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$Cp^{\star}$Mo-halide chemistry. Rapid halide scrambling during the conproportionation of $Cp^{\star}_2Mo_2Y_4$ (Y = Cl, Br, I) and $Cp^{\star}MoX_4$(X = Cl, Br): a paramagnetic ^{1}H NMR study *

Heinz-Bernhard Kraatz and Rinaldo Poli

Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742 (USA)

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Abstract

The reaction of the d^1 four-legged piano-stool complexes $Cp^{\star}MoX_4$ (X = Cl, Br) with the d^3–d^3 binuclear complexes $Cp^{\star}_2Mo_2Y_4$ (Y = Cl, Br, I) results in electron transfer and formation of the salts $[Cp^{\star}_2Mo_2Y_2]^+[Cp^{\star}MoX_4]^-$. Solutions of $[Cp^{\star}_2Mo_2I_4]^+[Cp^{\star}MoX_4]^-$ (X = Cl, Br) are stable indefinitely in chlorocarbon solvents. However, for the $Cp^{\star}_2Mo_2Y_4/Cp^{\star}MoX_4$ (Y, X = Cl, Br) systems, conversion to the complexes $Cp^{\star}_2Mo_2Y_{6-n}X_n$ is observed together with halide exchange reactions between the cation and the anion. The formation of $Cp^{\star}_2Mo_2Y_{6-n}X_n$ and the halide exchange are postulated to proceed via a common associative intermediate. The rate of formation of $Cp^{\star}_2Mo_2Y_{6-n}X_n$ depends mostly on the Lewis acidity of the cation $[Cp^{\star}_2Mo_2Y_4]^+$, which varies in the order $[Cp^{\star}_2Mo_2Cl_4]^+ \gg [Cp^{\star}_2Mo_2Br_4]^+ \gg [Cp^{\star}_2Mo_2I_4]^+$, and has little dependence on the nature of X.

Key words: Molybdenum; Conproportionation; Cyclopentradienyl; Halide; Paramagnetism; Nuclear magnetic resonance

1. Introduction

The development of transition metal cyclopentadienyl chemistry is mostly due to the pioneering work of Fischer and Wilkinson. Group 6 metals have had a prominent role in this development, since the discovery and early investigations of chromocene [1]. Compounds that contain halide ligands in addition to the Cp ring are particularly useful as synthons to other organometallic systems [2]. The first chromium compounds of this type, $CpCrX_2$ (X = Cl, Br, I), were reported by Fischer *et al.* in 1963 [3], whereas $CpMoCl_4$ was reported only a year later by Cousins and Green [4]. Within the molybdenum system, cyclopentadienyl halides of the metal in the oxidation state IV have remained undeveloped until recently when we reported convenient syntheses of $CpMoX_3$ (X = Cl, Br, I) [5] and detailed studies of the more soluble $Cp^{\star}$ systems [6–8].

Unlike most of the previously reported cyclopentadienylmetal halide compounds [2], the $Cp^{\star}Mo^{IV}$ halide system gives rise to a complex solution behavior whose elucidation has required detailed electrochemical and paramagnetic ^{1}H NMR investigations. In brief, the equilibria illustrated in eqns. (1) and (2) are established for this system. For X = Cl, both eqn. (1) and (2) are completely shifted to the left ($Cp^{\star}_2Mo_2Cl_6$ is a stable compound in the solid state and in solution) [6]. For X = Br, all species participating to equilibrium (1) are observable, whereas eqn. (2) is shifted completely to the left [8b]. Finally, for X = I, eqn. (2) is shifted completely to the right (although $Cp^{\star}_2Mo_2I_6$ has been isolated under kinetically controlled conditions) whereas eqn. (1) is not established because $Cp^{\star}MoI_4$ is able to oxidize its own I^- ligands to afford the products of eqn. (2) [8b].

$$2Cp^{\star}_2Mo_2X_6 \rightleftharpoons [Cp^{\star}_2Mo_2X_4]^+ + [Cp^{\star}MoX_4]^- + Cp^{\star}MoX_4 \quad (1)$$

$$2Cp^{\star}_2Mo_2X_6 \rightleftharpoons 2[Cp^{\star}_2Mo_2X_4]^+ + X^- + X_3^- \quad (2)$$

Correspondence to: Professor R. Poli.

* Herrn Prof. Dr. h.c. mult. E.O. Fischer zum 75. Geburtstag gewidmet.

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The following new complexes have been isolated during our studies: $Cp^*_2Mo_2X_6$ (X = Cl, Br, I), $[Cp^*_2Mo_2X_4]^+$ (X = Br, I), $[Cp^*MoX_4]^-$ (X = Cl, Br, I) and Cp^*MoBr_4 and several of these have been crystallographically characterized either by themselves ($Cp^*_2Mo_2Cl_6$ [6] and $Cp^*_2Mo_2Br_6$ [8b]), in combination with other ions ($[Cp^*_2Mo_2I_4]I_3$ and $[NMe_3Ph][Cp^*MoI_4]$) [8] or in combination with each other ($\{[Cp^*_2Mo_2Br_4]^+[Cp^*MoBr_4]^-\}_2 \cdot Cp^*MoBr_4$) [7].

A study of the reaction between $Cp^*_2Mo_2X_4$ and Cp^*MoX_4 for X = Cl and Br proved rather informative. In both cases, the salt $[Cp^*_2Mo_2X_4]^+[Cp^*MoX_4]^-$ is immediately formed. However, the subsequent transformations are different. The chloride-containing salt rapidly rearranges to a mixture of $Cp^*_2Mo_2Cl_6$ and $Cp^*_2Mo_2Cl_5$ (eqn. (3)). In the presence of an additional equivalent of Cp^*MoCl_4, the pentachlorodimolybdenum complex is further oxidized to the Mo^{IV} product $Cp^*_2Mo_2Cl_6$. For the bromide system, on the other hand, the initial salt is stable (a hypothetical equilibrium (3) is shifted completely to the left). However, addition of more Cp^*MoBr_4 produces the mixture of equilibrium (1). The difference between chloride and bromide systems can be due either to a greater Lewis acidity of $[Cp^*_2Mo_2X_4]^+$ in the order Cl > Br, or to a greater Lewis acidity of $Cp^*_2Mo_2X_6$ in the opposite order (see eqn. (3)).

$$[Cp^*_2Mo_2X_4]^+ + [Cp^*MoX_4]^+ \rightleftharpoons Cp^*_2Mo_2X_5 + 1/2Cp^*_2Mo_2X_6 \quad (3)$$

In order to better delineate the factors determining this difference, we have examined the reactivity of the mixed-halide salts $[Cp^*_2Mo_2Y_4][Cp^*MoX_4]$ (Y = Cl, Br, I; X = Cl, Br), that were generated by electron transfer from the corresponding neutral precursors, and report the results of our findings here. A strong dependence of the rate of their transformation on the nature of Y and a much smaller dependence on the nature of X determine the importance of the Lewis acidity of the cation. During these investigations, we also uncovered an unexpected rapid halide scrambling process, the mechanistic implications of which are examined and discussed.

