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The First Electron Transfer Chain Catalyzed Ligand Substitution Reaction That Occurs by Transforming an Odd-Electron System into an Even-Electron One

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Abstract: The substitution of I^- by Cl^- in $CpMoI_2(PMe_3)_2$ to afford $CpMoCl_2(PMe_3)_2$ is catalyzed by 1-electron oxidation, which produces the paramagnetic 16-electron $[CpMoI_2(PMe_3)_2]^+$ complex. Halide substitution is more rapid on the 16-electron cationic complex than on the 17-electron neutral one to produce $[CpMoCl_2(PMe_3)_2]^+$, and an endoergic electron transfer step follows to close a catalytic cycle with constitutes the first reported electron transfer chain catalytic pathway in ligand substitution where exchange is made faster by going from an odd- to an even-electron system. The efficiency of the catalysis is low because of the endoergic electron transfer and because the 16-electron dichloride cation is decomposed by excess chloride. The $[CpMoI_2(PMe_3)_2]^+$ complex has been isolated in salts with the PF_6^-, I_3^-, and I^- counterions. The interaction between $CpMoI_2(PMe_3)_2$ and I_2 in a 2:1 molar ratio shows that, after rapid formation of the $[CpMoI_2(PMe_3)_2]^+I^-$ salt, slow disproportionation occurs with formation of $CpMoI_2(PMe_3)_2$ and $[CpMoI_2(PMe_3)_2]^+I_3^-$. The interaction between $[CpMoCl_2(PMe_3)_2]^+$ and Cl^- has been investigated by NMR and cyclic voltammetry, which indicate the formation of the 18-electron $CpMoCl_3(PMe_3)_2$, in equilibrium with the paramagnetic 16-electron $CpMoCl_3(PMe_3)$. The same equilibrium mixture has also been obtained from $CpMoCl_2(PMe_3)_2$ and $PhI{\cdot}Cl_2$ in a 2:1 molar ratio.

Introduction

We have recently[1] described a kinetic investigation of the halide substitution reaction on the $CpMoX_2(PMe_3)_2$ system (X = Cl, I). The aim of this investigation was to elucidate the mechanism of ligand substitution in a stable 17-electron organometallic radical which is atypical among the organometallic radicals so far investigated in having a metal in a relatively high oxidation state and in showing a preference for being oxidized to a 16-electron system rather than being reduced to a closed-shell configuration.[2] All low-valent organometallic 17-electron radicals studied before show associative ligand substitution[3] unless the system is too sterically encumbered.[4,5] Although the kinetic data that we have gathered are not sufficient to distinguish between an associative and a dissociative mechanism, the large acceleration observed on going from the Cp system to the Cp* system shows that the mechanism for the Cp* system cannot proceed through 19-electron intermediates/transition states.[1]

During the kinetic investigations alluded to above,[1] we have witnessed a catalytic effect on ligand substitution caused by adventitious oxidation. We report here our investigations of this catalytic effect and some related studies.

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. Cyclic voltammograms were carried out with a EG&G potentiostat connected to a Macintosh computer through MacLab hardware/software. EPR measurements were carried out with a Bruker ER200 spectrometer calibrated with diphenylpicrylhydrazyl radical. The compounds $CpMoCl_2$, $CpMoCl_2(PMe_3)_2$, $CpMoClI(PMe_3)_2$, $CpMoI_2(PMe_3)_2$,[6] $[CpMoCl_2(PMe_3)_2]PF_6$,[2] and $Cp^*MoCl_2(PMe_3)_2$[1] were prepared as described previously. PPN^+Cl^- was purchased from Aldrich Chemicals and recrystallized from CH_2Cl_2. The Zn/Cu couple was prepared according to LeGoff, substituting 20-mesh Zn instead of the indicated 30 mesh.[7]

EPR Kinetic Study of the $CpMoI_2(PMe_3)_2/PPN^+Cl^-$ Exchange in the Presence of a Catalytic Amount of $[CpMoCl_2(PMe_3)_2]^+PF_6^-$. $CpMoI_2(PMe_3)_2$ (4.43 mg, 7.81×10^{-3} mmol), 2.60 mL of CH_2Cl_2, and some Zn/Cu couple were placed in a Schlenk tube. The sample was stirred at room temperature for 5 min, then cooled to −78 °C, and transferred into a second Schlenck tube which contained PPN^+Cl^- (135.26 mg, 0.2356 mmol) and $[CpMoCl_2(PMe_3)_2]^+PF_6^-$ (0.42 mg, 0.79×10^{-3} mmol). The solution was stirred at −78 °C for 3 min, and then an aliquot was transferred into a 3-mm-o.d. glass EPR tube which was sealed under argon and kept in liquid nitrogen until the time of the kinetics run. The kinetics run of the halide substitution reaction was carried out, and the resulting data were treated as described in the previous paper,[1] giving an observed pseudo-first-order rate constant of 1.9×10^{-4} s^{-1}. A second sample was prepared in an identical manner from 9.83 mg of $CpMoI_2(PMe_3)_2$ (17.3×10^{-3} mmol), 200.60 mg of PPN^+Cl^- (0.3495 mmol), 0.91 mg of $[CpMoCl_2(PMe_3)_2]^+PF_6^-$ (1.7×10^{-3} mmol), and 5.80 mL of CH_2Cl_2. This gave an observed pseudo-first-order rate constant for the halide exchange of 1.3×10^{-4} s^{-1}.

Preparation of $[CpMoI_2(PMe_3)_2]PF_6$. $CpMoI_2(PMe_3)_2$ was prepared in situ from $CpMoCl_2$ (351 mg, 1.51 mmol), PMe_3 (0.30 mL, 3.0 mmol), and NaI (816 mg, 5.44 mmol) in THF (20 mL) as already described.[6] The THF solvent was completely removed under reduced pressure and the residue extracted with CH_2Cl_2 (10 mL) and filtered. To the resulting solution was added a solution of $AgPF_6$ (388 mg, 1.53 mmol) in CH_2Cl_2 (20 mL), resulting in a color change to dark emerald green and the formation of a gray precipitate. The solution was filtered, the solvent was partially removed by evaporation under reduced pressure, and the product was crystallized by the addition of Et_2O. After the mixture was cooled to −20 °C overnight, the solid was collected by decanting off the mother liquor, washed with Et_2O, and dried in vacuo. Yield: 506 mg (47%). NMR (CD_2Cl_2, room temperature, δ): 181.0 (5 H, Cp), −11.1 (18 H, PMe_3). The cyclic voltammogram (CH_2Cl_2, 0.1 M n-Bu_4PF_6, room temperature) shows a reversible reduction wave at −0.425 V relative to the internal ferrocene standard. The addition of PPN^+I^- to the solution does not affect this electrochemical process.

