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Synthesis and Crystal Structure of $\text{MoCpICl}(\text{PMe}_3)_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) and Equilibrium of Disproportionation to $\text{MoCpCl}_2(\text{PMe}_3)_2$ and $\text{MoCpI}_2(\text{PMe}_3)_2$

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**SYNTHESIS AND CRYSTAL STRUCTURE OF $\text{MoCp}(\text{Cl})\text{I}(\text{PMe}_3)_2$
($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) AND EQUILIBRIUM OF HALIDE RE-
DISTRIBUTION TO $\text{MoCpCl}_2(\text{PMe}_3)_2$ AND $\text{MoCpI}_2(\text{PMe}_3)_2$ (*) (**)**

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(**) Atomic coordinates for $\text{MoCpICl}(\text{PMe}_3)_2$ have been deposited with the Cambridge Crystallographic Data Centre and can be obtained upon request From: The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 IEW, U.K.

(°) To whom correspondence should be addressed. Camille and Henry Dreyfus Distinguished New Faculty, 1987-92; Presidential Young Investigator, 1990-95.

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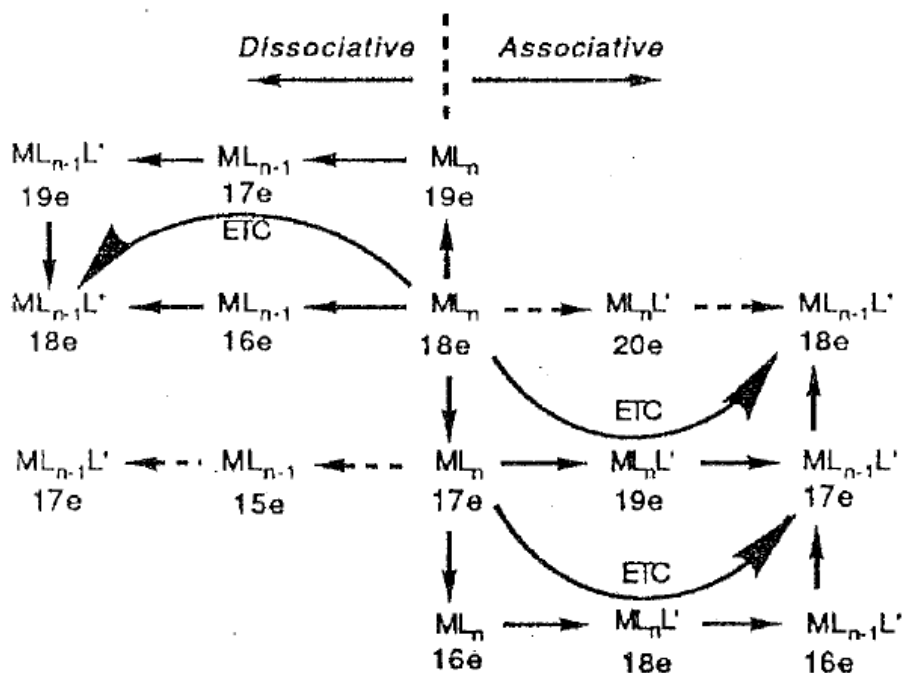
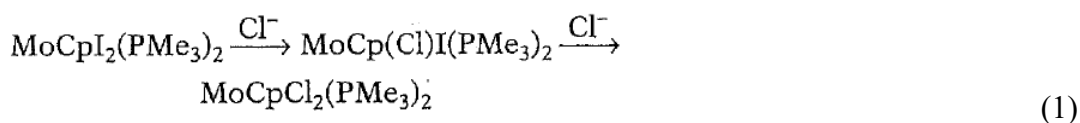
^c To whom correspondence about the crystallographic study should be addressed.

Summary - The mixed halide MoCp(Cl)I(PMe₃)₂ compound has been synthesized by selective halide exchange from MoCpCl₂(PMe₃)₂. It slowly establishes a halide redistribution equilibrium in solution to a mixture containing the two homogeneous halide compounds, MoCpCl₂(PMe₃)₂ and MoCpI₂(PMe₃)₂. The equilibrium position has been determined in both CH₂Cl₂ and THF media at different I/Cl ratios in the temperature range 22-35 °C. The value of the redistribution equilibrium constant is close to the expected statistical value but it slightly favours the mixed halide species, which is estimated to be *ca.* 0.5 kcal more stable than the average enthalpy of the two homogeneous halide compounds. The crystal structure of MoCpICl(PMe₃)₂ has been determined: monoclinic, space group *P2*₁/*c*, *a* = 12.310(3), *b* = 10.551(3), *c* = 13.682(3) Å, *β* = 105.04(2)°, *V* = 1716.2(8) Å³, *Z* = 4, *D*_{calc} = 1.840 g cm⁻³, *μ* (Mo *Kα*) = 28.9 cm⁻¹, *R* = 0.0388, *R*_w = 0.0425 for 145 parameters and 2926 observed reflections. The compound has a four-legged piano stool geometry and its structural parameters are compared with those of the two homogeneous halide systems.