2. Experimental details

2.1. General

Unless otherwise stated, all manipulations were carried out under a nitrogen atmosphere using standard Schlenk line techniques. Solvents were purified by conventional techniques and distilled under nitrogen prior to use. NMR spectra were obtained using Bruker WP200, AF200 and AMX400 spectrometers and referenced to the residual proton resonance in $CDCl_3$. Integrated peak intensities were analyzed with respect to the integrated peak intensity of the residual proton resonance of the NMR solvent $CDCl_3$, which was arbitrarily fixed. Cp^*MoCl_4 [9], Cp^*MoBr_4 [7], $Cp^*_2Mo_2Cl_4$ [6], $Cp^*_2Mo_2Br_4$ [7] and $Cp^*_2Mo_2I_4$ [8b] were prepared according to published procedures.

2.2. ^1H NMR investigation of the interaction between $Cp^*_2Mo_2Y_4$ with Cp^*MoX_4 (Y = Cl, Br, I; X = Cl, Br)

All reactions were carried out in a similar manner. In the following a detailed description is given for the reaction where X = Cl and Y = Br.

2.2.1. Reaction of $Cp^*_2Mo_2Cl_4$ with Cp^*MoBr_4 (1:2)

$Cp^*_2Mo_2Cl_4$ (17 mg; 0.028 mmol) was dissolved in 10 ml of degassed $CDCl_3$ to give a red-brown solution. Upon addition of solid Cp^*MoBr_4 (31 mg; 0.056 mmol) to the cooled solution (0°C), the reaction mixture turned brown immediately. An aliquot of the reaction solution was transferred into a nitrogen-flushed thin-walled 5 mm o.d. NMR tube *via* a cannula and then flame-sealed. The reaction was immediately monitored by ^1H NMR spectroscopy. ^1H-NMR (δ, 293 K, $CDCl_3$): 5.58, 4.99, 4.63, 4.28, 1.40, 1.34, −3.33, −3.89, −4.08, −4.52, −4.82, −5.18, −5.39, −5.65, −5.92, −6.08, −6.41, −17.4, −19.2. The assignment and the time evolution of the relative intensities of these resonances is described in detail in Section 3.

2.2.2. Reaction of $Cp^*_2Mo_2Br_4$ with Cp^*MoBr_4 in various molar ratios

A reaction in a 1:2 ratio was set up with $Cp^*_2Mo_2Br_4$ (31 mg; 0.040 mmol) and Cp^*MoBr_4 (44 mg; 0.080 mmol) in 10 ml of $CDCl_3$. The time evolution of this reaction has been previously described [8b]. After *ca.* 7 h an equilibrium is reached and no further changes in the spectrum are observed. An initial rate of $4.3 \cdot 10^{-8}$ mol l^{-1} s^{-1} was measured for this reaction at 20 ± 1°C from the time evolution of the integrated intensity of the $Cp^*_2Mo_2Br_6$ product. The final ratio between $[Cp^*_2Mo_2Br_4]^+$ and $Cp^*_2Mo_2Br_4$ was 4.8 ± 0.2, giving equilibrium concentrations of $3.62 \cdot 10^{-3}$ M for $[Cp^*_2Mo_2Br_4]^+$ (and consequently also for $[Cp^*MoBr_4]^-$and Cp^*MoBr_4, see eqn. (1)) and $0.76 \cdot 10^{-3}$ M for $Cp^*_2Mo_2Br_6$. A second experiment was carried out with a 1:3 ratio and a third experiment with a 2:3 ratio of Mo^{III} and Mo^V. The initial rates measured for these two runs were $3.4 \cdot 10^{-8}$ mol l^{-1} s^{-1} and $6.2 \cdot 10^{-8}$ mol l^{-1} s^{-1}, respectively.

2.2.3. Reaction of $Cp^*_2Mo_2Br_4$ with Cp^*MoCl_4 (1:2)

$Cp^*_2Mo_2Br_4$ (9 mg; 0.012 mmol); Cp^*MoCl_4 (9 mg; 0.024 mmol); 5 ml of $CDCl_3$. ^1H NMR (δ, 293 K, CDCl$_3$): $+3.95$ ($w_{1/2} = 108$ Hz, $[\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{Br}_4]^+$), -3.25, -3.62, -3.87, -4.44, -4.65, -5.19, -5.36 (see Section 3 for details on the time evolution of these resonances). The resonance intensities did not further change after *ca.* 2 days from the start of the reaction. From the monitoring of the growth of the $\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{Br}_{6-n}\mathrm{Cl}_n$ resonances (see Section 3), an initial rate of $2.1 \cdot 10^{-8}$ mol l^{-1} s^{-1} was measured for this reaction at 20 ± 1°C. The final ratio between $[\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{Br}_4]^+$ and the combined $\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{Br}_{6-n}\mathrm{Cl}_n$ is 2.4 ± 0.2.

2.2.4. Reaction of $Cp^*_2Mo_2I_4$ with Cp^*MoCl_4 (1:2)

$\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{I}_4$ (26 mg; 0.027 mmol); $\mathrm{Cp}^*\mathrm{MoCl}_4$ (21 mg; 0.056 mmol). ^{1}H NMR (δ, 293 K, CDCl$_3$): 2.32 (br, $w_{1/2} = 29$ Hz, $[\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{I}_4]^+$), -14.2 (br, $w_{1/2} = 164$ Hz, $[\mathrm{Cp}^*\mathrm{MoCl}_4]^-$). This spectrum did not change further.