Preparation of $[CpMoI_2(PMe_3)_2]I_x$ (x = 1,3). (a) x = 3. $CpMoI_2(PMe_3)_2$ (134 mg, 0.236 mmol) was dissolved in 15 mL of CH_2Cl_2 and the resultant mixture treated with I_2 (103 mg, 0.406 mmol). The brown solution immediately turned dark forest green, and a dark crystalline

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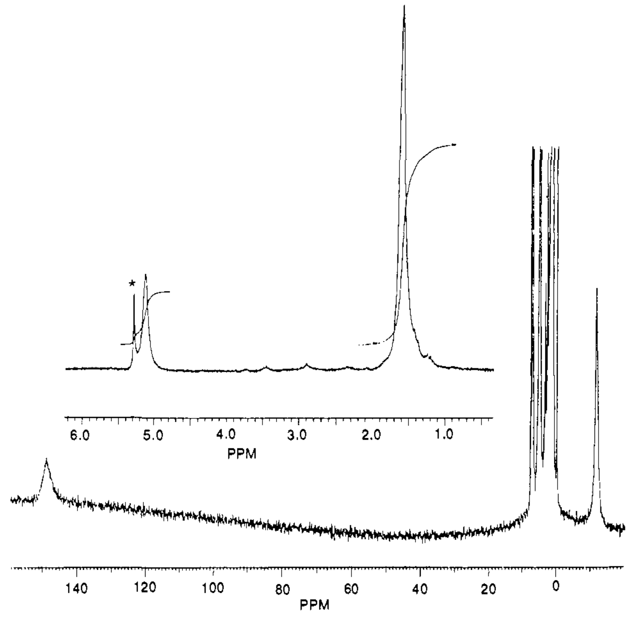

Figure 1. ^{1}H NMR of the products of the reaction between $CpMoCl_2(PMe_3)_2$ and $PhI{\cdot}Cl_2$ in CH_2Cl_2 (see Experimental Section). Solvent = $CDCl_3$; temperature = 298 ± 2 K. The starred peak is residual CH_2Cl_2.

precipitate started to form after a few minutes. After being stirred briefly at room temperature, the mixture was cooled to −20 °C overnight. The solid was recovered by filtration, washed with *n*-heptane, and vacuum dried. Yield: 153 mg (68%). Anal. Calcd for $C_{11}H_{23}I_5MoP_2$: C, 13.94; H, 2.45. Found: C, 13.68; H, 2.14.

(b) $x = 1$. $CpMoI_2(PMe_3)_2$ (336 mg, 0.593 mmol) was dissolved in 5 mL of CH_2Cl_2 and the resultant mixture treated with I_2 (75 mg, 0.30 mmol). The brown solution became immediately dark forest green. The solution was promptly layered with 10 mL of *n*-heptane and set at ca. 0 °C. After 2 days, the crystals that had formed were collected and dried. Inspection with the microscope revealed two types of crystals, both black. The mother liquor was red-brown. One crystal habit was parallelepipedal and was identical to the habit of the triiodide salt described above. The other crystals were larger cubes, and one of these was selected for an X-ray analysis, which confirmed the identity of the compound as the monoiodide salt; see Results.

EPR Spectroscopic Study of the Reaction between $CpMoI_2(PMe_3)_2$ and I_2. Stock solutions of $CpMoI_2(PMe_3)_2$ and I_2 in THF were combined at −80 °C to obtain a solution that was 2.97×10^{-3} M in $CpMoI_2(PMe_3)_2$ and 1.47×10^{-3} M in I_2. This solution was transferred at −78 °C into a 3-mm-o.d. glass EPR tube which was then further cooled to the liquid nitrogen temperature and flame sealed. The tube was thawed immediately before the introduction of the tube into the EPR cavity. After thawing, the solution was green and the EPR spectrum showed the characteristic triplet due to $CpMoI_2(PMe_3)_2$ at very low intensity. With time, the shape of the EPR spectrum did not change but the intensity increased until, after ca. 3 h, it reached a constant intensity which was about 68% of the intensity observed for a standard solution containing the diiodide complex at the same concentration and no diiodine. The same experiment with a solution that was initially 2.48×10^{-3} M in $CpMoI_2(PMe_3)_2$ and 2.46×10^{-3} M in I_2 gave a final concentration of the neutral diiodide complex equal to 35% of the amount that was present initially.

Preparation of $CpMoCl_3(PMe_3)$. $CpMoCl_2(PMe_3)_2$ was prepared in situ from $CpMoCl_2$ (292 mg, 1.26 mmol) and PMe_3 (0.30 mL, 3.0 mmol) in 10 mL of THF.[6] The THF solvent was completely removed by evaporation and replaced with 10 mL of CH_2Cl_2. A small amount of undissolved material was removed by filtration. To the resulting red-brown solution was slowly added a solution of $PhI{\cdot}Cl_2$ (145 mg, 0.53 mmol) in 3 mL of CH_2Cl_2 with stirring. When each drop of the $PhI{\cdot}Cl_2$ solution came in contact with the solution of the molybdenum complex, a dark green color immediately developed in the local volume that contained a temporary excess of Cl_2. Upon stirring, however, the solution went rapidly back to a red-brown color. At the end of the addition of $PhI{\cdot}Cl_2$, the solution had a different tonality of red-brown. An aliquot of this solution was stripped and redissolved in $CDCl_3$ for an NMR investigation, the results of which are shown in Figure 1 (see also Results). Upon standing at room temperature, the CH_2Cl_2 solution changed color further to orange-red while a white solid separated out. After several days the solution was filtered, concentrated to a few milliliters, and layered with *n*-heptane. Upon completion of the diffusion process, the solution was cooled to −20 °C to produce a small amount of well-formed brown crystals of $CpMoCl_3(PMe_3)$. ^{1}H NMR ($T = 298 \pm 2$ K, CD_2Cl_2, δ): 145.4 (5 H, Cp), −11.6 (9 H, PMe_3).

