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Kinetic Investigation of Halide Substitution in the 17-Electron $MoCpX_2(PMe_3)_2$ System

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The substitution of I^- by Cl^- in the 17-electron organometallic complex $CpMoI_2(PMe_3)_2$ ($Cp = \eta^5\text{-}C_5H_5$) has been investigated kinetically by using (PPN)Cl as the chloride source in CH_2Cl_2 with quantitative electron paramagnetic resonance spectroscopy monitoring. Under strictly controlled conditions (absence of traces of oxidants) the reaction is kinetically well-behaved and the iodochloro complex, $CpMoICl(PMe_3)_2$, can be observed as an intermediate. The rate constants of both substitution steps (k_1 and k_2) can be expressed as the sum of two second-order pathways that involve the solvated chloride ion and the (PPN)Cl ion pair, respectively, as nucleophiles: $k_{n\mathrm{obs}} = k_{n\mathrm{i}}[Cl^-] + k_{n\mathrm{ip}}[PPN^+Cl^-]$ ($n = 1, 2$). The rate constant of the second substitution has been independently obtained starting from the isolated iodochloro complex. Eyring analysis of the first substitution step shows the activation parameters $\Delta H_{1\mathrm{i}} = 13.2 \pm 1.8$ kcal·mol^{-1} and $\Delta S_{1\mathrm{i}} = -26.0 \pm 5.7$ cal·K^{-1}·mol^{-1}. The corresponding halide exchanges in the Cp* system ($Cp^* = \eta^5\text{-}C_5Me_5$) proceed about 10^5 times faster, indicating that the formation of 19-electron intermediates/transition states does not occur. Other mechanistic possibilities are discussed.

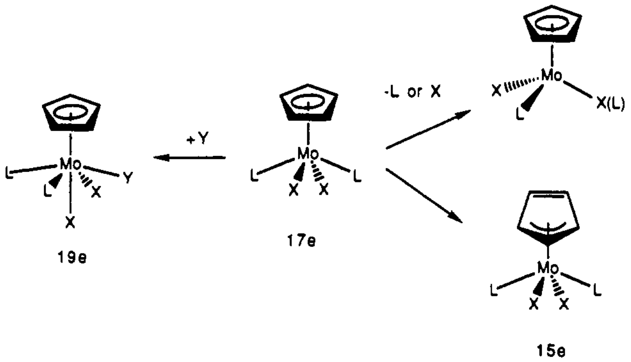
Introduction

Ligand substitution on organometallic compounds is a topic of long-standing interest.[1] Tolman's 16/18-electron rule[2] is of excellent guidance for the mechanism of substitution on even-electron systems in that the most typical paths are associative for 16-electron compounds and dissociative for 18-electron compounds. Relatively recently, the mechanism of substitution in organometallic compounds with a 17-electron configuration has attracted considerable attention.[3,4] It has been shown that ligand exchange usually proceeds through an associative path and that, in most cases, it is much faster than similar substitutions on analogous 18-electron systems. The lower activation barrier for substitution in 17-electron systems has been related to the positive bonding interaction between incoming ligand and metal center in the intermediate or transition state.[5] Associative substitutions suffer mainly from steric problems. For example, while CO substitution in $V(CO)_6$ is 10^{10} times faster than in $Cr(CO)_6$,[4c] the more sterically encumbered Cp(pd)V(CO) exchanges CO at about the same rate as Cp(pd)Cr(CO) (pd = η^5-pentadienyl).[4m] When the steric impediment to an associative mechanism becomes too great, the dissociative mechanism becomes lower in energy. For instance, associative and dissociative CO substitutions are competing in $(pd)_2V(CO)$, while a dissociative pathway prevails in $(2,4\text{-}Me_2pd)V(CO)$.[4l]

All the 17-electron organometallic compounds investigated to date are low-valent, carbonyl-based radicals. We have recently prepared a series of stable 17-electron compounds of the $CpMoX_2L_2$ class (X = halogen, L = phosphine) and investigated their ground-state properties.[6] They markedly differ from classical organometallic 17-electron radicals in that they are not strong oxidizing agents. Rather than being reduced to 18-electron Mo(II) anions, they are easily oxidized to stable 16-electron cations and therefore behave as mild reducing agents. This behavior can be related to the absence of strong π acceptors in the coordination sphere, which results in a relatively high energy for the HOMO.[6a]

Because of the high energy of the HOMO, we reasoned that the energetic stabilization of the intermediate in an associative ligand substitution by a nucleophile Y ought to be reduced. In addition, $CpMoX_2L_2$ *could* suffer from a steric impediment during the formation of the 19-electron $[CpMoX_2L_2Y]$ intermediate (Scheme I), although isostructural 18-electron $CpMoCl_3L_2$ (L_2 = dmpe, dppe) compounds are known.[7] Finally, a 15-electron intermediate in a dissociative pathway may gain stability through crystal field stabilization and electronic correlation effects if the pseudooctahedral geometry allows a high-spin ($S = {}^3/_2$) ground state. This intermediate could arise from either dissociation of a monodentate ligand or "slippage" of the Cp ring. Analogous chromium derivatives, e.g. $[CpCrX_3]^-$ (X = Cl, Me, Ph)[8] and $Cp^*CrMe_2(PMe_3)$,[9] are stable as 15-electron pseudooctahedral species with three unpaired electrons, and 15-electron octahedral Mo(III) derivatives without the Cp ring, e.g. $MoX_3(PMe_3)_3$ (X = Cl, Br, I),[10] are well-known.