We have recently become interested in the chemistry and properties of odd-electron organometallic systems and have focussed our attention on the 17-electron MoCpX₂L₂ system where X = halide and L = neutral 2-electron donor. Systems of this type had been briefly described earlier, *i.e.* MoCp'Cl₂L₂ [Cp' = η⁵-C₅H₄-*i*-Pr; L = PMe₃, PMe₂Ph, L₂ = (*i*-Pr)₂CH₂CH₂(*i*-Pr)₂],¹ Mo(η⁵-C₅Me₅)Cl₂(PMe₃)₂,² and MoCpX₂(diene); (X = Cl, Br, I, SC₆F₅, S-*p*-C₆H₄CH₃; diene = butadiene).³ An isoelectronic system with the π-allyl ligand, MoCp(η³-C₃H₅)₂, had also been described.⁴ We have recently reported a comprehensive investigation of the MoCpX₂(PMe₃)₂⁵ and MoCpX₂(dppe)⁶ [X = Cl, Br, I; dppe = 1,2- bis(diphenylphosphino)ethane] systems. This investigation included EPR, electrochemical and crystallographic characterization, as well as Fenske-Hall semi-empirical molecular orbital calculations. One interesting result of this study was the discovery of significant Mo-P π and Mo-Cp δ interactions. Additional evidence for a metal-phosphine π interaction in these and other cyclopentadienyl derivatives was obtained by analyzing the angular distortions of the four monodentate ligands in crystal structures of existing four-legged piano stool structures.⁷

Since there is great current interest in ligand substitution reactions of 17-electron systems *vis-à-vis* their 18-electron saturated analogues,⁸ we are investigating ligand substitution reactions on our stable 17-electron Mo(III) systems. In general, ligand substitutions on 17-electron systems are much faster than the corresponding processes on 18-electron analogues and proceed through an associative mechanism. Ligand substitutions on 18-electron systems are often accelerated by catalytic oxidation or reduction, in which 17-electron and 19-electron systems, respectively, are generated.⁹ This effect has been properly named electron-transfer catalysis (ETC).

We have discovered that, for our Mo(III) compounds, the substitution of I⁻ with Cl⁻ (equation 1) proceeds very slowly, but the process is greatly accelerated by catalytic oxidation to the 16-electron Mo(IV) system.¹⁰ Thus, this is the first example of an ETC process where ligand substitution is faster in the even-electron manifold than in the odd-electron one (see the scheme). Within this investigation, we have been able to establish that the intermediate mixed-halide species can be selectively generated in solution and isolated in crystalline form. We wish to report in this paper a full account of the studies carried out on this mixed-halide species, including its crystal and molecular structure, and equilibrium studies of its ligand redistribution to the homogeneous halide compounds.



SCHEME

EXPERIMENTAL

All operations were carried out under an atmosphere of dinitrogen or argon. Solvents were purified by conventional methods and distilled under dinitrogen prior to use. Instruments used were as follows: FTIR, Nicolet 5DXC; EPR, Bruker ER200; scanning potentiostat, EG&G 362.

Quantitative EPR analyses were carried out in the following manner: the raw data were the signal-to-baseline separations at various magnetic field values and were related to the concentration

through the use of calibration curves, which were found to be linear in the range of concentrations (10^{-4} - 5×10^{-3} M) investigated. For each pure compound, an “extinction coefficient” at the desired position was defined as

$$\varepsilon(H) = I(H)/[RG \times MA \times C]$$

where $I(H)$ = measured intensity of the signal (cm) at the desired value of the magnetic field H , RG = Receiver Gain, MA = Modulation Amplitude, and C = molar concentration. For equilibrium mixtures of $\text{MoCpCl}_2(\text{PMe}_3)_2$, $\text{MoCpI}_2(\text{PMe}_3)_2$, and $\text{MoCp(Cl)I}(\text{PMe}_3)_2$, the measurement of the intensity at three different values of the magnetic field (H_i ; $i = 1, 2, 3$) allowed the calculation of each individual concentration.

$$I(H_i) = RG \times MA [\varepsilon_{\text{I}_2}(H_i)C_{\text{I}_2} + \varepsilon_{\text{ClI}}(H_i)C_{\text{ClI}} + \varepsilon_{\text{Cl}_2}(H_i)C_{\text{Cl}_2}] \quad (i = 1, 2, 3)$$

Measurements were carried out in 3 mm 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 data reproducibility. 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, thereby keeping the sample volume constant in the cavity. Measurements for quantitative purposes were carried out after the instruments had been allowed to equilibrate for at least four hours after powering.