Cyclic Voltammetric Investigations of the $CpMoI_2(PMe_3)_2$ + PPN^+Cl^- System. The electrochemical cell was a standard Schlenk tube with a screw-threaded joint at top for fitting of the flat surface working Pt electrode. The Pt auxiliary electrode and a Ag pseudoreference electrode were fitted through Pt/uranium glass/Pyrex glass seals. The CH_2Cl_2 solution used for the electrochemical investigation was prepared by using the same technique employed for setting up the kinetic runs described in the previous paper[1] by using 13 mg of $CpMoI_2(PMe_3)_2$ in 1.55 mL of CH_2Cl_2 with the additional introduction of supporting electrolyte (ca. 0.1 M *n*-Bu_4NPF_6). During the experiment, aliquots from a solution containing 48.5 mg of PPN^+Cl^- in 1.0 mL of CH_2Cl_2 were added. All the solutions were maintained in permanent contact with Zn/Cu couple. At the end of the cyclic voltammetric experiment (ca. 1 h), EPR analysis showed that only negligible halide exchange had occurred.

Reaction between $[Cp^*MoI_2(PMe_3)_2]^+$ and PPN^+Cl^-. A solution of $[CpMoI_2(PMe_3)_2]^+$ in CH_2Cl_2 was prepared in situ as follows: $Cp^*MoCl_2(PMe_3)_2$ (28 mg, 0.062 mmol) and excess anhydrous NaI (35 mg, 0.23 mmol) were reacted to afford the corresponding amount of $Cp^*MoI_2(PMe_3)_2$ as described previously.[1] The mixture was evaporated to dryness, and the residue was extracted with CH_2Cl_2 (5 mL). After filtration, I_2 (22 mg, 0.17 mmol) was added. The color changed immediately from red-brown to purple, which is the same color observed for a CH_2Cl_2 solution of $[Cp^*MoI_2(PMe_3)_2]BF_4$, of which the X-ray structure has been determined.[8] In particular, absorption maxima at 550 (sh) and 575 nm are observed, which are absent in solutions of either $[Cp^*MoCl_2(PMe_3)_2]^+$ (obtained from equimolar amounts of $Cp^*MoCl_2(PMe_3)_2$ and $AgBF_4$) or $PPN^+I_3^-$ (obtained from equimolar amounts of PPN^+I^- and I_2) at the same concentration. An aliquot of this solution (1 mL) was added to a solution containing an excess of PPN^+Cl^- (45 mg, 0.078 mmol, in 4 mL of CH_2Cl_2). No significant exchange took place within 2 h at 20 °C (UV/vis monitoring on the absorptions at 550 and 575 nm).

Results

Catalytic Phenomenon. The substitution of iodide with chloride in $CpMoI_2(PMe_3)_2$ proceeds quantitatively according to eq 1. The kinetic investigation of this process is illustrated in the previous report.[1]

$$CpMoI_2(PMe_3)_2 \xrightarrow[k_1]{(PPN)Cl/CH_2Cl_2} CpMoClI(PMe_3)_2 \xrightarrow[k_2]{(PPN)Cl/CH_2Cl_2} CpMoCl_2(PMe_3)_2 \quad (1)$$

While carrying out these studies, we realized that the halide exchange was being catalyzed under certain conditions. While the uncatalyzed process has similar rate constants for the two subsequent exchanges ($k_2 \approx 5k_1$),[1] so that the intermediate mixed-halide compound builds up significantly at intermediate times, there is *no* observed mixed-halide intermediate under catalyzed conditions, showing that the catalytic efficiency is much greater for the second exchange than for the first one. Under catalyzed conditions, the half-life of the halide exchange starting from $CpMoI_2(PMe_3)_2$ is typically a few hours, whereas when starting with preformed pure $CpMoClI(PMe_3)_2$ the exchange is over in just a few seconds.

That the source of catalysis is oxidation is immediately suggested by the known chemical behavior of this system. $CpMoI_2(PMe_3)_2$ is easily oxidizable (−0.415 V with respect to the ferrocene/ferrocenium couple),[2a] and the product of oxidation is the corresponding 16-electron monocation. For the corresponding dichloride complex, the $[CpMoCl_2(PMe_3)_2]PF_6$ oxidation product was isolated and crystallographically characterized,[2a] and we have now isolated the corresponding 16-electron diiodide complex in salts with the PF_6^-, I^-, and I_3^- counterions (vide infra). It is reasonable to anticipate a faster halide substitution on the 16-electron $[CpMoI_2(PMe_3)_2]^+$ complex with respect to its 17-electron neutral conterpart because of the available coordination site and the positive charge on the complex. Finally, if electron cross-transfer can occur between different $[CpMoXY(PMe_3)_2]^{n+}$ (X, Y = Cl, I; n = 0, 1) species, then the initial 1-electron oxidation

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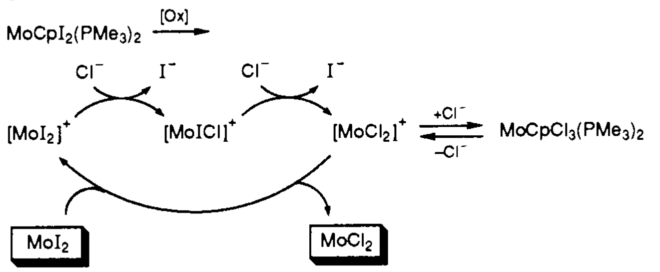
[8] Unpublished results from this laboratory.

Scheme I



of $CpMoI_2(PMe_3)_2$ provides a path for catalyzed halide exchange (see Scheme I, Cp and PMe_3 ligands omitted).

It is worth noting that this mechanism represents a case of electron transfer chain (ETC) catalyzed ligand substitution, numerous examples of which have been reported in recent years.[9] However, no example has been reported where ligand exchange is faster in the even-electron manifold than it is in the odd-electron manifold.

A first experimental support for this suggested catalysis by oxidation comes from our reported[1] kinetic studies: We were able to eliminate the catalytic effect under rigorously inert conditions and in the presence of a stabilizing *reductant* (Zn/Cu couple). Furthermore, we observed a ca. 6-fold acceleration of the exchange in eq 1 by introduction of ca. 10% of preoxidized dichloride material, $[CpMoCl_2(PMe_3)_2]^+PF_6^-$. We thus proceeded to test each of the individual steps of the proposed Scheme I stoichiometrically.