Scheme I



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On the basis of the above considerations, we considered it interesting to examine the mechanism of ligand exchange for this class of compounds. We report here the results of our investigations on the halide exchange reactions. During these investigations, we have uncovered a catalytic acceleration of this reaction by oxidation. Detailed investigations of the latter phenomenon will be reported in a separated paper.[11]

Experimental Section

All operations were carried out under an atmosphere of dinitrogen or argon. Solvents were dehydrated by standard methods and distilled under dinitrogen prior to use. The compounds $CpMoCl_2(PMe_3)_2$, $CpMoClI(PMe_3)_2$, $CpMoI_2(PMe_3)_2$,[12] and Cp^*MoCl_4[13] were prepared as described previously. PPN^+Cl^- was purchased from Aldrich Chemicals and recrystallized from CH_2Cl_2. The copper-coated zinc was prepared according to LeGoff, substituting 20-mesh Zn instead of the indicated 30-mesh zinc.[14] EPR measurements were carried out with a Bruker ER200 spectrometer calibrated with diphenylpicrylhydrazyl radical; UV/vis experiments were performed on Shimadzu UV-240 and Hewlett-Packard diode-array spectrometers.

Preparation of $Cp^*MoCl_2(PMe_3)_2$. This compound was prepared by a slight modification of the literature method, the most important difference being that an atmosphere of argon was used to avoid overreduction with formation of the molybdenum(II) dinitrogen complex $Cp^*MoCl(PMe_3)_2(N_2)$.[15] Cp^*MoCl_4 (1.933 g, 5.18 mmol) was introduced into a flask containing amalgamated sodium (244 mg, 10.7 mmol, 0.5% by weight), and 30 mL of THF and the suspension was stirred at room temperature. The color changed from pink to yellow-green. After ca. 1 h, PMe_3 (1.2 mL, ca. 12 mmol) was introduced, causing a further color change to brown. After an additional 1 h of stirring at room temperature, the solvent was completely removed by evaporation, and the residue was extracted with several 20-mL portions of hot *n*-heptane, which were filtered through Celite, until the filtrate was no longer colored. The combined filtrates were concentrated until crystallization began (remaining volume ca. 100 mL), warmed to reflux to completely redissolve the crystalline material, and slowly cooled to room temperature and then to −80 °C. The brown crystals were recovered by decanting off the solvent and dried under vacuum. Yield: 1.848 g (78.5%). EPR (*n*-heptane, room temperature): very broad featureless signal centered at $g = 1.984$. Cyclic voltammetry (CH_2Cl_2, Pt working electrode, Ag/AgCl reference, $n\text{-}Bu_4NPF_6$ supporting electrolyte): reversible oxidations (equal number of electrons) at $(E_{1/2})^1 = -0.84$ V and $(E_{1/2})^2 = +0.84$ V vs the internal Cp_2Fe standard.

Reaction of $Cp^*MoCl_2(PMe_3)_2$ with NaI (1 equiv). Formation of $Cp^*MoClI(PMe_3)_2$. $Cp^*MoCl_2(PMe_3)_2$ (591 mg, 1.30 mmol) was dissolved in 20 mL of THF and treated with 182 mg (1.21 mmol) of anhydrous NaI. The mixture was stirred at room temperature for ca. 3 days. The solvent was completely removed and the residue was extracted with 30 mL of hot *n*-heptane. Filtration, followed by evaporation to ca. 10 mL and cooling to −80 °C, afforded 521 mg of product (73% yield). EPR (THF, room temperature): $g = 2.009$. Cyclic voltammetry (THF, Pt working electrode, Ag/AgCl reference, $n\text{-}Bu_4NPF_6$ supporting electrolyte): reversible oxidation at $E_{1/2} = -0.70$ V vs the internal Cp_2Fe standard. The electrochemical experiment showed that the material is contaminated by ≤20% of unreacted dichloride precursor.

Preparation of $Cp^*MoI_2(PMe_3)_2$. Cp^*MoCl_4 (183 mg, 0.491 mmol) was placed in THF (10 mL) and treated with PMe_3 (100 μL, 1.0 mmol). This solution was transferred into a Schlenk tube containing Na (20 mg, 0.87 mmol) amalgamated with 4.7 g of Hg. Stirring at room temperature for 3.5 h caused complete reduction to $Cp^*MoCl_2(PMe_3)_2$, as shown by EPR. After filtration through Celite, NaI (340 mg, 2.27 mmol) was added and the mixture stirred at room temperature overnight. The solvent was completely removed under reduced pressure and the residue treated with *n*-heptane (10 mL). Warming to the reflux temperature, followed by filtration and cooling to −20 °C, afforded 154 mg of brown crystals (49%), which were isolated by decanting off the mother liquor and dried under vacuum. Anal. Calcd for $C_{16}H_{33}I_2MoP_2$: C, 30.2; H, 5.1. Found: C, 30.1; H, 5.1. EPR (THF, room temperature): $g = 2.037$, $a_P = 19$ G, $a_{Mo} = 32$ G. Cyclic voltammetry (THF, Pt working electrode, Ag/AgCl reference, $n\text{-}Bu_4NPF_6$ supporting electrolyte): reversible oxidations (equal number of electrons) at $(E_{1/2})^1 = -0.61$ V and $(E_{1/2})^2 = +0.71$ V vs the internal Cp_2Fe standard.