2.2.5. Reaction of $Cp^*_2Mo_2I_4$ with Cp^*MoBr_4 (1:2)

$\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{I}_4$ (21 mg; 0.022 mmol); $\mathrm{Cp}^*\mathrm{MoBr}_4$ (21 mg; 0.038 mmol). ^{1}H NMR (δ, 293 K, CDCl$_3$): 2.55 ($w_{1/2} = 64$ Hz, $[\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{I}_4]^+$), -19.2 ($w_{1/2} = 178$ Hz, $[\mathrm{Cp}^*\mathrm{MoBr}_4]^-$). This spectrum did not change further.

3. Results

The stoichiometric oxidation of the binuclear Mo$^{\mathrm{III}}$ complexes $\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{Y}_4$ (Y = Cl, Br, I) by solutions of the four-legged piano-stool Mo$^{\mathrm{V}}$ complexes $\mathrm{Cp}^*\mathrm{MoX}_4$ (X = Cl, Br) in CDCl$_3$ have been monitored by paramagnetic ^{1}H NMR spectroscopy. By analogy with the previously investigated all-chloro and all-bromo reactions, the mixed-halogen reactions also result in an immediate electron transfer to give the complex salts $[\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{Y}_4]^+[\mathrm{Cp}^*\mathrm{MoX}_4]^-$ (X = Cl, Br; Y = Cl, Br, I) according to eqn. (4).

$$\mathrm{Cp}^*_2\mathrm{Mo}_2^{\mathrm{III}}\mathrm{Y}_4 + \mathrm{Cp}^*\mathrm{Mo}^{\mathrm{V}}\mathrm{X}_4 \longrightarrow \left[\mathrm{Cp}^*_2\mathrm{Mo}_2^{\mathrm{III/IV}}\mathrm{Y}_4\right]^+\left[\mathrm{Cp}^*\mathrm{Mo}^{\mathrm{IV}}\mathrm{X}_4\right]^- \quad (4)$$

The Me-groups of the Cp* ligand are valuable spectroscopic probes. The ^{1}H NMR resonances of the $[\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{Y}_4]^+$ and $[\mathrm{Cp}^*\mathrm{MoX}_4]^-$ ions have been previ-

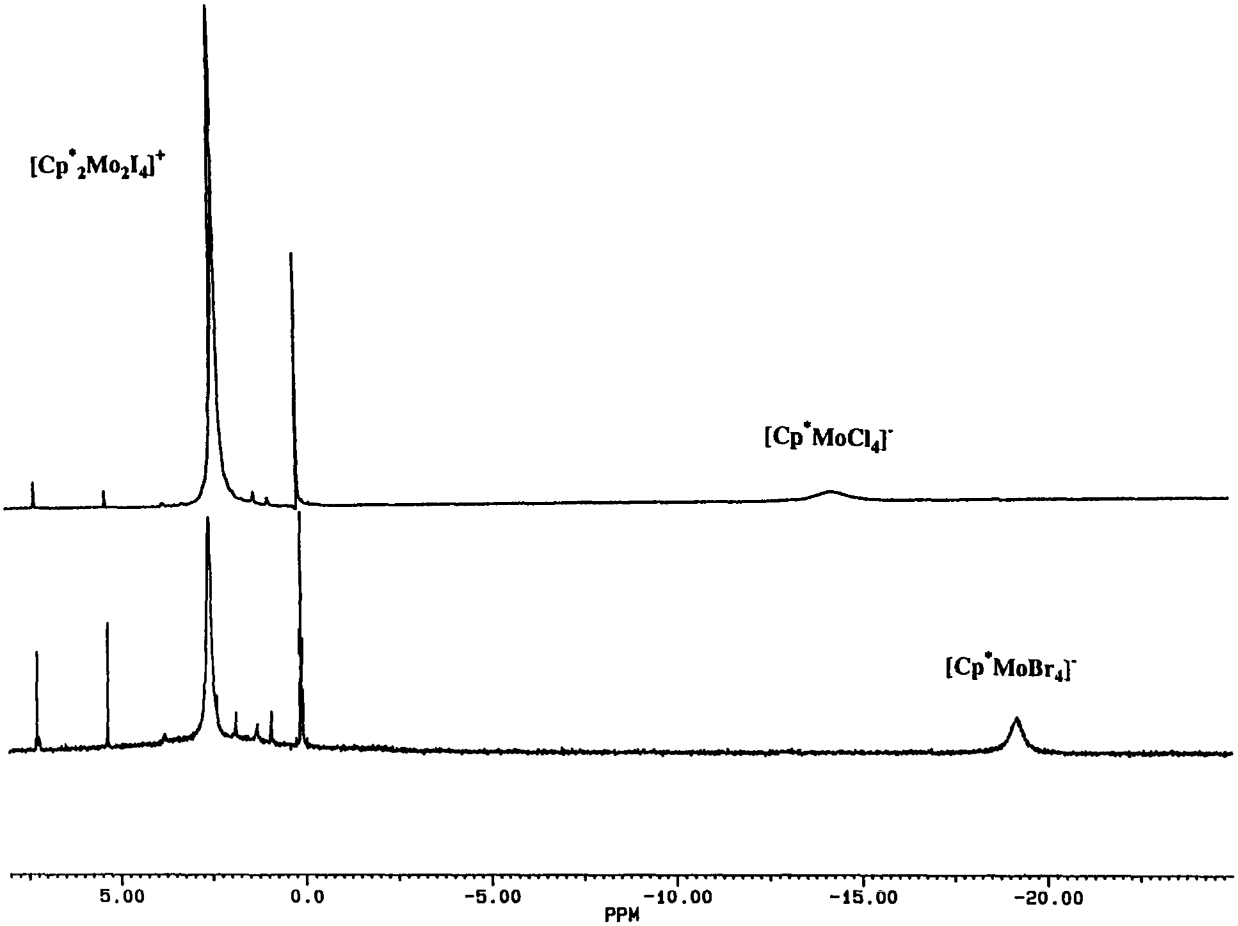


Fig. 1. The ^{1}H NMR obtained from the reactions: (top) $\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{I}_4 + \mathrm{Cp}^*\mathrm{MoCl}_4$; (bottom) $\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{I}_4 + \mathrm{Cp}^*\mathrm{MoBr}_4$.

ously reported [6–8]. For the mixed-valence $\mathrm{Mo^{III}}$–$\mathrm{Mo^{IV}}$ cations $[\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{Y}_4]^+$ (Y = Cl, Br, I), broad signals are observed downfield of tetramethylsilane (TMS). The shielding increases in the order Cl < Br < I (δ + 6.0 for $[\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{Cl}_4]^+$ [6], +4.4 − 4.0 for $[\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{Br}_4]^+$ [7], and 2.7–2.5 for $[\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{I}_4]^+$ [8]). The exact position of the resonances depends on the nature of the other paramagnetic species present in solution. The anions $[\mathrm{Cp^*MoX_4}]^-$ (X = Cl, Br) exhibit very broad singlets at much higher frequency with line widths of 100–200 Hz (δ −13 to −14 for $[\mathrm{Cp^*MoCl_4}]^-$ and −18 to −19.5 for $[\mathrm{Cp^*MoBr_4}]^-$).