Preparation and Investigations of the $[CpMoI_2(PMe_3)_2]^+$ Cation. The 17-electron diiodide compound can be oxidized by $AgPF_6$ in analogy to the dichloride compound reported earlier[2a] (see eq 2).

$$CpMoI_2(PMe_3)_2 + AgPF_6 \rightarrow [CpMoI_2(PMe_3)_2]PF_6 + Ag \qquad (2)$$

The product is a characteristic dark forest green, and in analogy to the dichloride species described before,[2a] it is paramagnetic as shown by the NMR resonance in CD_2Cl_2 at δ 181.0 (Cp) and −11.1 (PMe_3) at room temperature. The corresponding resonances for the dichloride system (for which the presence of two unpaired electrons was confirmed by a magnetic susceptibility measurement) have been found at δ 179.5 and −6.6.

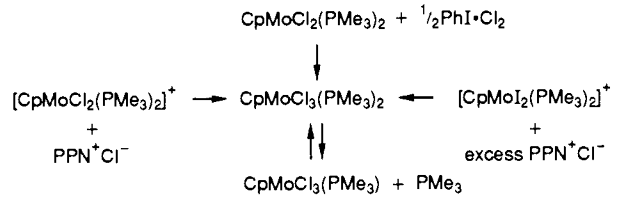
The 16-electron diiodide complex is also produced by oxidation with diiodine. EPR monitoring of the reaction with only one oxidizing equivalent of I_2 showed that the 17-electron starting material was initially consumed completely, but at later times it slowly formed again. This behavior, combined with a quantitative EPR determination (ca. two-thirds of the initial 17-electron complex was regenerated at equilibrium when 1 equiv of I_2 was employed and ca. one-third when 2 equiv was employed), is consistent with the mechanism shown in Scheme II.

Scheme II

$$CpMoI_2(PMe_3)_2 + {}^1\!/_2 I_2 \overset{\text{fast}}{\rightleftarrows} [CpMoI_2(PMe_3)_2]^+I^-$$

$$[CpMoI_2(PMe_3)_2]^+I^- + I_2 \xrightarrow{\text{slow}} [CpMoI_2(PMe_3)_2]^+I_3^-$$

Scheme III



Further evidence for the mechanism illustrated in Scheme II comes from isolation of the pure triiodide when the reaction is carried out with 3 equiv of iodine and the isolation of a mixture of monoiodide and triiodide salts when using only 1 equiv of iodine. The monoiodide salt has been crystallographically characterized.[10]

The three salts with the I^-, I_3^-, and PF_6^- anions exhibit identical UV/vis spectra, and the ^1H NMR spectra in CD_2Cl_2 of the I^- and I_3^- salts compare with that of the PF_6^- salt. The triiodide salt shows peaks at δ 175.8 (5 H) and −10.6 (18 H), and the monoiodide shows analogous resonances at δ 165.0 and −10.6. The minor changes in chemical shift between the three salts could be due to counterion effects or to a slight temperature difference between the various runs. We found no peaks in the diamagnetic region of the ^1H NMR spectrum that could be assigned to a $CpMoI_3(PMe_3)_2$ complex in *slow* equilibrium with the 16-electron cation, but we cannot exclude that such equilibrium is fast on the NMR time scale and is responsible for the slight shift in the Cp and PMe_3 proton resonances on going from the PF_6^- to the I_3^- to the I^- salt. Even if some neutral triiodide complex is formed, however, the small shift shows that the 16-electron $[CpMoI_2(PMe_3)_2]^+$ is the dominant species in solution. Cyclic voltammetry also confirms that the three salts contain the same 16-electron $[CpMoI_2(PMe_3)_2]^+$ cation: The same reversible reduction wave is observed for the three salts at a potential which corresponds to that reported earlier[2a] for the reversible oxidation of the neutral diiodide complex. The fact that the salt structure for the monoiodide salt is preferred with respect to an 18-electron neutral complex has relevance for the explanation of the catalytic effect in the halide substitution (see Discussion).

Halide Exchange in the 16-Electron $[CpMoI_2(PMe_3)_2]^+$ Complex. The next proposed step in Scheme I is halide exchange in $[CpMoI_2(PMe_3)_2]^+$, to generate $[CpMoClI(PMe_3)_2]^+$ and $[CpMoCl_2(PMe_3)_2]^+$. Treatment of $[CpMoI_2(PMe_3)_2]PF_6$ with (PPN)Cl in CH_2Cl_2 at room temperature results in the immediate quenching of the deep green color of the diiodide cation to generate a pale red color. The UV/visible spectrum of this solution *does not* correspond to that of $[CpMoCl_2(PMe_3)_2]PF_6$ but is identical to that obtained when the latter compound is treated in CH_2Cl_2 with an excess of (PPN)Cl. These observations establish that $[CpMoI_2(Me_3)_2]^+$ exchanges iodide with chloride to produce the corresponding dichloride cation and that the latter reacts further with the chloride anion. The rate of halide exchange was established semiquantitatively by visually observing the rate of disappearance of the green color of $[CpMoI_2(PMe_3)_2]^+$ at −37 and −51 °C and at various concentrations of Cl^-. The exchange appears to have a first-order dependence on the free chloride concentration,[1] and the second-order rate constant is estimated to be ca. 1×10^4 M^{-1} at 25 °C, assuming the dissociation constant for the PPN^+Cl^- ion pairing can be extrapolated to the lower temperatures. The associative nature of this halide exchange is further indicated by a strong retardation effect on the rate on going from the Cp system to the Cp* system. A solution of $[Cp^*MoI_2(PMe_3)_2]^+$ was generated from the neutral complex and I_2 (3 equiv) in analogy to formation of the analogous Cp triiode salt. Addition of excess PPN^+Cl^- did not result in any observable exchange at 20 °C within 2 h.