Kinetic Determinations for the Cp System. General Data. The kinetic runs were monitored by EPR. Measurements were carried out in medium-walled 3-mm-o.d. sealed glass tubes; the use of larger tubes with the CH_2Cl_2 solvent generally did not allow accurate instrument tuning, a condition that was found to be necessary for the reproducibility of the quantitative determinations. The tubes were filled to a sample height of ca. 10 cm and were adjusted in the sample holder such that the entire instrument cavity was occupied with sample. The instrument was allowed to stabilize for at least 4 h after powering up before carrying out quantitative measurements. When standard solutions were measured under these conditions, we found a level of reproducibility of 1% or better. The concentration of the various species was determined from the signal to baseline separation, which was found to be linear from calibration curves in the range of concentrations investigated. For the solutions containing mixtures of $CpMoCl_2(PMe_3)_2$, $CpMoClI(PMe_3)_2$, and $CpMoI_2(PMe_3)_2$, the concentration of each species was determined by measuring the signal height at three different positions and solving the three simultaneous equations; details are given in the supplementary material.

Kinetic Determinations. $CpMoI_2(PMe_3)_2$ + (PPN)Cl. A 6.60 mM stock solution of the molybdenum complex was prepared by placing 22.5 mg (0.0396 mmol) of the compound in 6.0 mL of CH_2Cl_2 inside a Schlenk tube under an atmosphere of dinitrogen in the presence of a small amount of Zn/Cu. The solution was stirred for 5 min at room temperature to assure complete reduction of any oxidized impurity before it was cooled to −78 °C. In separate Schlenk tubes, an analogous procedure was repeated for five different solutions of (PPN)Cl in CH_2Cl_2 at known concentration. A 0.50-mL aliquot of the Mo stock solution was added by syringe to each (PPN)Cl solution, which was stirred for 2 min and then transferred by cannula to four different tubes containing Zn/Cu, which were then cooled further to liquid-nitrogen temperature and flame sealed under dinitrogen or argon. To initiate reactions, a tube was taken to the desired temperature in a water bath. To monitor reaction progress, the tube was removed from the water bath and placed into the EPR sample cavity, a spectrum taken, and the tube then returned to the water bath. This process was repeated periodically.

Kinetic Determinations. $CpMoClI(PMe_3)_2$ + (PPN)Cl. The procedure described above proved ineffective in this case, and very fast exchanges were observed before the Zn/Cu couple could eliminate the source of catalysis (see Results). We were successful in this case by reducing transfers to the minimum and by avoiding the use of syringes. We carried out these reactions under argon. For each run, two separate solutions, one containing $CpMoClI(PMe_3)_2$ and the other (PPN)Cl, were prepared over Zn/Cu and stirred at room temperature for 5 min. The solutions were then cooled to −78 °C, combined by cannula transfer, and stirred for an additional 2 min. They were then transferred via cannula to EPR tubes containing Zn/Cu. These tubes were then cooled further to 77 K and flame sealed under argon.

Kinetic Determinations for the Cp* System. Substitution in the Cp* system was too fast for EPR techniques, so spectrophotometric techniques were used. Solutions of $Cp^*MoI_2(PMe_3)_2$ or $Cp^*MoICl(PMe_3)_2$ in CH_2Cl_2 in the millimolar range were prepared over Zn/Cu and stored at dry ice temperatures. Immediately prior to initiation of a kinetic run, a sample was withdrawn by cannula into a deoxygenated spectrophotometric cell containing Zn/Cu and thermostated. Syringe techniques were used to add the CH_2Cl_2 solution of PPN^+Cl^- which had been prepared and stored over Zn/Cu. The progress of the reaction was monitored in the 400–450-nm region.

Results

Preliminary Studies. We have reported previously[12] that halide exchange occurs smoothly in the $CpMoX_2(PMe_3)_2$ system (X = Cl or I). The dichloride compound can be converted stepwise to the mixed iodochloro complex and to the diiodo derivative on treatment with NaI in THF (eq 1).[12] The first exchange is much more rapid than the second, allowing the selective formation of the mixed halide system to be accomplished.

$$CpMoCl_2(PMe_3)_2 \xrightarrow[1/2\ h,\ room\ temp]{NaI/THF} CpMoClI(PMe_3)_2 \xrightarrow[1\ d,\ reflux]{NaI/THF} CpMoI_2(PMe_3)_2 \quad (1)$$

The exchange of halide from the dichloride to the diiodide complex with the NaI/THF system occurs only because of the

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Table I. Kinetic Runs for the Double Halide Substitution of Eq 2

run	T, °C	$10^3[\mathrm{CpMoI_2(PMe_3)_2}]$,[a] M	$10^3[\mathrm{(PPN)Cl}]$, M	$10^5 k_{1\mathrm{obs}}$, $\mathrm{s^{-1}}$	$10^4 k_{2\mathrm{obs}}$,[b] $\mathrm{s^{-1}}$
1	22.0	0.95	5.46	0.340 ± 0.018	...
2		1.13	12.24	0.380 ± 0.016	0.14
3		1.17	23.72	0.625 ± 0.011	0.21
4		0.93	34.00	0.769 ± 0.005	0.29
5		1.13	64.90	1.23 ± 0.03	0.44
6	30.0	1.20	5.46	0.60 ± 0.06	...
7		1.05	12.24	0.92 ± 0.05	0.30
8		1.00	23.72	1.48 ± 0.03	0.49
9		1.05	34.00	1.83 ± 0.14	0.61
10		1.12	64.90	3.00 ± 0.05	1.0
11	33.0	1.13	5.46	0.74 ± 0.06	0.22
12		0.98	12.24	1.14 ± 0.04	0.38
13		1.14	23.72	1.98 ± 0.03	0.64
14		1.27	34.00	2.29 ± 0.03	0.80
15		1.10	64.90	3.36 ± 0.04	1.1
16[c]		2.17	64.6	3.61 ± 0.05	...
17[c]				3.64 ± 0.05	...
18	37.5	1.04	5.46	1.17 ± 0.05	0.47
19		1.14	12.24	1.83 ± 0.03	0.61
20		1.04	23.72	2.70 ± 0.03	0.89
21		1.08	34.00	3.67 ± 0.05	1.2
22		1.05	64.90	5.19 ± 0.08	1.9