3.1. *The reaction between* $\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{I}_4$ *and* $\mathrm{Cp^*MoX_4}$ *(X = Cl, Br)*

The reactions of $\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{I}_4$ with $\mathrm{Cp^*MoCl_4}$ and with $\mathrm{Cp^*MoBr_4}$ result in the formation of characteristic dark green solutions indicating the presence of $[\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{I}_4]^+$ [8b]. The NMR of these solutions show the resonances due to $[\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{I}_4]^+$ and the respective anion when the reactions are carried out in 1:1 ratios (Fig. 1). When a 1:2 ratio is utilized, the spectrum of the $\{[\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{I}_4]^+[\mathrm{Cp^*MoBr_4}]^- + \mathrm{Cp^*MoBr_4}\}$ solution is identical to that shown in Fig. 1, whereas that of the $\{[\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{I}_4]^+[\mathrm{Cp^*MoCl_4}]^- + \mathrm{Cp^*MoCl_4}\}$ solution shows only the resonance of the cation. This difference is attributed to the faster self-exchange rate between $[\mathrm{Cp^*MoX_4}]^-$ and excess $\mathrm{Cp^*MoX_4}$ in the order Cl > Br. Since the $S = 1/2$ $\mathrm{Mo^V}$ $\mathrm{Cp^*MoX_4}$ materials have relatively long electronic relaxation times giving rise to sharp EPR resonances and, as a consequence, to very broad (unobserved) ^{1}H NMR lines, a rapid self-exchange process results in the ^{1}H NMR resonance of the $\mathrm{Mo^{IV}}$ anion being washed out. The slow self-exchange of the $[\mathrm{Cp^*MoBr_4}]^-/\mathrm{Cp^*MoBr_4}$ couple was noted previously [8b] and attributed to the large difference observed in the Mo–Br bond length between the two complexes.

Both these solutions are stable and their ^{1}H NMR spectra do not change over a period of 2 days at room temperature. Thus, after electron transfer to form $[\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{I}_4]^+[\mathrm{Cp^*MoX_4}]^-$ (X = Cl, Br), no further transformation is induced by additional $\mathrm{Cp^*MoX_4}$ under these conditions.

3.2. *The reaction between* $\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{Cl}_4$ *and* $\mathrm{Cp^*MoX_4}$ *(X = Cl, Br)*

The two reactions described in this section are at the opposite end of the scale with respect to those described in the previous section. The reaction with X = Cl has already been previously reported [6], and a summary of the results has been given in the Introduction. Compound $\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{Cl}_6$ shows a broad ^{1}H NMR resonance at δ −3.88 ($w_{1/2}$ *ca.* 60 Hz), whereas the pentachloro-complex $\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{Cl}_5$ shows a broad signal at δ 1.34 ($w_{1/2}$ *ca.* 30 Hz).

Significant ^{1}H NMR spectra for the reaction with X = Br are shown in Fig. 2. The first important observation is that the reaction does not stop at the formation of $[\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{Cl}_4]^+[\mathrm{Cp^*MoBr_4}]^-$, but follow-up

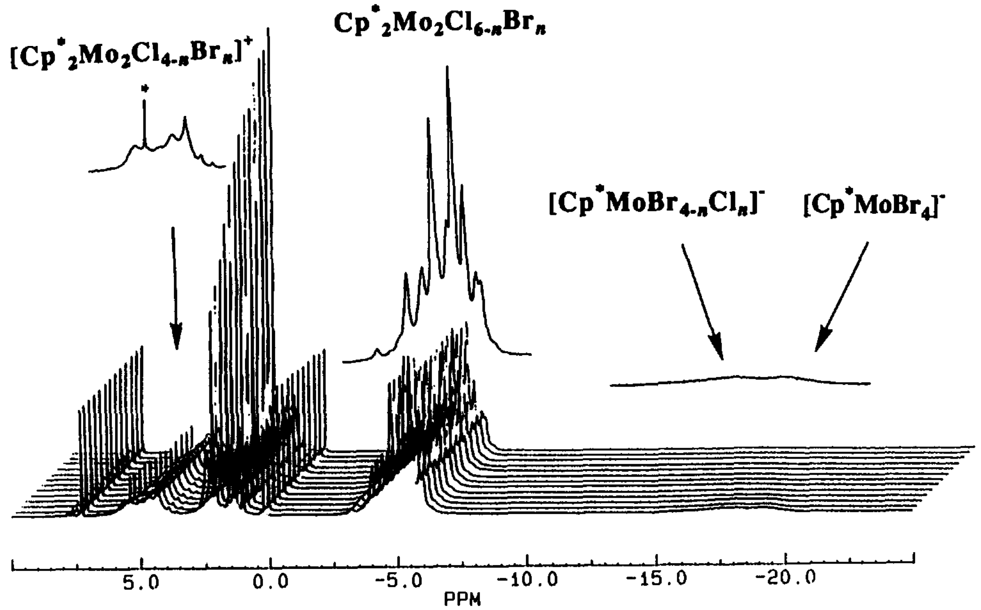
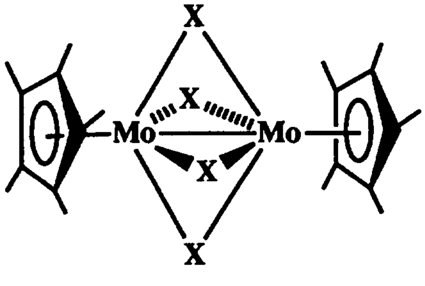