As shown in Scheme I, the logical proposal is that the reaction of $[CpMoCl_2(PMe_3)_2]^+$ with excess Cl^- produces the neutral trichloride species. However, our more detailed studies show that this is only the first step in a series of reactions. We have generated the "trichloride" complex in an NMR tube by three independent

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routes (using CD_2Cl_2 as solvent) (see Scheme III): (i) by treatment of $[CpMoCl_2(PMe_3)_2]^+PF_6^-$ with PPN^+Cl^-; (ii) by treatment of $[CpMoI_2(PMe_3)_2]^+I_x^-$ (mixture of monoiodide and triiodide salts, see Experimental Section) with excess PPN^+Cl^-; (iii) by oxidation of $CpMoCl_2(PMe_3)_2$ with $PhI{\cdot}Cl_2$. In each case, immediate NMR analysis showed slightly broadened prominant peaks at δ 5.1 (5 H) and 1.6 (18 H) in the ^1H NMR spectrum and a broadened peak in the range between δ −1 and −4 in the ^{31}P NMR spectrum; these peaks can be assigned to a diamagnetic $CpMoCl_3(PMe_3)_2$ molecule with equivalent PMe_3 ligands. In each case, however, the ^1H NMR spectra show additional peaks at ca. δ 150 and −12 (see Figure 1). The latter integrate satisfactorily for 5:9 protons (1 Cp:1 PMe_3). Due to their position relative to the 16-electron $[CpMoX_2(PMe_3)_2]^+$ (X = Cl, I) complexes, we believe they are also due to a 16-electron complex and we assign them to $CpMoCl_3(PMe_3)$. These peaks increase with time at the expense of those assigned to the bis(phosphine) complex. Fresh solutions indicated a $CpMoCl_3(PMe_3)_2/CpMoCl_3(PMe_3)$ ratio of ca. 6, whereas after 2-h standing at room temperature the same ratio decreased to ca. 2.5. Standing of a CH_2Cl_2 solution prepared as in method iii above for several days at room temperature, followed by crystallization by diffusion of *n*-heptane, gave brown crystals of pure $CpMoCl_3(PMe_3)$ as indicated by ^1H NMR.

It is reasonable to assume that an equilibrium exists between the bis- and mono(phosphine) complexes. The equilibrium is not fast on the NMR time scale because the two complexes are independently observed, but a slow exchange probably occurs as indicated by the progressive shift of the equilibrium toward the paramagnetic mono(phosphine) complex, presumably caused by the reaction of free PMe_3 with the chlorinated solvent. The reaction of PMe_3 with CH_2Cl_2 is known to result in the slow formation of white insoluble $[Me_3PCH_2Cl]^+Cl^-$.[11] The instability of $CpMoCl_3(PMe_3)_2$ is at variance with the stability of the analogous complexes with chelating diphosphines, $CpMoCl_3$(L-L) (L-L = dppe,[12] dmpe[13]), with the "cage phosphite", $CpMoCl_3[P(OCH_2)_3CEt]_2$,[14] or with phosphines and CO, $CpMoCl_3(CO)L$ (L = PEt_3, PMe_2Ph).[15] The $CpMoCl_3(PMe_3)_2$ complex could not be obtained from the reaction between $CpMoCl_3$ and 2 equiv of $PMe_3)_2$ in CH_2Cl_2.[14]

Related to these NMR studies is the result of a cyclic voltammetric investigation of $CpMoCl_2(PMe_3)_2$ in the presence of PPN^+Cl^- in CH_2Cl_2 (see Figure 2). Addition of Cl^- has several effects: It shifts the half-way potential of the reversible oxidation wave (labeled A) in a negative direction with respect to the internal acetylferrocene standard (labeled S), it makes the process chemically irreversible by diminishing the size of the back-reduction wave, it generates a new oxidation wave at ca. −0.15 V (labeled B) with respect to acetylferrocene, and it generates new, small reduction waves (labeled C and D). The internal standard had to be used because addition of Cl^- causes a shift of the Ag pseudoreference potential. The negative potential shift of the $[CpMoCl_2(PMe_3)_2]^{n+}$ (n = 0,1) couple is consistent with a fast equilibrium between $[CpMoCl_2(PMe_3)_2]^+$ and an adduct arising from the interaction with Cl^-. The trichloride neutral complex is the most likely candidate for this adduct, given the NMR experiment described above. The stability constant for the trichloride complex, $K = [CpMoCl_3(PMe_3)_2]/\{[CpMoCl_2(PMe_3)_2{}^+][Cl^-]\}$, cannot be calculated without knowing the association constants of all the ion pairs involved (PPN^+Cl^-, $Bu_4N^+Cl^-$, $Bu_4N^+PF_6^-$) at the temperature of the experiment, but the NMR experiment described above suggests that this constant has a large value. The formation of the neutral trichloride complex is fast with respect to the voltammogram time scale. This is verified by the insensitivity of the potential shift to the scan rate for rates ≤100 mV/s. The second oxidation wave, B in Figure 2, is chemically reversible up until 1 equiv of Cl^- has been added to the solution. The intensity of this wave depends on the amount of added Cl^- and reaches a maximum value when $[Cl^-] \geq [CpMoCl_2(PMe_2)_2]$, being of about the same size as the first oxidation. This establishes the 1-electron nature of this process. When an excess of Cl^- is added (Figure 2c), wave B does not further increase in intensity and it becomes chemically irreversible. The size of the return wave is strongly dependent on the scan rate, being greater at faster scan rates. These observations are consistent with Scheme IV. The potential of wave B shifts negatively upon addition of Cl^- in analogy to the potential of wave A, indicating that the first step of the decomposition of the $[CpMoCl_3(PMe_3)_2]^+$ ion is likely to be addition of Cl^-.