[a] Observed values, obtained by adding up the concentration of the three EPR active speices (diiodo, dichloro, and iodochloro complexes) at the initial stages of the kinetic runs. [b] Errors from the graphical analysis are estimated to be ≤5%. [c] In the presence of free $\mathrm{PMe_3}$: $[\mathrm{PMe_3}] = 22.7 \times 10^{-3}$ M. Values not used for the kinetic analysis of Table II.

precipitation of the less soluble sodium chloride. We now find that in an homogeneous system [using the THF-soluble $(n\text{-Bu})_4\mathrm{NI}$ that produces the corresponding soluble chloride] only a small portion of the dichloride compound is converted to the mixed halide system even with a $\mathrm{I^-{:}CpMoCl_2(PMe_3)_2}$ ratio of 50:1. We have thus focused our attention on the kinetic investigation of the reverse reaction, i.e. substitution of the iodide ions in $\mathrm{CpMoI_2(PMe_3)_2}$ with chloride.

$$\mathrm{CpMoI_2(PMe_3)_2} \xrightarrow[k_1]{\mathrm{(PPN)Cl/CH_2Cl_2}} \mathrm{CpMoClI(PMe_3)_2} \xrightarrow[k_2]{\mathrm{(PPN)Cl/CH_2Cl_2}} \mathrm{CpMoCl_2(PMe_3)_2} \quad (2)$$

We have investigated several combinations of chloride sources and solvents and found the $\mathrm{PPN^+Cl^-/CH_2Cl_2}$ system to suit best our needs (see eq 2). The $\mathrm{PPN^+Cl^-}$ salt is known to be highly associated in $\mathrm{CH_2Cl_2}$ but, as will be shown later, this fact did not provide a major obstacle for the interpretation of the kinetic data. The reasons for this choice have to do with a compromise between solubility and stability of all the reagents at the concentration levels necessary for the kinetic studies, the resolution of the EPR lines, and the tunability of the EPR instrument.

Our initial experiments showed that the conversion of diiodide to dichloride (eq 2) occurs without significant accumulation of the intermediate mixed-halide species, suggesting that the first exchange is the slow one. Complete disappearance of the diiodide species occurred within the span of a few hours whereas, operating under the same conditions, we found that the isolated mixed-halide complex[12] exchanged the iodide within seconds (by UV/vis spectroscopy). However, the observed kinetic constants for either the first or the second halide exchange, obtained by working under pseudo-first-order conditions, were not reproducible and did not show a clear dependence on the concentration of the chloride salt. These observations indicated to us that the exchange was being catalyzed.[11] To eliminate the source of the catalytic effect, we pretreated all our solutions with solid zinc/copper couple (metallic zinc whose surface has been covered with metallic copper)[14] and maintained them over zinc/copper inside the sealed EPR tubes. We found the zinc/copper couple to be an efficient reducing agent for the 16-electron $[\mathrm{CpMoX_2(PMe_3)_2}]^+$ cations which play a role in the catalyzed substitution,[11] regenerating the 17-electron neutral species. Furthermore, neither the solid reductant nor its inorganic oxidation products interfere with the EPR measurements.

Kinetic Analysis. The halide exchange reactions in the presence of Zn/Cu were much slower than kinetic runs carried out by operation under inert atmosphere without Zn/Cu. In addition, in contrast to the initial studies, there was significant accumulation of the intermediate $\mathrm{CpMoClI(PMe_3)_2}$ (see Figure 1). Thus, the two halide exchange steps occur at similar rates in the uncatalyzed exchange.

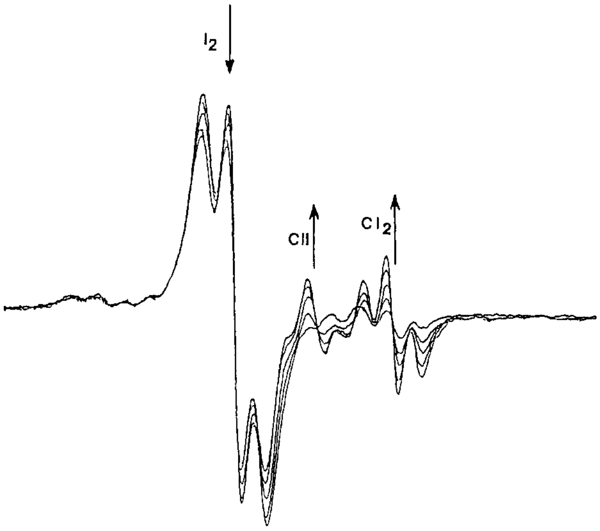

Figure 1. Representative EPR monitoring of the initial stages of a kinetic run for eq 2. T = 37.5 °C; time interval = 4.5 h.

Kinetic runs for the reaction of $\mathrm{CpMoI_2(PMe_3)_2}$ were performed over the temperature range 22.0–37.5 °C with excess $\mathrm{PPN^+Cl^-}$. The rate of disappearance of the diiodide starting complex was fit to a pseudo-first-order rate law. In the case of the samples where the concentration of chloride was small, data points for only the early part of the reaction were used (it is to be noted that the ion-pairing of $\mathrm{PPN^+Cl^-}$ acts to "buffer" the concentration of free $\mathrm{Cl^-}$, the species responsible for the dominant fraction of the reactivity—see below). The rate constants that result from a non-linear least-squares analysis for the first step in eq 2 are given in Table I.

