^5\text{-}MeCp)Mn(CO)_2(PMe_3)$**: ν (CO)IR (THF) in cm^{-1}: 1915 (s), 1849 (s). ^1H NMR (DMSO-d_6) in δ (ppm): 4.44 (4H, d), 1.88 (3H, s), 1.39 (9H, d). Mass, m/e [relative intensity, assignment]: 266 [10, $(\eta^5\text{-}MeCp)Mn(CO)_2(PMe_3)$], 210 [85, $(\eta^5\text{-}MeCp)Mn(PMe_3)$], 134 [100, $(\eta^5\text{-}MeCp)Mn$]. **$(\eta^5\text{-}MeCp)Mn(CO)_2[P(OEt)_3]$**: ν (CO)IR (THF) in cm^{-1}: 1935 (s), 1870 (s). ^1H NMR (DMSO-d_6) in δ (ppm): 4.47 (4H, s), 3.85 (6H, m), 1.87 (3H, s), 1.19 (9H, m). Mass, m/e [relative intensity, assignment]: 356[13, $(\eta^5\text{-}MeCp)Mn(CO)_2[P(OEt)_3]$], 300 [100, $(\eta^5\text{-}MeCp)Mn[P(OEt)_3]$], 134 [44, $(\eta^5\text{-}MeCp)Mn$]. **$(\eta^5\text{-}MeCp)Mn(CO)_2(PPh_3)$**: ν (CO)IR (THF) in cm^{-1}: 1927 (s), 1963 (s). ^1H NMR ($CDCl_3$) in δ (ppm): 7.56 (15H, m), 4.18 and 4.04 (4H, 2s), 1.93 (3H, s). Mass, m/e [relative intensity, assignment]: 452 [6.34, $(\eta^5\text{-}MeCp)Mn(CO)_2(PPh_3)$], 396 [100, $(\eta^5\text{-}MeCp)Mn(PPh_3)$], 134 [39, $(\eta5\text{-}MeCp)Mn$].

Kinetic Measurements. 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 an anionic transition metal carbonyl complex was loaded into a 10 mL volumetric flask in a drybox. The flask was removed from the drybox, and the respective THF solution of triethylphosphine, trimethylphosphine, triphenylphosphine, or triethylphosphite of known concentration was added by a syringe. This solution was stirred until it was homogeneous and placed in a Haake water bath equipped with a constant-temperature controller (± 0.1 ℃). Samples for IR spectral analysis were withdrawn periodically with a syringe and placed in a sealed 0.1 mm pathlength KBr or CaF_2 infra-

Table 1. Solution IR Spectral Data for $M^+(\eta^5\text{-MeCp})Mn(CO)_2Cl^-$ ($M^+ = K^+$, PPN^+, K^+(18-C-6)) and $(\eta^5\text{-MeCp})Mn(CO)_2PR_3$ (R = Me, Et, OEt, Ph) in THF

Complexes	ν(CO), cm^{-1}
$(\eta^5\text{-MeCp})Mn(CO)_3$	2010(s), 1924(s)
$(\eta^5\text{-MeCp})Mn(CO)_2(THF)$	1920(s), 1845(s)
$K^+(\eta^5\text{-MeCp})Mn(CO)_2Cl^-$	1891(s), 1814(s), 1802(s)
$K^+(18\text{-C-6})(\eta^5\text{-MeCp})Mn(CO)_2Cl^-$	1895(s), 1816(s)
$PPN^+(\eta^5\text{-MeCp})Mn(CO)_2Cl^-$	1893(s), 1816(s)
$(\eta^5\text{-MeCp})Mn(CO)_2(PMe_3)$	1915(s), 1849(s)
$(\eta^5\text{-MeCp})Mn(CO)_2(PEt_3)$	1918(s), 1852(s)
$(\eta^5\text{-MeCp})Mn(CO)_2(P(OEt)_3)$	1935(s), 1870(s)
$(\eta^5\text{-MeCp})Mn(CO)_2(PPh_3)$	1927(s), 1863(s)

red solution cell. Rates of reaction were observed by following the disappearance in absorbance of the reactant's ν (CO) IR which did not overlap with the other carbonyl bands: $PPN^+(\eta^5\text{-MeCp})Mn(CO)_2Cl^-$ at 1816 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 $[A_t\text{-}A_\infty]$ *vs* time, where A_t is the absorbance at time t and A_∞ is the absorbance at time infinity.