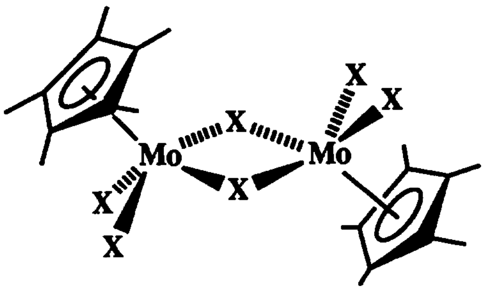
Fig. 2. ^{1}H NMR monitoring of the reaction of $\mathrm{Cp}^*_2\mathrm{Mo}_2\mathrm{Cl}_4 + 2\mathrm{Cp^*MoBr_4}$ in $\mathrm{CDCl_3}$ at room temperature. Spectra are recorded in 5 min time intervals. * denotes $\mathrm{CH_2Cl_2}$ impurity.

processes occur very rapidly. The initial spectrum exhibits resonances in regions characteristic for $[Cp^*_2Mo_2Cl_{4-n}Br_n]^+$ (δ 4 to 6), $Cp^*_2Mo_2Cl_{5-n}Br_n$ (δ 1.40 and 1.34, $Cp^*_2Mo_2Cl_{6-n}Br_n$ (δ −3 to −7), and $[Cp^*MoBr_{4-n}Cl_n]^-$ (δ −17.4 and −19.2). The complexity of this spectrum indicates that a fast halogen scrambling reaction between cation and anion occurs before further rearrangement processes take place. According to the reported shielding trend for the $[Cp^*\text{-}MoX_4]^-$ anions, the signal at δ −19.2 is assigned to $[Cp^*MoBr_4]^-$, whereas the signal at δ −17.4 is likely due to the mixed halide species $[Cp^*MoBr_3Cl]^-$. These resonances disappear from the spectrum rather rapidly. The signals in the δ +4 to +6 region are assigned to different $[Cp^*_2Mo_2Cl_{4-n}Br_n]^+$ species, with the more chlorine-rich complexes having the more downfield resonances. Given the symmetry of the cation (structure I) [7,8], six possible resonances are expected for the Cp* protons (Cl_4, $ClBr_3$, *cis*- and *trans*-Cl_2Br_2, $ClBr_3$, and Br_4) and at least four resonances are clearly observed. Two of these (the most downfield shifted ones, i.e., those assigned to the chlorine-rich species) disappear rapidly, whereas the others are more persistent and are still observed after 1 h. It is interesting to observe in Fig. 2 that the disappearance of chloride-rich (and corresponding growth of bromide-rich) $[Cp^*_2Mo_2Y_4]^+$ species parallels the disappearance of the bromide-rich $[Cp^*MoX_4]^-$ species but no chloride-rich anion resonance appears. As pointed out in section 3.1, the rate of $[Cp^*MoX_4]^-/Cp^*MoX_4$ self-exchange appears to increase as more chloride replaces bromide in this system, thus we propose that line broadening by self-exchange is responsible for the inability to observe the resonances of $[Cp^*MoBr_{4-n}Cl_n]^-$ species with $n \geq 2$ in the advanced phases of the reaction.



I

For the $Cp^*_2Mo_2Cl_{6-n}Br_n$ systems (δ −3 to −7 region) at least 11 resonances are distinctly observed. Given the geometry of the system (structure II) a total of 24 distinct complexes are possible when both bridging and terminal positions are considered (one Cl_6, two Cl_5Br, six Cl_4Br_2, six Cl_3Br_3, six Cl_2Br_4, two $ClBr_5$ and one Br_6) and a few of these are asymmetric, giving rise to two rather than one Cp* resonance each. However, only the complexes with $n \geq 2$ are expected to form in this reaction. Again, the more downfield-shifted resonances are assigned to the Cl-richer systems, since the resonances for the all-chloro and all-bromo complexes are reported at δ −3.9 and δ −5.7, respectively [6,8b]. No significant change of the relative intensities for these resonances is observed as the reaction progresses.



II

The resonances at δ 1.40 and δ 1.34 are assigned to the $Cp^*_2Mo_2Cl_{5-n}Br_n$ species, presumably with $n = 1$ and 2. No significant change in their relative intensities is noticeable as the reaction progresses. The lack of resonances due to bromide-rich pentahalide dimers can be rationalized with a decreased rate and less favorable thermodynamics for the halide transfer equilibrium (eqn. (3), see section 4). Finally, a sharp single resonance at δ 1.99 is observed to increase throughout the experiment. By analogy with the behavior of the all-chloro and all-bromo systems [6,8b], this resonance is attributed to a by-product which probably derives from the slow reduction of minor hydrolytic impurities in the Cp^*MoX_4 materials.

3.3. The reaction between $Cp^*_2Mo_2Br_4$ and Cp^*MoX_4 ($X = Cl$, Br)

The reaction between $Cp^*_2Mo_2Br_4$ and Cp^*MoBr_4 has been reported earlier and the relative results have been summarized in the Introduction (eqn. (5)) [8b]. We have now carried out a kinetic and equilibrium analysis of this transformation. Measurement of the equilibrium concentrations by ^1H NMR establishes $K = 12\ mol^{-1}\ l$ for equilibrium (5). The initial rate of formation of the product $Cp^*_2Mo_2Br_6$ does not depend on the initial concentration of the Mo^V complex but increases when the initial concentration of the salt is increased. This establishes that the Mo^V complex is not involved in the slow step during the forward process.

$$[Cp^*_2Mo_2Br_4]^+ + [Cp^*MoBr_4]^- + Cp^*MoBr_4 \rightleftharpoons 2Cp^*_2Mo_2Br_6 \quad (5)$$

For the mixed-halide reaction (X = Cl) a dark brown solution containing the salt $[Cp^*_2Mo_2Br_4]^+[Cp^*Mo\text{-}$