To determine the dependency of the rate on the concentration of $\mathrm{Cl^-}$, we needed to account for the partial ionization of (PPN)Cl in dichloromethane.[17,18] Attempts to fit the pseudo-first-order

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Table II. Results of the Kinetic Analysis According to Eq 4

T, °C	10^3k_{1i}, M^{-1}·s^{-1}	10^4k_{1ip}, M^{-1}·s^{-1}
22.0	1.33 ± 0.17	0.98 ± 0.07
30.0	3.90 ± 0.27	1.33 ± 0.30
33.0	4.92 ± 0.43	1.63 ± 0.50
37.5	8.26 ± 0.42	1.80 ± 0.50

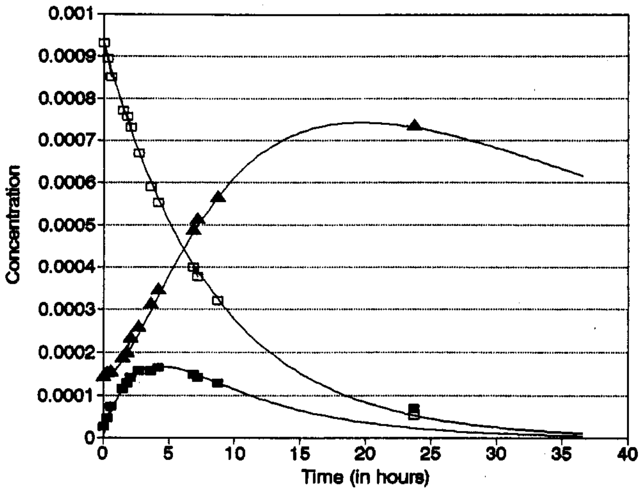

Figure 2. Representative variation of the concentration of CpMoI$_2$(PMe$_3$)$_2$ (open squares), CpMoICl(PMe$_3$)$_2$ (dark squares), and CpMoCl$_2$(PMe$_3$)$_2$ (dark triangles) with time, from the EPR monitoring of reaction 2. The data shown relate to run 15 of Table I.

rate constants to an expression first order in "dissociated" Cl$^-$ by non-linear least-squares analysis of eq 3, where C_s is the nominal

$$k_{1obs} = k_1[\mathrm{Cl}^-] \qquad (3a)$$

$$[\mathrm{Cl}^-]^2 = K_d(C_s - [\mathrm{Cl}^-]) \qquad (3b)$$

concentration of (PPN)Cl salt and K_d is the dissociation constant of the (PPN)Cl ion pair, provided values for the second order rate constants k_1 and afforded ion pair dissociation constants K_d that are close to the literature values[17] at the various temperatures. However, the Eyring plot of the k_1 values failed to provide a reasonable straight line. In analogy to the treatment of Algra and Balt,[17b] we then considered that both the free chloride and the (PPN)Cl ion pair can act as nucleophiles. Thus, the k_{1obs} values were fit by least-squares analysis to the two-term rate law

$$k_{1obs} = k_{1i}[\mathrm{Cl}^-] + k_{1ip}(C_s - [\mathrm{Cl}^-]) \qquad (4)$$

which corresponds to two independent second-order pathways (an *ion* pathway and an *ion pair* pathway). Because our attempts to fit all three independent parameters (k_{1i}, k_{1ip}, and K_d) led to instability, we chose to fix the K_d parameter at the various temperatures to the literature values.[17b] The independent fit on the two kinetic parameters led to the values reported in Table II and to the activation parameters ΔH_{1i} = 13.2 ± 1.8 kcal·mol^{-1}, ΔS_{1i} = −26.0 ± 5.7 cal·K^{-1}·mol^{-1} for the ion path. The ion pair path is, as expected, much less important, and an Eyring analysis was not meaningful because of the high uncertainty of the k_{1ip} values.

Thermal decomposition occurs as shown by the gradual decrease of the total concentration of EPR-active molybdenum species. The diiodide starting material, however, is stable under these conditions as shown by control experiments, and the observed rate constants k_{1obs} reported in Table I are therefore meaningful. A representative graph of concentration of the three EPR active species as a function of time is shown in Figure 2. This graph shows one of the runs carried out at the highest temperature (37.5 °C), where thermal decomposition is most noticeable. This decomposition is noticed only when the majority of the CpMoX$_2$(PMe$_3$)$_2$ is in the form of CpMoCl$_2$(PMe$_3$)$_2$. This result is consistent with the known thermal instability of CpMoCl$_2$(PMe$_3$)$_2$ in warm THF.[5a] Under the assumption that the only cause for the decrease of total EPR-active molybdenum is the thermal decomposition of the dichloride species, we have fit the Cl$^-$ substitution of I$^-$ in CpMoI$_2$(PMe$_3$)$_2$ to the scheme

Table III. Kinetic Runs for the Substitution of Iodide with Chloride in CpMoClI(PMe$_3$)$_2$

run	T, °C	10^3[CpMoICl(PMe$_3$)$_2$], M	10^3[(PPN)Cl], M	10^5k_{2obs}, s^{-1}
1	31.5	4.61	27.0	6.81 ± 0.14
2				5.75 ± 0.06
3		4.19	42.5	8.08 ± 0.11
4				8.17 ± 0.14
5				8.19 ± 0.08
6		4.22	64.2	10.3 ± 0.1
7				10.8 ± 0.1
8				10.1 ± 0.1
9		4.52	93.6	12.8 ± 0.2