Results and Discussion

The synthesis of the anionic transition metal carbonyl complexes was achieved by the simple addition of labile ligand to the derivatives of group 7 metal carbonyls, $(\eta^5\text{-MeCp})Mn(CO)_2(THF)$ with PPN^+Cl^- or $K^+(18\text{-C-6})Cl^-$ as depicted in equation (4).

$$PPN^+Cl^-/CH_2Cl_2 + (\eta^5\text{-MeCp})Mn(CO)_2(THF) \rightarrow PPN^+(\eta^5\text{-MeCp})Mn(CO)_2Cl^- \qquad (4)$$

The reactions were complete at time of mixing (ambient temperature), yielding products which were isolated by precipitation in 50 to 80% yield. The brown crystalline products were stable for a few days under nitrogen.

Comparison of the ν (CO)IR for $(\eta^5\text{-MeCp})Mn(CO)L$ ($L = Cl^-$, THF, CO, PMe_3, PEt_3, $P(OEt)_3$, PPh_3). For a series of analogous $\eta^5\text{-MeCpMn(CO)}_2L$ ($L = CO$, Cl^-, PR_3; R = Me, Et, OEt, Ph) complexes, CO stretching frequencies are employed as a means to assess the relative electron density at the metal center. (See Table 1.) The assumption made here is that the increased electron density at Mn will be reflected by the increased back donation into the π* orbital of the CO ligand resulting in lower ν (CO)IR (cm^{-1}). Based on this assumption, the relative electron donating ability of ligands is as follows:

$$Cl^- > PMe_3 \sim PEt_3 > THF > PPh_3 > P(OEt)_3 > CO$$

In the case of $M^+(\eta^5\text{-MeCp})Mn(CO)_2Cl^-$ ($M^+ = K^+(18\text{-C-6})$, PPN^+) in Table 1, two ν (CO)IR bands (1895, 1816 for $M^+ = K^+(18\text{-C-6})$ salt; 1893, 1816 for PPN^+ salt) were observed; however, the spectrum of $K^+(\eta^5\text{-MeCp})Mn(CO)_2Cl^-$ shows three bands (1891, 1814, 1802), among which one band (1802 cm$^-$) may be ascribed to the interaction between Mn-CO and K^+. (See Figure 1(a).) In this case, those contributions from the interactions depicted in Figure 1(b) and (c) may essentially be minimal because the stretching frequencies of the two peaks (1891, 1814 cm^{-1}) are not higher than those of $K^+(18\text{-C-6})(\eta^5\text{-MeCp})Mn(CO)_2Cl^-$ (1895, 1816 cm^{-1}). Even the interaction shown in Figure 1(a) vanishes in the case of K^+(18-C-6) salt, where the crown ether (18-C-6) effectively interrupts the interaction by complexing K^+ cation.

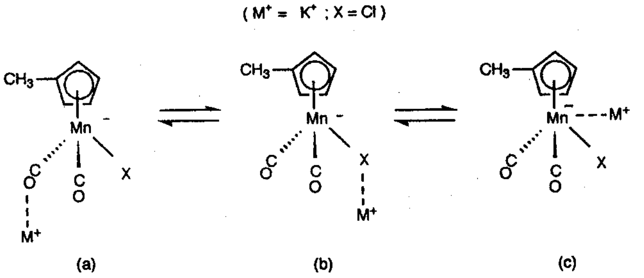

Figure 1. Interaction modes of cation with $(\eta^5\text{-MeCp})Mn(CO)_2Cl^-$ anion.