Elemental analyses were carried out by Galbraith Laboratories, 5-Knoxville, TN, and by Midwest Microlab, Indianapolis, IN. MoCpCl_4 was prepared as described previously.⁶ PMe_3 was purchased from Strem Chemicals and trap-to-trap distilled prior to use.

SYNTHESIS OF $[\text{MoCpCl}_2]_n$

MoCpCl_4 (2.21 g, 7.31 mmol) and Zn powder (0.48 g, 7.3 mmol) were suspended in THF (50 ml). The mixture was stirred at room temperature for *ca.* 20 h, during which time the metallic zinc was completely consumed and a golden yellow precipitate replaced the partially dissolved red MoCpCl_4 . The product was filtered, washed thoroughly with THF to remove the soluble ZnCl_2 by-product, and dried in vacuo. Yield 1.46 g (86%). *Elem. anal.*, found % (calcd for $\text{C}_5\text{H}_5\text{Cl}_2\text{Mo}$): C, 25.5 (25.9); H, 2.5 (2.2). The product is insoluble or only sparingly soluble in all common organic solvents.

SYNTHESIS OF $\text{MoCpCl}_2(\text{PMe}_3)_2$

To 1.097 g (4.73 mmol) of MoCpCl_2 in 20 ml of toluene was added PMe_3 (1.0 ml, 10 mmol) and the resulting mixture was stirred at room temperature. The molybdenum material dissolved within *ca.* 15 minutes to yield a red-brown solution. After filtration, the solution was evaporated until formation of the crystalline product was observed (*ca.* 3 ml). At this point, heptane (10 ml) was added

and the mixture was placed at $-20\text{ }^{\circ}\text{C}$ overnight. The resulting precipitate was separated by filtration, washed with heptane and dried *in vacuo*. Yield 0.87 g (48%). This material shows identical spectroscopic properties to those reported earlier⁵ for $\text{MoCpCl}_2(\text{PMe}_3)_2$.

SYNTHESIS OF $\text{MoCp}(\text{Cl})\text{I}(\text{PMe}_3)_2$

To 0.349 g (1.51 mmol) of MoCpCl_2 in 20 ml of THF was added PMe_3 (320 μl , 3.20 mmol) and the formation of $\text{MoCpCl}_2(\text{PMe}_3)_2$ was allowed to take place as described in the preceding paragraph. At this point, anhydrous NaI (0.230 g, 1.53 mmol) was added and the resulting mixture stirred at room temperature under a dinitrogen atmosphere. EPR monitoring showed the smooth conversion of $\text{MoCpCl}_2(\text{PMe}_3)_2$ to the product (ca. 2 h) without further substitution to the diiodide material. After removal of the solvent by evaporation under reduced pressure, the residue was dissolved in toluene and the resulting solution filtered. The product was crystallized by the addition of heptane. Yield 0.326 g (46%). EPR (THF): g , 2.015; a_M , 39.3 G; a_P , 11.9 G.

SYNTHESIS OF $\text{MoCpI}_2(\text{PMe}_3)_2$

MoCpCl_2 (0.686 mg, 2.96 mmol), PMe_3 (650 μl , 6.50 mmol), and anhydrous NaI (1.160 g, 7.74 mmol) were stirred in THF (20 ml) overnight at $50\text{ }^{\circ}\text{C}$. At this point the major EPR active species in solution was the mixed halide species, with minor amounts of $\text{MoCpI}_2(\text{PMe}_3)_2$ also being present. The mixture was then refluxed until halide substitution was complete (EPR monitoring, ca. 10 h). The solvent was then evaporated under reduced pressure, the residue was dissolved in toluene and the resulting solution was filtered. The product was then crystallized by the addition of heptane. Yield 1.144 g (68%). The spectroscopic properties of this material are identical to those reported earlier⁵ for $\text{MoCpI}_2(\text{PMe}_3)_2$.

X-RAY DATA COLLECTION AND STRUCTURE REFINEMENT OF $\text{MoCp}(\text{Cl})\text{I}(\text{PMe}_3)_2$

Crystallographic data are presented in table 1. A deep red crystal of $\text{MoCp}(\text{Cl})\text{I}(\text{PMe}_3)_2$ obtained by recrystallization from toluene/heptane was mounted on a glass fibre and found to belong to the monoclinic system. The space group, $P2_1/c$, was uniquely determined from systematic absences in the diffraction data. An empirical absorption correction^{11a} was applied to the data.