Table IV. Results of the Kinetic Analysis According to Eq 5

T, °C	10^2k_{2i}, M^{-1}·s^{-1}	T, °C	10^2k_{2i}, M^{-1}·s^{-1}
22.0	0.44[a]	33.0	1.3[a]
30.0	0.94[a]	37.5	3.5[a]
31.5	1.73 ± 0.21[b]		

[a] From the data of Table I. Errors are estimated to be ±15%. [b] From the data of Table III. k_{2ip} = (2.05 ± 1.08) × 10^{-4} M^{-1}·s^{-1}.

$$\mathrm{CpMoI_2(PMe_3)_2} \xrightarrow{k_1} \mathrm{CpMoICl(PMe_3)_2} \xrightarrow{k_2} \mathrm{CpMoCl_2(PMe_3)_2} \xrightarrow{k_3} \text{decomposition} \qquad (5)$$

The observed values of the concentration of the three dihalo complexes, obtained from EPR analysis, were fit graphically to this scheme with k_{1obs} determined from the least-squares analysis and k_{2obs} and k_3 variables. This analysis differs from the normal A → B → C system in that some CpMoCl$_2$(PMe$_3$)$_2$ was present at the "zero" time reading due to catalysis of the reaction[11] before the Zn/Cu was able to reduce the catalyst; this was accounted for in the integration of the equations. The k_{2obs} values obtained by this treatment are reported in Table I. The values of the rate constant for the k_3 path, the decomposition of CpMoCl$_2$(PMe$_3$)$_2$, are about a factor of 10–20 less than k_2 and show, at best, only a mild dependence on chloride ion.

We also obtained the pseudo-first-order rate constant for the substitution of I$^-$ by Cl$^-$ in the second step, k_{2obs}, directly from CpMoICl(PMe$_3$)$_2$ and (PPN)Cl at one temperature. These data are given in Table III. All of the pseudo-first-order rate constants for the second step were treated by the procedure given above for k_{1obs} (see eq 6); in Table IV we give the values of k_{2i} (values of k_{2ip} were too scattered to have any meaning). The calculated activations parameters on the k_{2i} pathway have too large standard deviations to be of any significance.

$$k_{2obs} = k_{2i}[\mathrm{Cl}^-] + k_{2ip}(C_s - [\mathrm{Cl}^-]) \qquad (6)$$

Kinetic Analysis of the Corresponding Cp* System. The substitution of iodide by chloride in Cp*MoI$_2$(PMe$_3$)$_2$ occurs significantly faster than does the corresponding substitution in the Cp case. Because of this increase in rate, we were forced to study the kinetics of this process by UV/vis spectroscopy and hence we are less certain about the assignment of the observed absorbance changes. We do observe two first-order processes when PPN$^+$Cl$^-$ is added to Cp*MoI$_2$(PMe$_3$)$_2$. At a concentration of PPN$^+$Cl$^-$ and a temperature comparable with the data on the Cp system, k_{1obs} and k_{2obs} are about 6 × 10^4 and 5 × 10^5, respectively, faster than those observed in the Cp system. The assignment of the two observed first-order processes to the two subsequent halide exchange steps was confirmed by the independent investigation of the single first-order exchange starting from isolated Cp*MoICl(PMe$_3$)$_2$. Because Zn/Cu was used in all steps of the handling and because the increase in rate on going from Cp to

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(18) Pearson, R. G.; Gray, H. B.; Basolo, F. *J. Am. Chem. Soc.* **1960**, *82*, 787.

Cp* system was significantly more striking than any catalysis by oxidation observed in the Cp system,[11] we believe that substitution in the Cp* system is significantly faster than is substitution in the Cp complexes.

Discussion

The choice of the halide exchange rather than the phosphine exchange for the investigation of the ligand substitution mechanism on the 17-electron CpMoX$_2$L$_2$ system was influenced by the choice of using EPR to obtain the kinetic data. Changing the nature of the halide has a much greater effect on the position of the EPR signal[6] than does changing the nature of the phosphine. As illustrated in the Results, the ion pairing of the halide reagent does not present a major obstacle to the analysis of the kinetic data. The Cl/I exchange was chosen instead of either the Cl/Br or Br/I exchanges because of the expected greater thermodynamic driving force and the greater changes in the EPR spectra.[6a] We elected to use EPR for obtaining kinetic data instead of the more classical UV/visible technique because (i) the spectral changes observed by EPR are much more indicative of the nature of the species that are present in solution than are UV/visible spectral changes and (ii) it is easier to protect the solutions against adventitious oxidation (especially considering the long half-lives of the kinetic runs) in flame-sealed EPR tubes than in UV/visible cells. The use of glass instead of quartz for the EPR tubes does not pose background problems at the signal amplification utilized, and the long recording times for each spectrum (ca. 2 min) do not affect the accuracy of the kinetic information given the long half-life of the reaction.