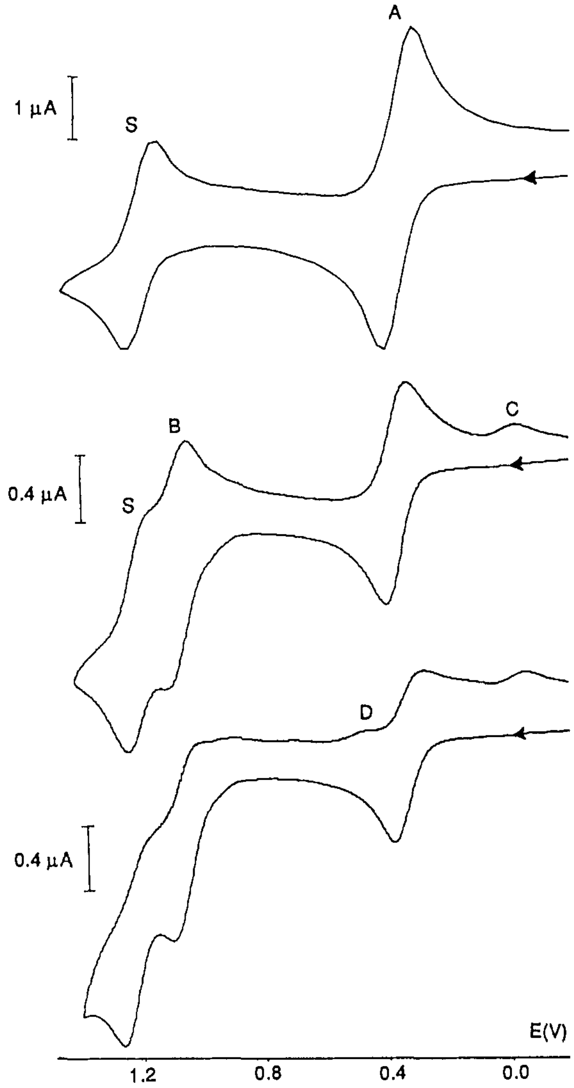

Figure 2. Cyclic voltammetric scans of mixtures of $CpMoCl_2(PMe_3)_2$ and (PPN)Cl. Solvent = CH_2Cl_2; supporting electrolyte = n-Bu_4NPF_6 (0.30 M); reference electrode = Ag/AgCl; working electrode = 3.5 mm^2 flat surface Pt; S = acetylferrocene (internal standard). Key: (a) $[CpMoCl_2(PMe_3)_2] = 6.0 \times 10^{-3}$ M; [(PPN)Cl] = 0. (b) $[CpMoCl_2(PMe_3)_2] = 5.4 \times 10^{-3}$ M; [(PPN)Cl] = 6.7×10^{-3} M. (c) $[CpMoCl_2(PMe_3)_2] = 4.1 \times 10^{-3}$ M; [(PPN)Cl] = 2.3×10^{-2} M. Scan rates: (a) 500 mV/s; (b–c) 50 mv/s.

Scheme IV

$$CpMoCl_2(PMe_3)_2 \rightleftarrows [CpMoCl_2(PMe_3)_2]^+ + e^- \quad E_1$$

$$[CpMoCl_2(PMe_3)_2]^+ + Cl^- \rightleftarrows CpMoCl_3(PMe_3)_2 \quad C_1 \text{ (fast)}$$

$$CpMoCl_3(PMe_3)_2 \rightleftarrows [CpMoCl_3(PMe_3)_2]^+ + e^- \quad E_2$$

$$[CpMoCl_3(PMe_3)_2]^+ + Cl^- \rightarrow \text{decomposition} \quad C_2 \text{ (slow)}$$

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The decrease of the return wave associated with the reduction of the $CpMoCl_3(PMe_3)_2/[CpMoCl_2(PMe_3)_2]^+$ equilibrium system to the Mo(III) neutral complex is due to an unknown process. The shape and intensity of this return wave do not greatly change if the potential scan is switched before the occurrence of process B or when the scan rate is varied in the 500–50 mV/s range, whereas they are strongly dependent on the concentration of Cl^- ions. Thus, it seems unlikely that the reason for this phenomenon is simply decomposition of $CpMoCl_3(PMe_3)_2$ by a first-order process. A possible way to rationalize this result is to invoke the equilibrium between $CpMoCl_3(PMe_3)_2$ and the 16-electron $CpMoCl_3(PMe_3)$ complex shown by the NMR experiment. This equilibrium, which favors the 18-electron species, might be shifted by the addition of Cl^- to form an electrochemically inactive species, for instance a $[CpMoCl_4(PMe_3)]^-$ ion, which subtracts electroactive $CpMoCl_3(PMe_3)_2$ from solution in a scan rate independent fashion. Waves C and D are probably due to decomposition products.

The decomposition of the $[CpMoCl_2(PMe_3)_2]^+$ ion, which is indicated by the NMR and cyclic voltammetric experiments described above, suggests that if the mechanism of catalysis illustrated in Scheme I is correct, the catalytic acceleration should decrease with time. In fact, in a few of the early kinetic studies when the precaution of protecting the solutions in the sealed EPR tubes with Zn/Cu was not taken,[1] we have observed that the exchange started off fast and without accumulation of the intermediate mixed-halide complex, but later slowed, approaching the rate of uncatalyzed process, and the intermediate mixed-halide complex started to accumulate, indicating that the catalyst was depleted.

The Electron Transfer Step. Next, we investigated the electron cross-transfer reaction illustrated in eq 3. From known[2a] half-way potentials, an equilibrium constant $K = 49$ can be calculated for equilibrium 3. Note that the redox step involved in the proposed catalytic cycle of Scheme I is the reverse of eq 3, and it is therefore an endoergic process.

$$[CpMoI_2(PMe_3)_2]^+ + CpMoCl_2(PMe)_2 \rightleftarrows [CpMoCl_2(PMe_3)_2]^+ + CpMoI_2(PMe_3)_2 \quad (3)$$

Reaction 3 was investigated kinetically, again in a semiquantitative fashion by visually estimating the time required to quench the intense green color of $[CpMoI_2(PMe_3)_2]^+$. The reaction is complete within 1 s at −50 °C, from which a second-order kinetic constant higher than 1×10^3 M^{-1} at −50 °C can be estimated. If we assume that the activation enthalpy is about 10 kcal/mol, a typical value for electron transfer reactions of this sort, then the value of k at room temperature is $>2 \times 10^5$ M^{-1} s^{-1}. From this number and the known equilibrium constant, the rate of electron transfer of reaction 3 in the opposite direction (right to left) is estimated as $>4 \times 10^3$ M^{-1} s^{-1} at room temperature. The high value for this rate was expected since the structures of $[CpMoX_2(PMe_3)_2]^{n+}$ (X = Cl, I) are identical on going from $n = 0$ to $n = 1$,[2a] the only differences being minor changes in the bond lengths; therefore, Franck–Condon effects are small. Since the mixed-halide complex has been shown to have a structure identical with those of the two homogeneous halide systems,[6] the rates of electron transfer between the MoI_2/MoICl or MoICl/$MoCl_2$ pairs are expected to be equally high. $E_{1/2}$ for the iodo–chloro complex (−0.48 V vs ferrocene) is approximately half-way between those of the dichloride and diiodide complexes.