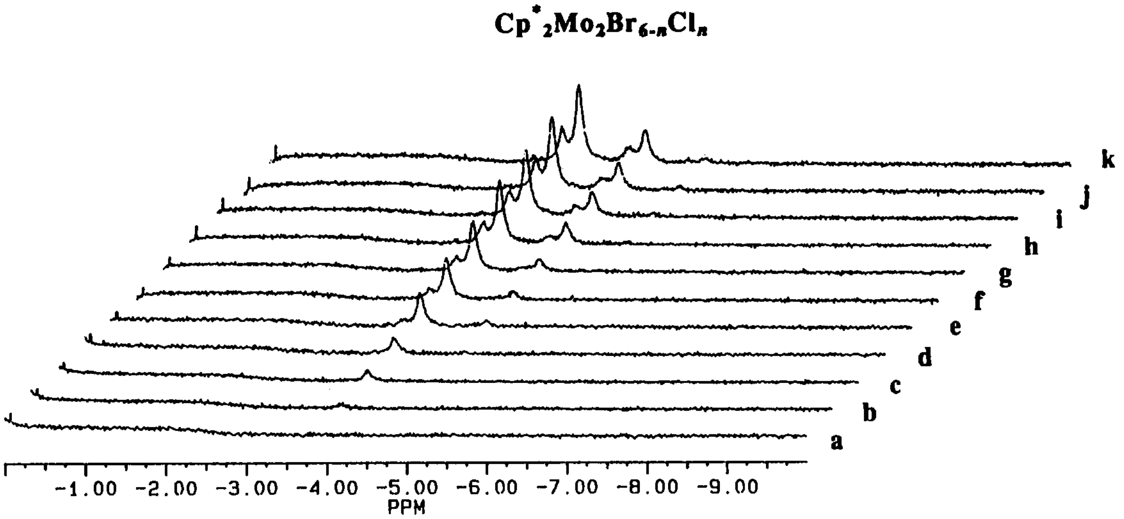


Fig. 3. ^{1}H NMR monitoring of the reaction of Cp$_2^*$Mo$_2$Cl$_4$ + 2Cp*MoBr$_4$ (CDCl$_3$, room temperature). The spectrum shows the Cp$_2^*$Mo$_2$Cl$_{6-n}$Br$_n$ region: (a) $t = 5$, (b) $t = 15$, (c) $t = 30$, (d) $t = 45$, (e) $t = 105$, (f) $t = 135$, (g) $t = 175$, (h) $t = 240$, (i) $t = 270$, (j) $t = 305$, (k) $t = 335$ min.

Cl$_4$]$^-$ and Cp*MoCl$_4$ in a 1:1 ratio, which is initially obtained by mixing Cp$_2^*$Mo$_2$Br$_4$ and Cp*MoCl$_4$ in a 1:2 ratio, changes approximately as slowly as the corresponding solution obtained for the all-bromo system. This solution shows the characteristic cation ^{1}H NMR resonance at δ 3.95. Contrary to the reaction with Cp*MoBr$_4$ described above, the resonance of the [Cp*MoCl$_4$]$^-$ anion is not observed if a second equivalent of Cp*MoCl$_4$ is present. However, this is again observed (δ −13.2) when the reaction is carried out in a 1:1 stoichiometry. This phenomenon may be attributed to a rapid self-exchange between Cp*MoCl$_4$ and the corresponding Mo^{IV} anion on the NMR time scale.

Figure 3 shows the progress of the ^{1}H NMR spectrum in the region of the Cp* resonances of Cp$_2^*$Mo$_2$Br$_{6-n}$Cl$_n$. The first change in the spectrum is noticeable after 15 min, when a peak appears at δ −3.87. After about 100 min, three more signals appear in the trihalide region (δ −3.62, −4.44, −4.65). Finally, after about 300 min, three more resonances appear at δ −3.25, −5.19, −5.36. At the same time, the concentration of [Cp$_2^*$Mo$_2$Br$_4$]$^+$ is decreasing. Complete consumption of [Cp$_2^*$Mo$_2$Br$_4$]$^+$ to form Cp$_2^*$Mo$_2$Cl$_{6-n}$Br$_n$ is not observed. An equilibrium was reached after 2 days between all species involved, with a final ratio between [Cp$_2^*$Mo$_2$Br$_4$]$^+$ and the combined Cp$_2^*$Mo$_2$Br$_{6-n}$Cl$_n$ of about 2.4:1. Although halide scrambling gives rise to Cp$_2^*$Mo$_2$Br$_{6-n}$Cl$_n$ species, no noticable chloride incorporation into the [Cp$_2^*$Mo$_2$Br$_4$]$^+$ cation was observed. This is in contrast to the Cp$_2^*$Mo$_2$Cl$_4$/Cp*MoBr$_4$ reaction system, where bromide incorporation into the cation was easily observable.

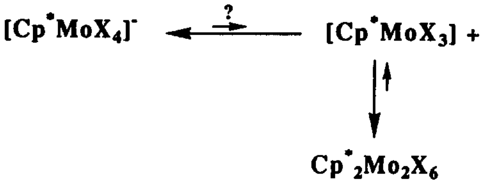
4. Discussion

4.1. ^{1}H NMR properties

The ^{1}H NMR resonances of the [Cp$_2^*$Mo$_2$Y$_{4-n}$X$_n$]$^+$, Cp$_2^*$Mo$_2$Y$_{5-n}$X$_n$, Cp$_2^*$Mo$_2$Y$_{6-n}$X$_n$, and [Cp*MoX$_{4-n}$Y$_n$]$^-$ are all broad and paramagnetically shifted because all these species are magnetically active. The [Cp$_2^*$Mo$_2$Y$_{4-n}$X$_n$]$^+$ (structure **I**) has a d^2–d^3 Mo$_2^{5+}$ core, which contains one unpaired electron [10]. No structural information is available for the Cp$_2^*$Mo$_2$Y$_{5-n}$X$_n$ system, but the d^2–d^3 configuration would lead in any case to a paramagnetic system with at least one unpaired electron. For the Cp$_2^*$Mo$_2$Y$_{6-n}$X$_n$ system (structure **II**), antiferromagnetic coupling between two $S = 1$ Mo^{IV} centers, leaving a substantial magnetic moment at room temperature, has been established for the all-chloro compound [6]. Finally, the [Cp*MoX$_4$]$^-$ complexes (X = Cl, Br) are mononuclear systems with a $S = 1$ ground state [6,8b].

4.2. The mechanism of Cp$_2^*$Mo$_2$Y$_{6-x}$X$_x$ formation

The formation of the dimolybdenum compounds Cp$_2^*$Mo$_2$X$_6$ by conproportionation of Cp$_2^*$Mo$_2$X$_4$ and



Scheme 1.