The second-order rate law obtained for the halide exchange and the negative value obtained for the activation parameter ΔS^{*}_{1i} suggest an associative slow step. However, as discussed elsewhere,[3] several mechanistic possibility are consistent with these observations. One possibility is formation of a 19-electron [CpMoClI$_2$(PMe$_3$)$_2$]$^-$ intermediate or transition state, which then loses an iodide ion to generate the mixed-halide complex. The latter exchanges the second iodide ion in an identical manner to produce the final dichloride complex. As mentioned in the Introduction, 18-electron analogues of the hypothetical intermediate of this mechanism, e.g. CpMoCl$_3$L$_2$ [L$_2$ = dmpe, dppe; L = P(OCH$_2$)$_3$CEt], are known;[7] thus the formation of the [CpMoX$_n$Y$_{3-n}$(PMe$_3$)$_2$]$^-$ (X, Y = Cl, I) species appears sterically possible. This mechanism would accommodate the experimental observation of $k_2 > k_1$ on steric grounds because, as the hypothetical 19-electron intermediate for this mechanism has increased steric crowding, the replacement of an iodide ligand with a chloride ligand should alleviate some steric strain and facilitate the attack by the second chloride ligand. However, as shown in a separate report,[11] the 18-electron CpMoX$_3$(PMe$_3$)$_2$ system is unstable, rearranging to the [CpMoI$_2$(PMe$_3$)$_2$]$^+$I$^-$ salt when X = I and being in equilibrium with the 16-electron CpMoCl$_3$(PMe$_3$) complex when X = Cl.[11]

A second possible mechanism is dissociation of an iodide ligand to generate a [CpMoX(PMe$_3$)$_2$]$^+$I$^-$ ion pair (X = I for the first substitution; X = Cl for the second one) in a fast preequilibrium, followed by rate-determining exchange of the anion in the ion pair. The negative activation entropy would be, in this case, determined by the preequilibrium, which presumably involves considerable reorganization of the solvent. Steric considerations would lead to the prediction, in this case, of $k_1 > k_2$ contrary to what is observed. Electronically, however, it is expected that the presence of Cl in the [CpMoX(PMe$_3$)$_2$]$^+$ intermediate would provide energetic stabilization through better π donation.

A third possible mechanism, which corresponds to the proposed mechanism for substitutions on several Cp-containing 18-electron complexes,[19] involves ring slippage from a η^5 to a η^3 conformation. A recent report shows kinetic acceleration of ring slippage upon one-electron oxidation of (CH$_3$)$_4$C$_2$(C$_5$H$_4$)$_2$Cr(CO) to the corresponding 17-electron cation.[20] The ring slippage could be either concomitant with the chloride attack or could precede it in a rapid reversible preequilibrium. The faster second exchange ($k_2 > k_1$) could be accommodated by either a steric alleviation to chloride attack during the second exchange or a greater stabilization of the 15-electron ring-slipped (η^3-C$_5$H$_5$)MoICl(PMe$_3$)$_2$ intermediate through π donation from Cl or both. An argument in favor of concomitant ring slippage with nucleophilic attack has been advanced, based on the observed faster slippage in 17-electron complexes with respect to 18-electron analogues and on the belief that 15-electron intermediates would be less favorable than those with 16 electrons.[3] We would like, however, to propose that 15-electron intermediates might be possible in cases, like the present one, where they may assume a high-spin ($S = {}^3/_2$) electronic configuration and thus gain stability through electronic correlation effects. It is therefore possible that ring slippage might precede nucleophilic attack.

Yet another possible dissociative pathway exists, namely equilibrium dissociation of a PMe$_3$ ligand, followed by rate-determining halide exchange and final PMe$_3$ recoordination. This possibility, however, is eliminated by at least two lines of evidence. First, such a mechanism is not consistent with a large negative activation entropy. Second, if this mechanism operates, a retardation effect of PMe$_3$ would be anticipated, but kinetic runs with a 10-fold excess of PMe$_3$ showed no significant variation in rate (compare the result of runs 16 and 17 with the value of $(3.52 \pm 0.50) \times 10^{-5}$ s^{-1} calculated from the values of k_{1i} and k_{1ip} of Table II under these experimental conditions).

A reviewer pointed out that a useful check of the validity of eq 4 would be a kinetic investigation of the reaction in the presence of an electrolyte with a common PPN$^+$ ion, e.g. (PPN)ClO$_4$. Although this is possible in principle, given the association constant of the PPN$^+$ClO$_4^-$ ion pair,[21] the concentration of free Cl$^-$ would not be lowered to an extent to affect the observed kinetics significantly at practical concentrations of the common ion salt. The association constant in CH$_2$Cl$_2$ of ion pairs containing the PPN$^+$ ion does not seems to depend strongly on the nature of the counterion. Another reviewer pointed out that there could be a medium effect on the rates, since the ionic strength of the solutions has not been kept constant in the different kinetic runs. We observe, however, that no ionic strength effect is predicted by theory when one of the interacting species is neutral.

In order to establish whether the mechanism is truly associative or involves preequilibrium dissociation of a ligand (either an iodide or part of the Cp ring) we considered that the replacement of the Cp ligand with the Cp* ligand should render an associative substitution more difficult, from both the steric and electronic points of view. On the other hand, a mechanism involving either halide predissociation or ring slippage should result in acceleration or show only a minor variation in rate. We have thus prepared Cp*MoI$_2$(PMe$_3$)$_2$ and performed a preliminary investigation of the rate of substitution of the iodide ligands with chloride ligands in the same solvent used for the Cp system. As shown in the Results, this exchange is *faster* than the corresponding exchange on the Cp system by a factor of at ca. 10^5. Thus, it appears that the mechanism for halide substitution is not proceeding through a 19-electron intermediate or transition state *for the Cp* system.* It is, of course, still possible that the mechanism is associative for the Cp system and becomes dissociative for the Cp* system. A situation in which the increase of steric bulk in the ancillary ligands changes the mechanism from associative to dissociative has been found previously for the 17-electron XYV(CO) complexes (X, Y = Cp, Cp*, pentadienyl, 2,4-dimethylpentadienyl).[41] In that case, however, the associative substitution was faster than the dissociative one and was being retarded by an increase in steric bulk so that in the more crowded systems only the dissociative mechanism was observable. In the case under study here, the more crowded system reacts *faster* by a mechanism that appears to show the same rate law as the less crowded system. Thus, these data

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(20) van Raaij, E. U.; Brintzinger, H.-H. *J. Organomet. Chem.* **1988**, *356*, 315.