Table 2. The Relationship between $P(OEt)_3$ Concentrations and the Rates(k_{obs}) of the Reaction of $PPN^+(\eta^5\text{-MeCp})Mn(CO)_2Cl^-$ in THF at 50 ℃

$[PPN^+(\eta^5\text{-MeCp})Mn(CO)_2Cl^-]$ M(×10^3)	$[P(OEt)_3]$ M(×10^3)	$k_{obs}\times10^6$, s^{-1}
5.0	25	16.4± 0.7
5.0	50	18.7± 0.6
5.0	100	15.8± 0.4
5.0	200	16.4± 1.0

Table 3. The Relationship between PPh_3 Concentrations and the Rates(k_{obs}) of the Reaction of $PPN^+(\eta^5\text{-MeCp})Mn(CO)_2Cl^-$ in THF at 50 ℃

$[PPN^+(\eta^5\text{-MeCp})Mn(CO)_2Cl^-]$ M(×10^3)	$[PPh_3]$ M(×10^3)	$k_{obs}\times10^6$, s^{-1}
5.0	25	10.1± 0.4
5.0	50	10.1± 0.4
5.0	100	12.0± 0.4
5.0	200	13.0± 0.6

Reaction of $PPN^+(\eta^5\text{-MeCp})Mn(CO)_2Cl^-$ with PR_3 (R = Et, Me, OEt, Ph). The reactions of $PPN^+(\eta^5\text{-MeCp})Mn(CO)_2Cl^-$ with an excess amount of PR_3 were carried out in THF solution at the various temperatures (r.t. to 60 ℃). The reaction products $(\eta^5\text{-MeCp})Mn(CO)_2(PR_3)$ were obtained as depicted in equation (5).

$$PPN^+(\eta^5\text{-MeCp})Mn(CO)_2Cl^- + PR_3 \rightarrow (\eta^5\text{-MeCp})Mn(CO)_2(PR_3) + PPN^+Cl^- \qquad (5)$$

Reactions of $PPN^+(\eta^5\text{-MeCp})Mn(CO)_2Cl^-$ with an excess of PR_3 (5 up to 40-fold excess compared with the concentration of the complex) were performed in THF and monitored with time by ν (CO)IR (Table 2, 3). As is shown in Table

Table 4. Temperature Dependence on the Rate of the Reaction of $PPN^+(\eta^5$-MeCp)$Mn(CO)_2Cl^-$ with $P(OEt)_3$ in THF[a]

Complex	Temp. (℃)	$k_{obs}\times10^6$, s^{-1}
$PPN^+(\eta^5$-MeCp)$Mn(CO)_2Cl^-$	40	6.4± 0.2
	45	10.1± 0.6
	50	16.4± 1.0
	60	45.2± 1.5

[a] [$PPN^+(\eta^5$-MeCp)$Mn(CO)_2Cl^-$]=5.0 mM; [$P(OEt)_3$]=100 mM.

Table 5. Temperature Dependence on the Rate of the Reaction of $PPN^+(\eta^5$-MeCp)$Mn(CO)_2Cl^-$ with PPh_3 in THF[a]

Complex	Temp. (℃)	$k_{obs}\times10^6$, s^{-1}
$PPN^+(\eta^5$-MeCp)$Mn(CO)_2Cl^-$	40	4.3± 0.2
	45	6.8± 0.3
	50	12.0± 0.4
	60	34.5± 0.9

[a] [$PPN^+(\eta^5$-MeCp)$Mn(CO)_2Cl^-$]=5.0 mM; [PPh_3]=100 mM.