Cp^*MoX_4 (X = Cl, Br) was found to proceed according to Eqns. (6)–(8) [6,8b]. However, the intimate mechanism of halide transfer in eqn. (7) could not be adequately addressed. The results of the mixed-halide reactions reported in this paper allow a more detailed analysis of this transformation.

$$Cp_2^*Mo_2X_4 + Cp^*MoX_4 \longrightarrow [Cp_2^*Mo_2X_4]^+[Cp^*MoX_4]^- \quad (6)$$

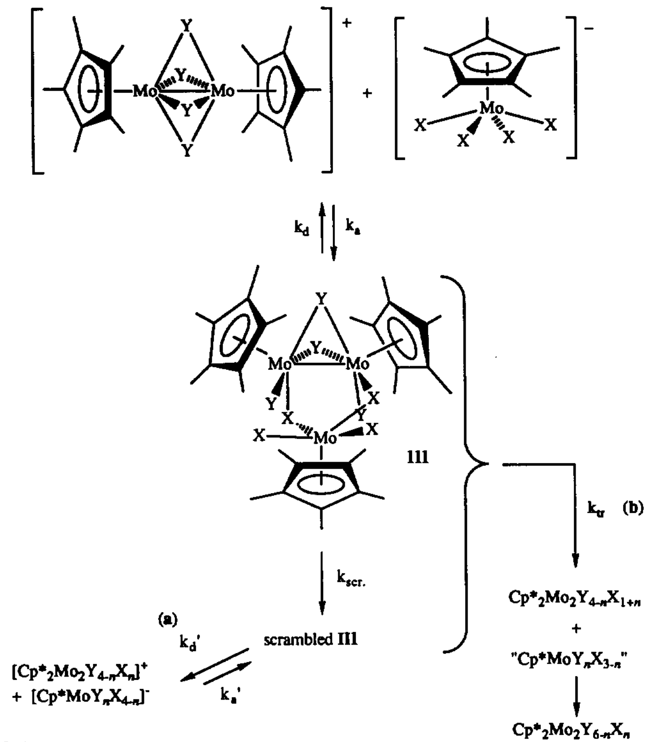
$$[Cp_2^*Mo_2X_4]^+[Cp^*MoX_4]^- \longrightarrow Cp_2^*Mo_2X_5 + 1/2Cp_2^*Mo_2X_6 \quad (7)$$

$$Cp_2^*Mo_2X_5 + Cp^*MoX_4 \longrightarrow 3/2Cp_2^*Mo_2X_6 \quad (8)$$

There are two conceivable mechanisms for reaction (7): (i) halide anion dissociation from $[Cp^*MoX_4]^-$ followed by addition to the $[Cp_2^*Mo_2Y_4]^+$ cation and (ii) an associative mechanism. We have shown that solutions of $[Cp^*MoX_4]^-$ (X = Cl, Br, I) in $CDCl_3$ are stable towards halide dissociation (Scheme 1) [6,8b]. In fact, the Mo^{IV} anion can be conveniently synthesized by the addition of halide anion to the trihalide dimer. However, this does not rule out mechanism (i) because it is still possible that a rapid and reversible equilibrium is present, although this will be strongly shifted towards the $[Cp^*MoX_4]^-$ anion. On the other hand, mechanism (i) cannot explain the observed halide scrambling reaction in the $[Cp_2^*Mo_2Y_4]^+/[Cp^*MoX_4]^-$ system, which precedes halide transfer. On the basis of this new finding, we must modify the earlier proposal [6] according to which the $[Cp^*MoX_4]^-$ would dissociate a halide ion to form a $[Cp_2^*Mo_2X_4]^+X^-$ ion pair.

The formation of $[Cp_2^*Mo_2Y_{4-n}X_n]^+$ and $[Cp^*MoX_{4-n}Y_n]^-$ can only be rationalized by invoking a reversible association between cation and anion to form a halide-bridged intermediate such as **III** in Scheme 2. Such an association requires the opening of at least one Mo–Y–Mo bridge and could be driven by the electrostatic attraction between the two charged species. This intermediate would then allow for the rapid halide redistribution among the different positions in the complex and it would then proceed in two possible ways. It can either revert to a mixture of halide-scrambled cation and anion (see path a) or it can accomplish the halide transfer to form neutral species as shown in path b. The relative rate of halide transfer (k_{tr}) *vs.* the rate of the scrambling process (k_{scr}) will determine the degree of halide scrambling.

Pathway b affords the aforementioned neutral pentachloride complex (e.g. $Cp_2^*Mo_2Y_4X$) and a short-lived trihalide monomer, which dimerizes to give trihalide dimers. This trihalide monomer has not been observed by ^1H NMR. However, the pentahalide complex has been observed for the all-chloro system, as discussed earlier [6], and also for the $Cp_2^*Mo_2Cl_4/Cp^*MoBr_4$ system, as evidenced by the two peaks at δ +1.34 and +1.40.



Scheme 2.

The drawing of structure **III** is only speculative at this point. However, we note that the occurrence of rapid halogen scrambling can be accounted for quite easily by this structure: the trinuclear complex has two singly-bridged and one doubly-bridged edges, therefore it can equilibrate the edges by concerted bridge-opening and -closing processes in a similar fashion to the "merry-go-round" mechanism of CO scrambling in metal carbonyls.

So far, we have not taken into account the second equivalent of the oxidizing agent Cp^*MoX_4. We have previously shown by cyclic voltammetry that the $Cp_2^*Mo_2Y_4$ complexes undergo two successive reversible or quasi-reversible one-electron oxidations, but the redox potential of Cp^*MoX_4 only allows the oxidation of $Cp_2^*Mo_2Y_4$ to the corresponding monocation (the dication is not accessible) [6–8]. However, Cp^*MoX_4 may be able to oxidize the product of addition of halide to the cationic species, since it is expected that such halide coordination increases the electron density at the metals and therefore lowers their oxidation potential. It has previously been suggested that Cp^*MoX_4 oxidizes the neutral pentahalide species (see eqn. (8)) and, at least for the all-chloro system, this possibility seems consistent with the ^1H

NMR observation of the $Cp^*_2Mo_2Cl_5$ intermediate and with the electrochemical properties of all species involved [6]. For the all-bromo and the $[Cp^*_2Mo_2Br_4]$ $[Cp^*MoCl_4]$ systems, however, there is no ^1H NMR evidence for the accumulation of a $Cp^*_2Mo_2Br_4X$ (X = Cl, Br) intermediate. This is possibly the result of the slow halogen transfer reaction in these cases, which would allow for $Cp^*_2Mo_2Br_4X$ to be consumed by reaction (8) before it can accumulate to a sufficient extent to be observed, but we may also consider the possibility that Cp^*MoX_4 is able to oxidize intermediate **III** directly (eqn. (9)).

$$\text{“}Cp^*_3Mo_3X_4Y_4\text{”} \xrightarrow{Cp^*MoX_4} 2Cp^*_2Mo_2Y_{6-n}X_n \qquad (9)$$

The observation that the initial rate of formation of $Cp^*_2Mo_2Br_6$ does not depend on the concentration of Cp^*MoBr_4 is consistent with the halide transfer (eqn. (7)) being the slow step of the reaction, consistent with the lack of accumulation of $Cp^*_2Mo_2Br_5$ or of an intermediate such as **III**.