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suggest that halide exchange does not involve the formation of 19-electron intermediates/transition states.

Whether the mechanism is more likely to involve predissociation of an iodide ligand or ring slippage is presently not clear. Attempts to dissociate an iodide ligand by interaction of $CpMoI_2(PMe_3)_2$ with Lewis acids have been unsuccessful. No reaction takes place with AlI_3, whereas the interaction with BF_3 either in toluene or in THF involves oxidation.[22]

Analogous kinetic investigations of phosphine exchange reactions and extension to other similar systems are planned for the near future. In particular, we are interested in investigating the halide exchange kinetics in the corresponding indenyl system to probe more directly for the ring slippage mechanism.

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Supplementary Material Available: Text giving details of the method of calculation of concentrations from EPR intensities for a generic mixture of $CpMoCl_2(PMe_3)_2$, $CpMoClI(PMe_3)_2$, and $CpMoI_2(PMe_3)_2$ and a figure showing a typical EPR spectrum of a mixture of the three complexes (3 pages). Ordering information is given on any current masthead page.

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[22] The isolated product of this reaction, $[Cp^*MoI_2(PMe_3)_2]BF_4$, has been characterized crystallographically: unpublished results from this laboratory.

Contribution from the Department of Chemistry,
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Ligand Effects on the Photoaquation of Tetrakis(amine)rhodium(III) Complexes $[Rh(L)_4XY]^+$

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Photolysis at the longest wavelength absorption band of aqueous solutions of complexes of the type *trans*-$[Rh(L)_4XY]^+$, where X and Y are Cl, Br, I, CN, or OH, and L is a heterocyclic amine, gave photoaquation of X, Y, and L. The quantum yield of photoaquation of the axial ligand X showed both a photochemical trans effect due to Y and a photochemical cis effect due to the heterocyclic amine ligands. The distribution of photoproducts depended strongly on the nature of X, Y, and L and significant differences were observed with the analogous $[Rh(NH_3)_4XY]^+$.

Introduction

Ligand field photolyses of complexes of Rh(III) of the type *trans*-$[RhL_4Cl_2]^+$, where L is a heterocyclic amine, give photoaquation of both chloride and amine, with the distribution of photoproducts strongly dependent on the nature of the amine.[2,3] Significant differences have been noted between these complexes and analogous complexes with L = NH_3.[4-10] Both *cis*- and *trans*-$[Rh(NH_3)_4XY)]^+$ isomers can be prepared,[11] and numerous examples of photoisomerization for the NH_3 complexes have been reported.[12-17] However, repeated attempts to prepare the analogous cis isomers of the tetrakis(pyridine) and other monodentate heterocyclic amine complexes of Rh(III) have been unsuccessful, and the dichloro complexes with heterocyclic amines were completely stereoretentive upon photolysis.[2,3] Thus, it seemed of interest to examine the effect of variation of the axial ligands on the photolysis products and quantum yields. In addition, complexes with derivatives of thiazole and imidazole were prepared for comparison with previously reported heterocyclic amine complexes.

Experimental Section

Physical Measurements. Absorption spectra in the visible–ultraviolet region were obtained with a Perkin-Elmer 200 spectrophotometer. Measurements of absorbance at selected wavelengths for determination of molar absorptivities were made with a Hitachi Perkin-Elmer 139 spectrophotometer. A Metrohm Herisau E512 pH meter was used for all potentiometric measurements.

Materials. The chemicals $RhCl_3{\cdot}3H_2O$ and $RhBr_3{\cdot}2H_2O$ (Strem Chemicals), pyridine (py) (J. T. Baker Chemicals Co.), and 1-methylimidazole (mim), thiazole (tz), and 2-bromothiazole (brtz) (Aldrich Chemical Co.) were used as received.

The complexes *trans*-$[Rh(L)_4Cl_2]Cl{\cdot}5H_2O$[18] and *trans*-$[Rh(L)_4Br_2]Br{\cdot}H_2O$,[18] and the corresponding haloaquao complexes of the type *trans*-$[Rh(L)_4(H_2O)X](ClO_4)_2$,[19] where L is py, mim, tz, or brtz and X is Cl or Br, were prepared by following the literature methods. However, the yields for these and the other complexes were improved when the reaction mixtures were kept under a N_2 atmosphere.

***trans*-$[Rh(py)_4Cl(OH)]ClO_4$**[20] was prepared from 50 mL of 2.8 mM *trans*-$[Rh(py)_4(H_2O)Cl](ClO_4)_2$. The pH of the solution was adjusted to 10.75 by addition of NaOH. Then 5 M $NaClO_4$ was added dropwise with stirring until the desired yellow product precipitated. Yield: 0.0562 g, 85%. The same method was used to prepare the analogous bromohydroxo complex, *trans*-$[Rh(py)_4Br(OH)]ClO_4$.

***trans*-$[Rh(py)_4ClBr]ClO_4{\cdot}H_2O$** was prepared from the chloroaquo complex. Under a N_2 atmosphere, a solution containing 0.191 g (0.284

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