Thus, we have shown that each of the proposed steps illustrated in Scheme I takes place at a rate that is faster than the rate of catalyzed halide exchange. Thus, Scheme I qualifies as a plausible mechanism for the catalytic effect. We have not measured the Coulombic yield of the process because the $[CpMoCl_2(PMe_3)_2]^+$ complex is decomposed by excess chloride as shown above.

Catalyzed Halide Exchange by Electrochemical Oxidation. Further and more direct evidence for the occurrence of the catalytic cycle illustrated in Scheme I is provided by a cyclic voltammetric experiment of $CpMoI_2(PMe_3)_2$ in the presence of Cl^- under conditions of uncatalyzed halide exchange (in the presence of Zn/Cu). Figure 3 illustrates selected runs. When the temperature is maintained low (−37 °C) and the scan speed relatively high (500 mV/s), the voltammogram shows only a practically reversible oxidation wave for $CpMoI_2(PMe_3)_2$ and the reversible wave of the internal standard. Underneath the wave of the internal standard some activity due to an uncharacterized process is observed, which was not present before the addition of Cl^-, but significant amounts of free I^- are not formed under these conditions. When the scan speed is lowered to 50 mV/s, a peak labeled I slightly increases. This peak is due to an oxidation process of the I^- ion, as shown by an independent study of PPN^+I^- under the same conditions. This peak is yet more evident at room temperature, especially at the lowest scan speed. Obviously, past the oxidation wave of the diiodide complex, the 16-electron diiodide cation which is formed on the electrode surface undergoes halide exchange generating free iodide. Exchange, on the other hand, does not occur significantly in the bulk as shown by EPR monitoring. Other features observed in the room-temperature scans are the decrease of the return wave associated with the reduction of the diiodide cation to the neutral complex and the appearance of several new features, labeled A–C. The reduction wave A occurs at ca. 120 mV to the negative direction of the reduction of $[CpMoI_2(PMe_3)_2]^+$, which is the potential expected for the reduction of $[CpMoCl_2(PMe_3)_2]^+$ ion to the corresponding neutral complex in the presence of excess chloride ions. Processes B and C correspond to the identically labeled processes observed during the electrochemical investigation of $CpMoCl_2(PMe_3)_2$ in the presence of Cl^- (see above) and shown in Figure 2. Thus, there is evidence for the formation of the $[CpMoCl_2(PMe_3)_2]^+$ ion, in addition to I^-, following the electrochemical oxidation of $CpMoI_2(PMe_3)_2$. There is no sign of the presence of the $[CpMoClI(PMe_3)_2]^{n+}$ (n = 0, 1) system in the cyclic voltammograms in Figure 2, in agreement with a much faster second halide substitution in the oxidized manifold (see Discussion).

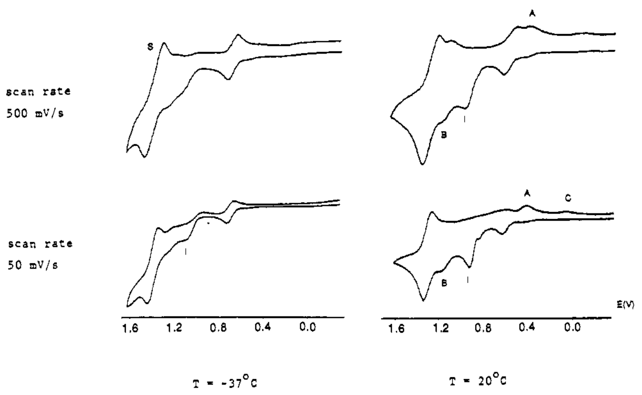

Figure 3. Cyclic voltammetric scans of mixtures of $CpMoI_2(PMe_3)_2$ and (PPN)Cl. Solvent = CH_2Cl_2; supporting electrolyte = n-Bu_4NPF_6; reference electrode = Ag/AgCl; working electrode = 3.5 mm^2 flat surface Pt; S = acetylferrocene (internal standard).

Discussion

The results obtained in this study prove that 1-electron oxidation catalyzes the exchange of iodide with chloride in the 17-electron $CpMoI_2(PMe_3)_2$ complex through the formation of the corresponding 16-electron $[CpMoI_2(PMe_3)_2]^+$ complex (Scheme I). Thus, this system provides the first example of an ETC-catalyzed ligand substitution where exchange is faster in the even-electron manifold than in the odd-electron manifold. In all the other ETC-catalyzed ligand substitution processes reported to date, substitution in a saturated complex is accelerated by either oxidation to a 17-electron species or by reduction to a 19-electron species.[9]

This observed reversal of reactivity (even faster than odd) has to do with several fortunate occurrences. Ligand substitution in the 17-electron system is slow.[1] Classical organometallic 17-electron radicals are typically fast in ligand substitution because the low-energy HOMO can establish a positive interaction with the incoming ligand in an associative mechanism, thus leading to a very low activation barrier. Our 17-electron system is sterically crowded and has a high-energy HOMO, and thus an associative mechanism is disfavored sterically and electronically.[1] The second fortunate occurrence is that, again due to the high-energy HOMO, the radical prefers to be oxidized rather than reduced and it does so reversibly; that is, the 16-electron product is stable. This stability may be at least in part due to the high-spin configuration. The third occurrence is that, in the presence of excess halide, the 16-electron dihalide cation, presumably because of the stringent steric situation, is either the preferred ground state (see the salt nature of the "triiodide" complex) or at most a low-energy intermediate. If a neutral 18-electron configuration were strongly favored, then large activation barriers for ligand substitution would exists also in the even-electron manifold. In addition to the above considerations, the positive charge that is present in the oxidized complex certainly favors attraction of the incoming halide and thus introduces a Coulombic bias for faster substitution in the oxidized system with respect to the neutral system, although analogous systems show only a mild acceleration of the second-order rates for the substitution by Cl^- due to increase in substrate positive charge.[16] It is also interesting to observe that when the steric bulk is increased further by going to the sterically more encumbered Cp* system, the exchange in the oxidized system (which must be associative) is strongly inhibited and the necessary conditions for ETC substitution are not met. The observed rates of exchange of iodide by chloride presented here and in the parallel investigation of the noncatalyzed exchange[1] can be summarized as follows:

$$\begin{array}{ccc} CpMoI_2(PMe_3)_2 & << & Cp^*MoI_2(PMe_3)_2 \\ \overset{\wedge}{\wedge} & & \overset{\vee}{\vee} \\ [CpMoI_2(PMe_3)_2]^+ & >> & [Cp^*MoI_2(PMe_3)_2]^+ \end{array}$$