Table 6. Activation Parameters from the Reaction of $PPN^+(\eta^5$-MeCp)$Mn(CO)_2Cl^-$ with PR_3 (R=OEt, Ph) in THF[a]

Ligand	Activation Parameters
$P(OEt)_3$	$\Delta H^{\dagger}=19.8\pm0.6$ kcal/mol
	$\Delta S^{\dagger}=-19.3\pm1.8$ e.u.
PPh_3	$\Delta H^{\dagger}=21.0\pm1.5$ kcal/mol
	$\Delta S^{\dagger}=-16.4\pm4.6$ e.u.

[a] [$PPN^+(\eta^5$-MeCp)$Mn(CO)_2Cl^-$]=5.0 mM; [PR_3]=100 mM.

2 (for $P(OEt)_3$) and Table 3 (for PPh_3), each reaction follows a first order dependence on [$(\eta^5$-MeCp)$Mn(CO)_2Cl^-PPN^+$] and no dependence on [PR_3], (R=OEt, Ph) within the experimental error range.

$$\text{rate}=k_1\ [PPN^+(\eta^5\text{-MeCp})Mn(CO)_2X^-] \qquad (6)$$

The reaction rate was also observed to be enhanced with temperature (Table 4, 5) under the pseudo-first-order conditions.

Determination of Activation Parameters. The first order rate constants, k_1, were measured for the reaction of $PPN^+(\eta^5$-MeCp)$Mn(CO)_2Cl^-$ with PR_3 (R=OEt, Ph) in THF as a function of temperature and the activation parameters were calculated from the Eyring plot. The activation parameters ($\Delta H^{\neq}=19.8\pm0.6$ kcal/mol, $\Delta S^{\neq}=-19.3\pm1.8$ e.u. for $P(OEt)_3$; $\Delta H^{\neq}=21.0\pm1.5$ kcal/mol, $\Delta S^{\neq}=-16.4\pm4.6$ e.u. for PPh_3, see Table 6) both suggest that the associative ligand substitution may take place at the rate-determing step. However, the rate solely depends on the concentration of the metal complex. These two apparently opposite results may be compromised by the introduction of the coordinating solvent, THF. The $PPN^+(\eta^3$-MeCp)$Mn(CO)_2Cl^-$ on heating may accomodate a THF molecule first, as is represented by the negative entropy change of activation and the overall first-order dependence on the concentration of the metal complex as well.

Table 7. Ligand Dependence on the Reaction of $PPN^+(\eta_5{}^-$MeCp)$Mn(CO)_2Cl^-$ with PR_3 (R=Me, Et, OEt, Ph) in THF[a]

Ligand	Temp. (℃)	Ligand Cone Angle (°)	$k_{obs}\times10^6$, s^{-1}
PMe_3	20	118	b
PEt_3	20	132	b
$P(OEt)_3$	40	106	6.4± 0.2
PPh_3	40	142	4.3± 0.2

[a] [$PPN^+(\eta^5$-MeCp)$Mn(CO)_2Cl^-$]=5.0 mM; [PR_3]=100 mM. [b] These reactions are too fast to measure the rates by the method used here.

Mechanistic Considerations. It looks rather surprising to observe that the incoming ligand PR_3 (R=Me, Et, OEt, C_6H_5) does have the major effect on the reaction rate as shown in Table 7.

It is generally accepted that in the associative ligand substitution reactions, there is a pronounced steric retardation with the increasing cone angle of PR_3, regardless of phosphine basicity; however, in this reaction, the dominant factor contributing to the enhanced reaction rate appears to be the basicity (or nucleophilicity) of the ligand, PR_3, definitely not the steric factor of the ligand.[3c] The fact that electronic factor of the incoming ligand determines the rate may partly be related to the electronic environment of the site for attack, Mn, by the incoming ligand. The manganese metal center should be electron-deficient, to some degree, at the time of attack by the ligand; therefore the better σ-donating ligand could more effectively attack the metal center than the other ligands ($P(OEt)_3$, $P(C_6H_5)_3$) do.