The I and Mo atoms were positioned from an auto-interpreted Patterson synthesis, and the Structure completed from difference Fourier computations. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as idealized, isotropic contributions. All computations used SHELXTL (5.1) software.^{11b} Positional and isotropic equivalent isotropic thermal parameters are in table 2, and selected bond distances and angles are listed in table 3.

TABLE 1 - CRYSTAL DATA FOR MoCp(Cl)I(PMe₃)₂

| (a) Crystal Parameters | |
|---|---|
| Formula | C ₁₁ H ₂₃ ClIMoP ₂ |
| Space group | <i>P2₁/c</i> |
| Crystal system | Monoclinic |
| Systematic absences | <i>0k0: k ≠ 2n; h0l: h+l ≠ 2n</i> |
| <i>a</i> , Å | 12.310(3) |
| <i>b</i> , Å | 10.551(3) |
| <i>c</i> , Å | 13.682(3) |
| β , deg | 105.04(2) |
| <i>V</i> , Å ³ | 1716.2(8) |
| <i>Z</i> | 4 |
| Cryst. size, mm | 0.36 x 0.40 x 0.42 |
| Cryst. Color | Deep red |
| <i>D</i> _{calc} , g/cm ³ | 1.840 |
| μ (Mo <i>K</i> α), cm ⁻¹ | 28.9 |
| Temp, °C | 23 |
| T(max)/T(min) | 1.39 |
| (b) Data Collection | |
| Data collection instrument | Nicolet R3m |
| Monochromator | Graphite |
| Scan method | Wyckoff |
| Radiation | Mo <i>K</i> α (λ = 0.71073 Å) |
| 2 θ scan range, deg | 4-55 |
| Data collected | ± 16 , +14, +18 |
| Rflns. Collected | 4321 |
| Indpt. rflns. | 3936 |
| <i>R</i> (merg.), % | 2.10 |
| Indpt. rflns. Obsvd. | 2926 |
| Std. rflns. | 3 std/197 rflns |
| Var. in stds, % | < 1 |
| (c) Refinement | |
| <i>R</i> (<i>F</i>), % | 3.88 |
| <i>R</i> (w <i>F</i>), % | 4.25 |
| Δ/σ (max) | 0.004 |
| $\Delta(\rho)$, eÅ ⁻³ | 1.25 |
| N _o /N _v | 20.13 |
| GOF | 1.183 |

TABLE 2 - ATOMIC COORDINATES (x10⁴) AND ISOTROPIC THERMAL PARAMETERS (Å²x10³) FOR MoCp(Cl)I(PMe₃)₂

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> ^a |
|------|-----------|-----------|-----------|-----------------------|
| I | 880.2(4) | 6305.4(5) | 6575.1(3) | 51.9(2) |
| Mo | 2411.4(4) | 5408.0(5) | 8339.9(3) | 31.0(1) |
| Cl | 4470(1) | 5430(2) | 8368(1) | 47(1) |
| P(1) | 2869(1) | 7714(2) | 8577(1) | 42(1) |
| P(2) | 2518(2) | 3588(2) | 7188(1) | 44(1) |

| | | | | |
|-------|---------|---------|----------|-------|
| C(1) | 1592(7) | 3815(8) | 9059(6) | 64(3) |
| C(2) | 2697(7) | 4068(8) | 9635(6) | 64(3) |
| C(3) | 2722(7) | 5294(8) | 10014(5) | 60(3) |
| C(4) | 1640(7) | 5828(8) | 9666(6) | 65(3) |
| C(5) | 952(6) | 4871(9) | 9070(5) | 66(3) |
| C(6) | 3946(7) | 8142(8) | 9716(6) | 73(3) |
| C(7) | 1793(7) | 8846(7) | 8630(6) | 60(3) |
| C(8) | 3413(7) | 8377(7) | 7575(6) | 66(3) |
| C(9) | 1268(7) | 2744(8) | 6546(6) | 67(3) |
| C(10) | 3417(7) | 2310(7) | 7788(7) | 74(3) |
| C(11) | 3098(7) | 4029(8) | 6146(6) | 64(3) |