4.3. *Reactivity trends*

The following trends are noteworthy. (a) halide exchange reactions leading to mixed halide cations are only observed for reactions involving the $[Cp^*_2Mo_2Cl_4]^+$ cation. In the case of Y = Br or I, there is no spectroscopic evidence for the formation of mixed halide cations. (b) the rate of consumption of $[Cp^*_2Mo_2Y_4]^+$ $[Cp^*MoX_4]^-$ and formation of $Cp^*_2Mo_2Y_{6-n}X_n$ is greatly dependent on the nature of Y. For Y = Cl, the complexes $Cp^*_2Mo_2Cl_{6-n}X_n$ (X = Cl, Br) are formed immediately, while in systems obtained from $Cp^*_2Mo_2Br_4$, the formation of Mo^{IV} dimers proceeds more slowly and, from $Cp^*_2Mo_2I_4$, not at all. (c) the rate of consumption of $[Cp^*_2Mo_2Y_4]^+[Cp^*MoX_4]^-$ and formation of $Cp^*_2Mo_2Y_{6-n}X_n$ has little dependence on the nature of X.

All these phenomena can be rationalized, based on Scheme 2, as follows: the acidity of $[Cp^*_2Mo_2Y_{4-n}X_n]^+$ is greater for more chloride-substituted species and smaller for species that are highly substituted with heavier halide ligands (*i.e.*, as the complex becomes richer with heavier halide ligands, k_a becomes smaller and k_d becomes larger). For each combination of halide ligands, however, k_a must be smaller than k_d, since in no instance is there any evidence for the accumulation of an intermediate such as **III**. Therefore, for the $[Cp^*_2Mo_2Cl_4]^+[Cp^*MoBr_4]^-$ combination, fast association is followed by fast scrambling and then fast dissociation of the bromide-richer cation and chloride-richer anion. For the opposite $[Cp^*_2Mo_2Br_4]^+$-$[Cp^*MoCl_4]^-$ combination, on the other hand, association is slow and the association product has the greatest tendency to dissociate back to the starting unscrambled ions.

We must remark at this point that solutions of $[Cp^*_2Mo_2Br_4]^+[Cp^*MoX_4]^-$ (X = Cl, Br) are indefinitely stable when an additional equivalent of Cp^*MoX_4 is not present. Only when excess Cp^*MoX_4 is present (*e.g.* in the $Cp^*_2Mo_2Br_4/Cp^*MoX_4$ reaction carried out in a 1:2 molar ratio) is any $Cp^*_2Mo_2Br_{6-n}X_n$ product formed. Solutions of $[Cp^*_2Mo_2I_4]^+[Cp^*MoX_4]^-$ (X = Cl, Br) are indefinitely stable even when an additional equivalent of Cp^*MoX_4 is present. On the other hand, when starting from $Cp^*_2Mo_2Cl_4$, both pentahalide and hexahalide dimers are formed immediately even when using only one equivalent of the oxidizing agent Cp^*MoX_4. This shows that equilibrium (10) is thermodynamically shifted towards the right when Y = Cl and towards the left when Y = Br or I.

$$[Cp^*_2Mo_2Y_4]^+[Cp^*MoX_4]^- \rightleftharpoons Cp^*_2Mo_2Y_4X + 1/2Cp^*_2Mo_2X_6 \qquad (10)$$

We also observe a thermodynamic trend in the position of equilibrium (11), where the formula on the right hand side represents a distribution of various compounds with different n values. For the X = Y = Br system, a constant $K = 12\ mol^{-1}\ l$ can be calculated from the initial concentrations and an equilibrium $[Cp^*_2Mo_2Br_4]^+/Cp_2Mo_2Br_6$ ratio of 4.8. For the X = Br, Y = Cl system a value of K cannot be calculated rigorously, but we observe that the equilibrium is qualitatively shifted towards the right with respect to the all-bromo system (equilibrium $[Cp^*_2Mo_2Br_4]^+/Cp_2Mo_2Br_{6-n}Cl_n$ ratio = 2.4). These numbers should be compared with the system described previously with X = Y = Cl [6], where no measurable concentration of $[Cp^*_2Mo_2Cl_4]^+[Cp^*MoCl_4]^-$ remains in solution.

$$[Cp^*_2Mo_2Y_4]^+[Cp^*MoX_4]^- + Cp^*MoX_4 \rightleftharpoons 2Cp^*_2Mo_2Y_{6-n}X_n \qquad (11)$$

Previous electrochemical studies have shown that the redox potentials of the $Cp^*_2Mo_2Y_4/[Cp^*_2Mo_2Y_4]^+$ and $Cp^*MoX_4/[Cp^*MoX_4]^-$ systems do not sharply depend on the nature of X and Y (Cp^*MoBr_4 is a stronger oxidant than Cp^*MoCl_4 by 20 mV, whereas the oxidation potential of the different $Cp^*_2Mo_2Y_4$ compounds to the corresponding cations varies within a 80 mV range) [2–4]. In conclusion, the difference in chemical reactivity between the different $Cp^*_2Mo_2Y_4/Cp^*MoX_4$ systems is mostly dominated by the different Lewis acidity of the $[Cp^*_2Mo_2Y_4]^+$ ion, which varies in the order $[Cp^*_2Mo_2Cl_4]^+ \gg [Cp^*_2Mo_2Br_4]^+ \gg [Cp^*_2Mo_2I_4]^+$.

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