The mechanistic studies of this catalytic effect are clouded by the decomposition of one of the key intermediates of the catalytic cycle, $[CpMoCl_2(PMe_3)_2]^+$, in the presence of excess chloride. Nevertheless, the validity of the argument put forward in the title of this paper is not undermined. This decomposition is one of the reasons for the observed decreased catalytic efficiency as the reaction progresses. Another reason for a gradual decrease of catalytic efficiency is the endoergic electron transfer step (reverse of eq 3). The concentration of $CpMoI_2(PMe_3)_2$ is maximal at the beginning of the reaction and gradually decreases as the exchange processes, whereas the reverse is true for the concentration of $CpMoCl_2(PMe_3)_2$. Thus, from equilibrium 3, the $[CpMoCl_2(PMe_3)_2]^+/[CpMoI_2(PMe_3)_2]^+$ ratio, which is already large at the beginning of the experiment, will become greater and greater as the exchange reaction progresses. In addition to this factor, the equilibrium between $[CpMoCl_2(PMe_3)_2]^+$ and its adduct with Cl^- diminishes even further the effective concentration of $[CpMoI_2(PMe_3)_2]^+$ and therefore the catalytic efficiency. The comparison of the $CpMoX_3(PMe_3)_2$ (X = Cl, I) compounds is interesting. Both complexes are sterically congested, but although the triiodide achieves steric relief by expelling an iodide ion and forming a salt, the trichloride complex prefers to expel a phosphine ligand. This difference is probably due to the better π-donor properties of the chloride ion with respect to the iodide ion.

We can summarize the observations made in this paper and our parallel study of the uncatalyzed exchange[1] in the reaction coordinate plot illustrated in Figure 4. Exchange of I^- with Cl^- in the 17-electron diiodide complex is difficult as shown by the high activation barriers represented by ΔG_7 and ΔG_9.[1] We also know from an independent equilibrium study[6] that $CpMoClI(PMe_3)_2$ is stabilized by 0.35 kcal with respect to the average energy of the two homogeneous halide complexes. $(\Delta G_3 + \Delta G_5) - (\Delta G_8 + \Delta G_{10})$, that is the free energy of eq 3, can be calculated from the half-way potentials determined in the cyclic voltammetric studies[2a] as -2.30 kcal.

The activation barriers for exchange in the oxidized system are smaller than those involved with the neutral system. Steric considerations are important to rationalize the trend in the exchange rates. The diiodide 16-electron complex has no tendency to coordinate a third iodide ion as shown by UV/visible and NMR studies and by the crystal structure of $[CpMoI_2(PMe_3)_2]^+I^-$.[10] When the steric bulk is reduced by replacing iodides with chlorides, the energy of a hypothetical 18-electron complex will presumably come closer to that of the salt with the 16-electron cation. Thus, ΔG_1 will be large and it is expected that $\Delta G_1 > \Delta G_2 > \Delta G_4 > \Delta G_6$, the last being a negative number. ΔG_2 is estimated to be about 12 kcal from the semiquantitative study of the stoichiometric halide exchange on the 16-electron $[CpMoI_2(PMe_3)_2]^+$ complex. The value of ΔG_2 must be greater than that of ΔG_4 because there is no accumulation of significant amounts of the mixed-halide neutral complex under catalytic conditions. The very fast exchange from pure $CpMoClI(PMe_3)_2$ under catalyzed conditions is the combined result of the lower activation barrier for exchange in the oxidized system and the lower difference in potentials for the endoergic electron transfer step, thus resulting in a less unfavorable equilibrium constant with respect to that of eq 3 and, consequently, a greater catalytic turnover.

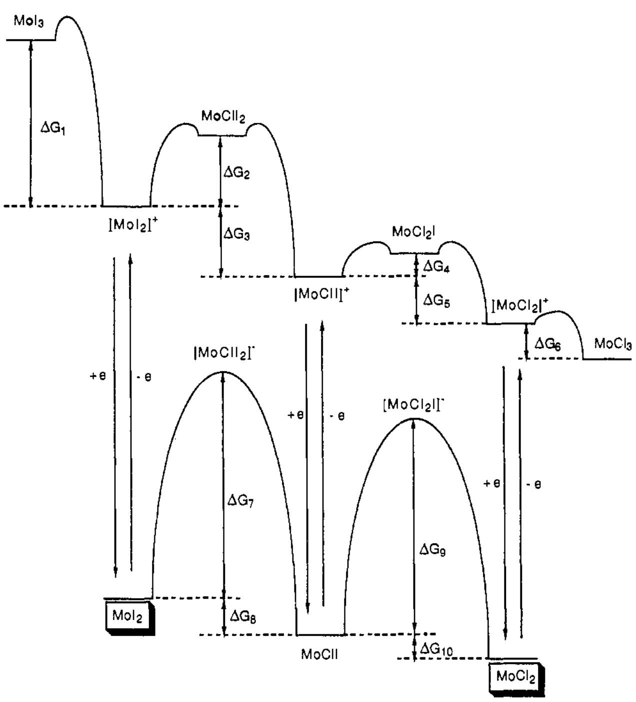

Figure 4. Reaction coordinate for the catalyzed and uncatalyzed halide substitution reaction on $CpMoI_2(PMe_3)_2$ with Cl^-.

The intermediates or transition states for halide exchange on the oxidized system are not necessarily 18-electron complexes. They might also be 16-electron complexes with the ring slipped to an η^3 coordination. If these complexes have an 18-electron configuration, a kinetic barrier to halide dissociation is predicted since the system changes spin state during this transformation and these complexes may be intermediates along the coordination pathway as represented in Figure 4. In case these complexes have a ring-slipped, 16-electron configuration, they might as well be located on maxima of the reaction coordinate; i.e., they might be mere transition states. However, NMR evidence points toward a diamagnetic trichloride complex, $CpMoCl_3(PMe_3)_2$, thus presumably having a 18-electron configuration, and the structurally characterized analogous $CpMoCl_3L_2$ complexes [L_2 = dppe,[12] dmpe;[13c] L = $P(OCH_2)_3CEt$[14]] have an η^5-Cp ligand and an 18-electron configuration.

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