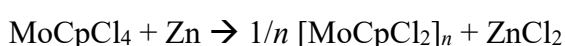
(^a) Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3 - SELECTED DISTANCES (Å) AND ANGLES (deg) FOR MoCp(Cl)I(PMe₃)₂

| a) Bond distances | | | |
|-------------------|-----------|----------------|-----------|
| I-Mo | 2.814(1) | Mo-Cl | 2.525(2) |
| Mo-P(1) | 2.500(2) | Mo-P(2) | 2.509(2) |
| Mo-C(1) | 2.307(9) | Mo-C(2) | 2.224(8) |
| Mo-C(3) | 2.226(7) | Mo-C(4) | 2.299(9) |
| Mo-C(5) | 2.341(8) | C(1)-C(2) | 1.409(11) |
| C(1)-C(5) | 1.367(12) | C(2)-C(3) | 1.393(11) |
| C(3)-C(4) | 1.419(12) | C(4)-C(5) | 1.430(11) |
| b) Bond angles | | | |
| I-Mo-Cl | 117.2(1) | I-Mo-P(1) | 82.1(1) |
| I-Mo-P(2) | 81.4(1) | I-Mo-C(1) | 110.0(2) |
| I-Mo-C(2) | 146.1(2) | I-Mo-C(3) | 143.1(2) |
| I-Mo-C(4) | 106.9(2) | I-Mo-C(5) | 91.7(2) |
| Cl-Mo-P(1) | 78.3(1) | Cl-Mo-P(2) | 78.5(1) |
| Cl-Mo-C(1) | 123.2(2) | Cl-Mo-C(2) | 92.5(2) |
| Cl-Mo-C(3) | 94.6(2) | Cl-Mo-C(4) | 127.2(2) |
| Cl-Mo-C(5) | 151.0(2) | P(1)-Mo-P(2) | 141.2(1) |
| P(1)-Mo-C(1) | 139.7(2) | P(1)-Mo-C(2) | 122.2(2) |
| P(1)-Mo-C(3) | 86.9(2) | P(1)-Mo-C(4) | 80.5(2) |
| P(1)-Mo-C(5) | 110.6(2) | P(2)-Mo-C(1) | 79.1(2) |
| P(2)-Mo-C(2) | 89.4(2) | P(2)-Mo-C(3) | 125.6(2) |
| P(2)-Mo-C(4) | 138.0(2) | P(2)-Mo-C(5) | 104.7(2) |
| C(2)-C(1)-C(5) | 108.4(7) | C(1)-C(2)-C(3) | 108.0(7) |
| C(2)-C(3)-C(4) | 108.5(7) | C(3)-C(4)-C(5) | 106.2(7) |
| C(1)-C(5)-C(4) | 108.9(7) | | |

RESULTS AND DISCUSSION

The materials utilized in this study have been prepared as described in equations 1-4.

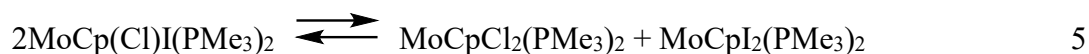




Reduction of MoCpCl_4 to $[\text{MoCpCl}_2]_n$ proceeds smoothly (equation 1) and affords a product of high purity provided no more than the stoichiometric amount of Zn is used and the Mo(V) material is pure. The latter condition is the most critical. We find that when MoCpCl_4 is contaminated by the PCl_5 material used for its generation,⁶ lower yields and a less pure material are obtained. When more than the stoichiometric amount of Zn is used for the reduction, the excess cannot be separated from the product and remains as an impurity in the isolated material. The ZnCl_2 co-product is easily separated since it remains dissolved in THF. The insolubility of MoCpCl_2 suggests an oligomeric or polymeric formulation analogous to that suggested for TiCpCl_2 ¹² and RuCp^*Cl_2 ,¹³ compounds of identical stoichiometry. The use of sodium amalgam as the reducing agent does not afford MoCpCl_2 but generates instead a soluble derivative, presumably an adduct of MoCpCl_2 with Cl^- . Independent reaction of MoCpCl_2 and Cl^- has been shown to yield the $[\text{Mo}_2\text{Cp}_2\text{Cl}_5]^-$ anion.¹⁴

The reaction of MoCpCl_2 with PMe_3 proceeds smoothly and represents a very convenient route to $\text{MoCpCl}_2(\text{PMe}_3)_2$ (reaction 2). The reaction does not require the use of forcing conditions and therefore does not result in the formation of by-products as observed in the previously published method.⁵ We have discovered that the chloride ions in the $\text{MoCpCl}_2(\text{PMe}_3)_2$ compound can be replaced by iodide upon reaction with anhydrous NaI .¹⁰ The driving force of the reaction must be the formation of the less soluble NaCl , because in a homogeneous system the halide substitution proceeds quantitatively in the opposite direction. The replacement of the second chloride ion is much slower than the replacement of the first (reaction 4 is much slower than reaction 3), so that the selective synthesis of the mixed-halide species can be accomplished by the interaction of $\text{MoCpCl}_2(\text{PMe}_3)_2$ and NaI in stoichiometric amounts with the use of shorter reaction times.