The relatively low electron density buildup on the Mn center could be achieved through the structural reorganization, where an appropriate energy is applied; e.g., the shift from η^5-MeCp to η^3-MeCp creating an open coordination site[5] and also the electron density on Mn can be pulled over by the electron withdrawing ligand, Cl^-, simultaneously.

This η^3-MeCpMn$(CO)_2Cl^-PPN^+$, although it is a charged species, is assumed to be a 16 electron species; therefore, this complex may accomodate another two electron donor ligand, either the coordinating solvent, THF, or PR_3. However, the Mn-Cl bond should be cleaved with the formation of PPN^+Cl^- leading to the stable neutral intermediate, η^5-MeCpMn$(CO)_2$(THF) prior to the attack at the metal center by PR_3 ligand.

The intermediate (η^5-MeCp)Mn$(CO)_2$(THF) can survive for hours at ambient temperature under N_2. At this stage, the electronic factor of the ligand, PR_3, may be little related to the reaction rate because the neutral intermediate, η^5-MeCpMn$(CO)_2$(THF), no longer demands either steric or electronic enhancements from the PR_3.

As no kinetic data could be obtained from the reactions with the PR_3 (R=Me, Et) due to the very fast reaction, (These reactions cannot be followed by the ν (CO) IR spectroscopic method employed here) it does not yet appear to be certain whether these reactions with PR_3 (R=Me, Et) are in the associative ligand substitution mode or not; however, the incredibly fast reaction ($k_{obs}\cong1.7\times10^{-2}$ s^{-1} for PMe_3 at 1 : 1 molar ratio with respect to [(MeCp)Mn$(CO)_2Cl^-$] at ambient temperature; this reaction rate is almost 10^3 times

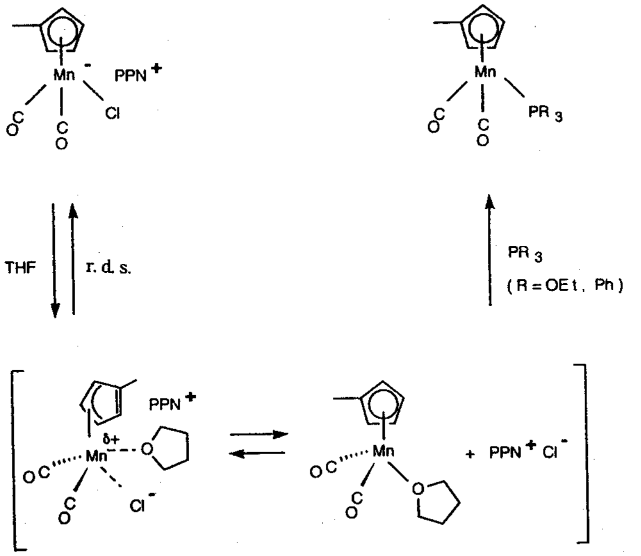

Figure 2. Proposed reaction sequencies for PPN$^+$(η^5-MeCp)Mn (CO)$_2$Cl$^-$ with PR$_3$ (R=Me, Et, OEt, Ph).

faster than that for P(OEt)$_3$. See Table 3) may drive us to believe that the strong nucleophile, PR$_3$ (R=Me, Et) may directly attack at the Mn center of the PPN$^+$(η^3-MeCp)Mn (CO)$_2$Cl$^-$ to yield the corresponding product, η^5-MeCpMn (CO)$_2$(PR$_3$). Therefore, the reaction mechanism involving a dissociative ligand substitution seems to be related to the weak nucleophilicity of the incoming ligand, PR$_3$ (Figure 2). This situation may as well be compared with the nucleophilic substitution reactions (S_N1 *vs* S_N2) depending on the structure of the substrate and the nucleophilicity of the nucleophile involved. More in-depth fast kinetic study at low temperature on the same reaction with PR$_3$ (R=Me, Et, etc.) should be done later in the near future.

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