The isolation of $\text{MoCp}(\text{Cl})\text{I}(\text{PMe}_3)_2$ immediately after its formation is crucial to the selectivity of the synthetic method, because the compound partially and slowly establishes a halide redistribution equilibrium in solution to afford a mixture of the two homogeneous halide derivatives (equation 5).



Since we have optimized the quantitative determination of each of the three species participating in equilibrium 5 by use of the EPR technique (quantitative analysis by EPR is precedented in the literature¹⁵) for the purpose of studying the kinetics of the halide substitution,¹⁰ we have decided to investigate equilibrium 5 in more detail. Measurements of the mixture composition were carried out in both THF and CH₂Cl₂ solvents. The EPR spectra were recorded until no further change was observed. Studies were carried out at variable temperatures and the equilibrium values obtained are reported in table 4. It was not possible to extend the temperature range above 35 °C because significant thermal decomposition of the dichloride system occurs by an as yet unknown pathway.¹⁰ Control runs indicate that the thermal decomposition of MoCpCl₂(PMe₃)₂ is not significant within the time required to reach equilibrium in the temperature range that we have utilized (22-35 °C).

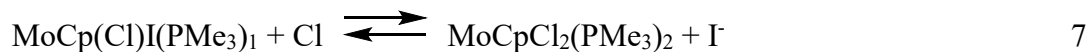
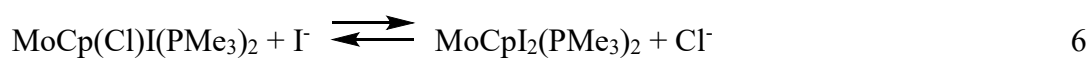
TABLE 4 - EQUILIBRIUM CONSTANTS FOR EQUILIBRIUM 5

| A. In CH ₂ Cl ₂ | | | | | |
|---------------------------------------|---|-------|-------|--------------------------------|-------------|
| Temp. (°C) | From [MoI ₂] ^b + [MoCl ₂] ^b | | | From [Mo(Cl)I] ^b | Average |
| | Cl/I ratio ^c | | | | |
| | 0.58 | 1.06 | 1.44 | | |
| 22.0 | 0.055 | 0.062 | 0.072 | 0.074 | 0.066±0.009 |
| 28.5 | 0.069 | 0.076 | 0.073 | 0.078 | 0.074±0.004 |
| 32.0 | 0.085 | 0.077 | 0.087 | 0.082 | 0.083±0.004 |
| 35.0 | 0.077 | 0.074 | 0.078 | 0.071 | 0.075±0.003 |
| B. In THF | | | | | |
| Temp. (°C) | From [MoI ₂] ^b + [MoCl ₂] ^b | | | Average | |
| | Cl/I ratio ^c | | | | |
| | 0.68 | 1.00 | 1.47 | | |
| 22.0 | 0.028 | 0.045 | 0.037 | | 0.036±0.008 |

| | | | | |
|------|-------|-------|-------|-------------|
| 28.5 | 0.051 | 0.048 | 0.054 | 0.051±0.003 |
| 32.0 | 0.047 | 0.049 | 0.049 | 0.048±0.001 |
| 35.0 | 0.052 | 0.046 | 0.047 | 0.048±0.004 |

(^a) Temperatures are accurate to ± 0.5 °C. (^b) Cp and PMe₃ ligands omitted in the formula. (^c) Ratios are based on the weighed amounts of materials. Variable amounts of oxidation resulted in a measured Cl/I ratio lower than the calculated amount (see text).

Equilibrium was reached at variable and erratic speeds but, in general, 48 hours were sufficient at all temperatures investigated. It has been proven¹⁰ that trace amounts of oxidizing agents catalyze halide substitution reactions in MoCpX₂(PMe₃)₂ complexes. Therefore, variable amounts of adventitious oxygen might also catalyze the halide exchange reaction 5. Furthermore, trace amounts of free halide ions might also catalyze equilibrium 5, especially in the presence of oxidants, through single halide exchange reactions (equations 6 and 7).



We have in fact observed that, in a comparative run, the equilibrium is reached at a considerable faster rate when an additional amount (*ca.* 1%) of Na⁺I⁻ in THF is present. No attempt was made to eliminate the catalytic impurities to control the equilibration rate. In fact, a faster equilibration rate was to our advantage in order to successfully compete with the unknown decomposition path(s).

The most important conclusion from the results listed in table 4 is that the equilibrium constant is in all cases lower than the statistical value of 0.25, that is the mixed halide system experiences an extra stabilization with respect to the average of the two homogeneous halide compounds. It can also be observed that the value of the equilibrium constant has little or no dependence on the temperature in the range investigated. This suggests that the enthalpic contribution must be small. Under the assumption that the deviation of K from the statistical value is enthalpically driven, a value for ΔH^o₂₉₈ for reaction 5 of *ca.* 0.7 kcal (CH₂Cl₂) or 1.0 kcal (THF) can be calculated from the equilibrium constant [ΔS^o = Rln(0.25) = -2.8 cal K⁻¹ for a thermoneutral reaction of the type 2A = B+C]. These

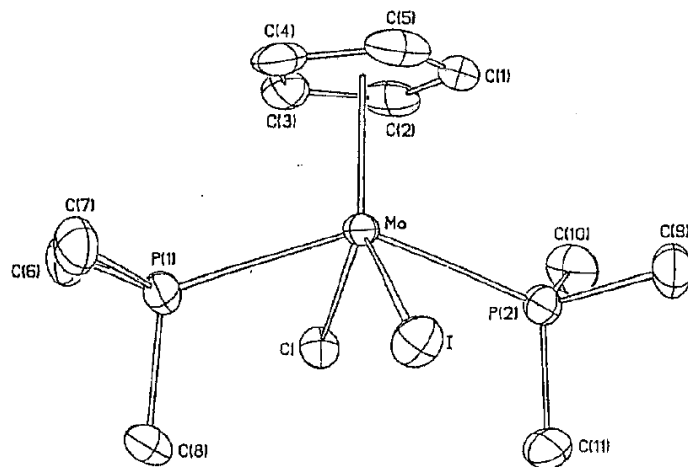
values are indeed small and result in a calculated change of K of less than 0.0039 unit (CH_2Cl_2) or 0.0033 units (THF) over the temperature range investigated, which are indeed comparable with the uncertainties on the averages in table 4. The assumption of insignificant entropic contribution appears reasonable considering that the same type and number of bonds are present on either side of equation 5. This situation is similar to, but more subtle than, other ligand redistribution equilibria that have been reported in the literature [equation 8, $E, E' = \text{PR}_2, \text{AsR}_2, \text{SbR}_2, \text{BiR}_2$ ¹⁶; $\text{Mn}(\text{CO})_5, \text{Re}(\text{CO})_5$ ¹⁷]. In these reactions, all the bonds of the molecule are maintained unaltered except for the single bond connecting the E and E' atoms. Curiously, the equilibration between tetraalkyl (or aryl) dipnictides is found to be endothermic, contrary to expectations based on Pauling's postulate that heteronuclear bonding is always stronger than homonuclear bonding.¹⁶ The scrambling between dimanganese and dirhenium decacarbonyls, on the other hand, seems to be essentially thermoneutral.^{17b}



Our exchange equilibrium can be described schematically by equation 9 and does not involve the formation or disappearance of bonds but merely their rearrangement among the various Mo(III) complexes. It can be compared with similar scramblings observed in the palladium systems $\text{Pd}(\text{dppm})\text{XY}$ and $\text{Pd}_2(\text{dppm})_2\text{XY}$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$; $X, Y = \text{Cl}, \text{Br}, \text{I}$) which show exothermic mixed-system formations for the Pd(I) dinuclear case but endothermic ones for the Pd(II) mononuclear complexes,^{18a} and with scramblings in the $\text{PtBr}_x\text{Cl}_{4-x}(\text{PEt}_3)(\text{py})$ system, in which the statistical distribution at equilibrium suggests that thermodynamic effects are relatively unimportant.^{18b} Similar equilibrium data can be calculated from thermochemical data¹⁹ for the exothermic (0.6 kcal/mol) redistribution of $\text{CH}_2\text{ClI}_{(g)}$ to $\text{CH}_2\text{Cl}_2_{(g)}$ and $\text{CH}_2\text{I}_2_{(g)}$: $\Delta S^\circ = -3.09 \text{ cal K}^{-1} \text{ mol}^{-1}$, $K = 0.6$.

In the hope to gain a better insight into the relative enthalpic stability of the mixed-halide system we have determined its crystal structure by X-ray diffraction methods for a comparison with the known structures of the dichloride and diiodide derivatives.⁵ A view of the molecular unit is reported in the figure. The molecule resides in a general position with no imposed crystallographic symmetry.

It has, however, idealized C_s symmetry with the mirror plane containing the Mo, Cl, I, and C(5) atoms. There is no sign of crystallographic disorder among the two halides.



An ORTEP view of the $\text{MoCp}(\text{Cl})\text{I}(\text{PMe}_3)_2$ molecule with the numbering scheme employed.

Selected bond distances and angles are listed in table 3. The geometry of the molecule can be described as pseudo-square pyramidal with the Cp ring occupying the apical position. The term “four-legged piano stool” is also commonly employed for this class of molecules. The geometry of this molecule is substantially identical to that of the corresponding homogeneous halide compounds. In particular, it shows the some tilting of the Cp ring with two carbon atoms closer, two at an intermediate distance, and one at a longer distance from the metal centre. This distortion has been predicted to occur when a significant metal-Cp δ back-bonding interaction exists.²⁰ The angles formed by the Mo-Cp (centre of gravity) and each of the individual Mo-X vectors (X = halide or PMe_3) are also similar and indicate significant Mo-to- PMe_3 π back-bonding and halide-to-Mo π bonding according to our recent MO analysis.⁷

The most relevant structural parameters for the mixed-halide molecule are compared with the corresponding ones for the two homogeneous halide molecules in table 5. Among these parameters, the Mo-Cl and Mo-I distances are perhaps the most interesting and intriguing ones. It was earlier discussed⁵ that the Mo-Cl distances in $\text{MoCpCl}_2(\text{PMe}_3)_2$ [average 2.471(3) Å] are longer than the usual Mo(III)-Cl separation (which is in the 2.43-2.45 Å range). In $\text{MoCp}(\text{Cl})\text{I}(\text{PMe}_3)_2$, this distance is even longer, that is 2.525(2) Å. On the other hand, the Mo(III)-I separation in $\text{MoCp}(\text{Cl})\text{I}(\text{PMe}_3)_2$ is shorter than for $\text{MoCpI}_2(\text{PMe}_3)_2$. It would appear that the mixed-halide system experiences a

destabilization of the Mo-Cl bond and a stabilization of the Mo-I bond with respect to the two homogeneous halide systems.^d

TABLE 5 - COMPARISON OF STRUCTURAL PARAMETERS OF MoCpXY(PMe₃)₂ MOLECULES (X, Y = Cl, I)

| | X = Y = Cl | X = Cl, Y = I | X = Y = I |
|-------------------------|------------|---------------|-----------|
| Mo-Cp (Å) | 1.933 | 1.943 | 1.951 |
| Mo-X (Å) | 2.468(2) | 2.525(2) | 2.831(1) |
| Mo-Y (Å) | 2.464(2) | 2.814(1) | 2.831(1) |
| Mo-P(1) (Å) | 2.484(2) | 2.500(2) | 2.500(2) |
| Mo-P(2) (Å) | 2.481(2) | 2.509(2) | 2.502(2) |
| X-Mo-P (°) ^a | 79.3(3) | 78.4(1) | 81.2(7) |
| Y-Mo-P (°) ^a | 79.8(4) | 81.8(3) | 81.2(7) |
| θ(X) (°) ^b | 117.6 | 120.8 | 117.2 |
| θ(Y) (°) ^b | 117.2 | 122.0 | 117.2 |
| θ(P1) (°) ^b | 113.2 | 109.6 | 112.7 |
| θ(P2) (°) ^b | 113.1 | 108.9 | 106.2 |

^a Average of the angles involving the two inequivalent P atoms. ^b θ is defined as the angle between the Mo-Cp (centre of gravity) vector and the bond between Mo and the ligand in parentheses.

Calculations based on the principle of electronegativity equalization²¹ using the absolute hardness parameters given by Pearson²² lead to the prediction of an increased ionic character for the Mo-Cl bond and a decreased ionic character for the Mo-I bond in the mixed-halide compound with respect to the two homogeneous halide derivatives. It is tempting to suggest that the charge redistribution is paralleled by an opposite redistribution of covalent strength, so that the structure of MoCp(Cl)I(PMe₃)₂ could be viewed as sitting along the reaction coordinate for the expulsion of a chloride ion and formation of the ionic isomer [MoCpI(PMe₃)₂]⁺Cl⁻.

^d An unrealistically long Mo-Cl bond and a comparatively short Mo-I bond would result if the chloride and iodide ligands were partially disordered among the two positions. However, a careful analysis of the electron density (thermal ellipsoids) did not show any evidence for partial disorder.

The Mo-P distances are similar for the mixed-halide and diiodide molecules, and slightly longer than for the dichloride molecule. The variations in the angular parameters are also interesting. In the mixed-halide structure, the P-Mo-Cl angles are slightly smaller and the P-Mo-I bonds slightly larger than all the P-Mo-X angles in the two homogeneous dihalide systems. This trend is in agreement with the idea of the chloride "expulsion" toward anionic isomer, although it could also be attributed to the different steric requirement of the two halide ligands.

We conclude that the structural changes observed on going from homogeneous halide compounds to the mixed-halide system do not allow the origin of the extra thermodynamic stability of the mixed-halide system to be assessed with certainty. The enthalpic difference calculated from the equilibrium data is very small and its effect on the structural parameters is probably inconsequential compared with other effects, which are probably caused by an energy redistribution within the molecule.

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