The Unusual Structure of the Novel [Mo$_2$Cp$_2$Cl$_5$]$^-$ Ion (Cp = C$_5$H$_5$)

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The novel [Mo$_2$Cp$_2$Cl$_5$]$^-$ ion (Cp = C$_5$H$_5$), obtained as the salt of the bis(triphenylphosphine)iminium (PPN) cation on reacting MoCpCl$_2$ with PPN$^+$Cl$^-$ in CH$_2$Cl$_2$, contains two equivalent molybdenum centres at a distance of 2.413(1) Å, which are bonded to two terminal Cl atoms and one η^5-C$_5$H$_5$ group and are bridged by a single Cl ligand; the electronic structure indicates a metal–metal triple bond, which is little perturbed by the bridging chloride ligand; the molecule provides a bridge between two diverse structures of M$_2$(η^5-C$_5$H$_4$Pr^i)$_2$Cl$_4$ (M = Mo: quadruply-bridged, Mo–Mo single bond; M = W: unbridged, W–W triple bond).

We have recently reported synthetic and structural studies on seventeen-electron Mo^{III}-Cp (Cp = C$_5$H$_5$) derivatives of formula MoCpX$_2$L$_2$ (X = Cl, Br, I; L = monodentate phosphine; L$_2$ = bidentate phosphine).[1,2] One of the synthetic routes that has been investigated is the reduction of MoCpCl$_4$ to the +3 oxidation state, followed by addition of the desired ligand. When a similar reduction is carried out with sodium (2 equiv.) in the absence of L, a soluble intermediate is obtained.[2] This compound, presumably a sodium salt, could not be isolated and work-up of the resulting solutions

generated an insoluble material that is probably a mixture of MoCpCl$_2$ and NaCl. We have now successfully generated pure MoCpCl$_2$ and investigated its reaction with Cl$^-$, which provides a clean route to an adduct that is believed to be related to the product of the sodium reduction of MoCpCl$_4$. The synthesis and the peculiar structure of this complex are described here.

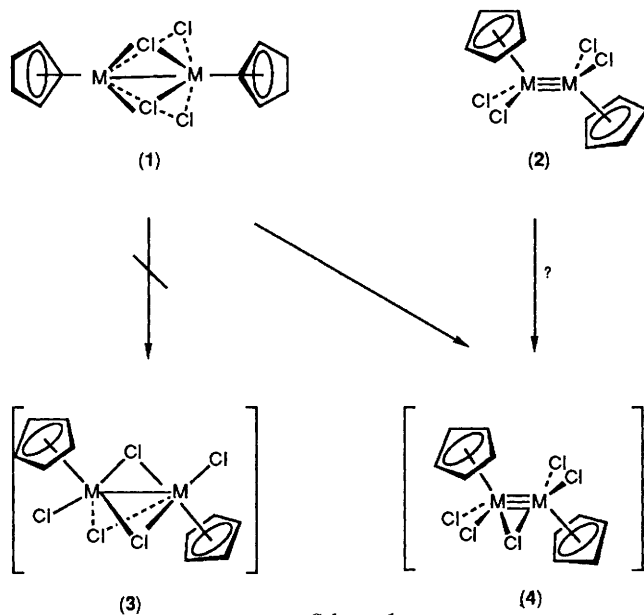The reduction of MoCpCl$_4$ with zinc powder (1 equiv.) proceeds smoothly and selectively at room temperature to produce insoluble 'MoCpCl$_2$' as a golden yellow microcrystal-
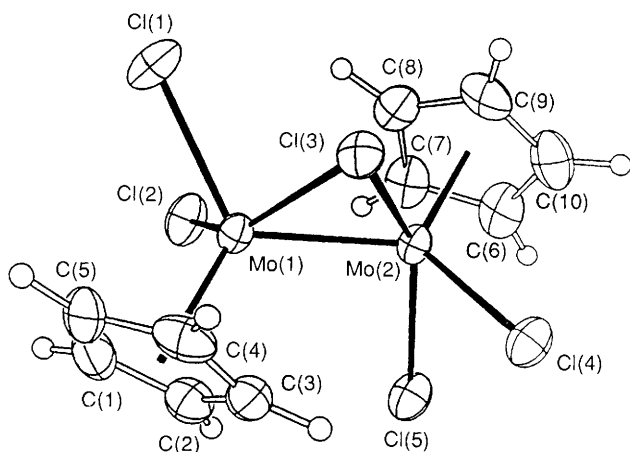
Figure 1. Structure of the anion from PPN[Mo₂Cp₂Cl₅]·THF.
Selected bond distances (Å) and angles (°): Mo(1)–Mo(2) 2.413(1),
Mo(1)–Cl(1) 2.460(3), Mo(1)–Cl(2) 2.422(2), Mo(1)–Cl(3) 2.436(2),
Mo(2)–Cl(3) 2.438(2), Mo(2)–Cl(4) 2.459(2), Mo(2)–Cl(5) 2.432(3),
CNT(1)–Mo(1) 2.039(9), CNT(2)–Mo(2) 2.036(9), Mo(1)–Cl(3)–
Mo(2) 59.3(1), CNT(1)–Mo(1)–Cl(1) 119.9(2), CNT(1)–Mo(1)–Cl(2)
106.7(2), CNT(1)–Mo(1)–Cl(3) 111.2(3), Cl(1)–Mo(1)–Cl(2) 83.4(1),
Cl(1)–Mo(1)–Cl(3) 81.1(1), Cl(2)–Mo(1)–Cl(3) 141.9(1), CNT(2)–
Mo(2)–Cl(3) 111.2(2), CNT(2)–Mo(2)–Cl(4) 122.3(2), CNT(2)–
Mo(2)–Cl(5) 105.5(3), Cl(3)–Mo(2)–Cl(4) 80.4(1), Cl(3)–Mo(2)–
Cl(5) 143.0(1), Cl(4)–Mo(2)–Cl(5) 83.7(1), P(1)–N–P(2) 143.2(4),
CNT(1)–Mo(1)–Mo(2)–CNT(2) 160.7. CNT = Cp ring centroid.

(1)   **(2)**

(3)   **(4)**

Scheme 1

line powder. The molybdenum product is easily separated
from ZnCl₂ since the latter remains dissolved in tetrahydrofu-
ran (THF), and a thorough washing affords analytically pure
material in high yields.† The MoCpCl₂ compound is insoluble
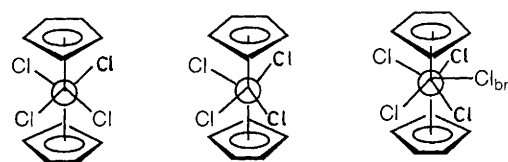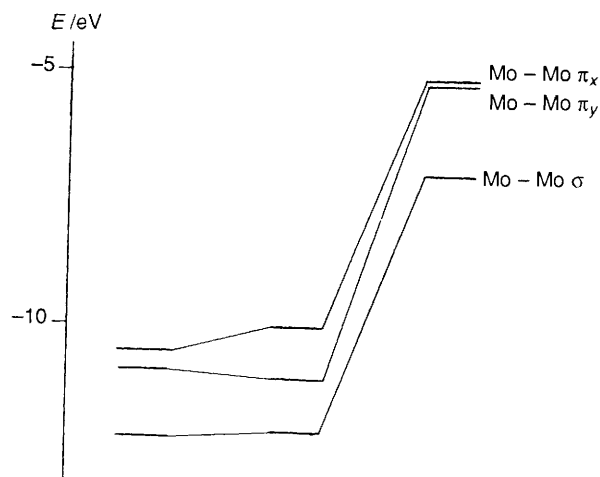
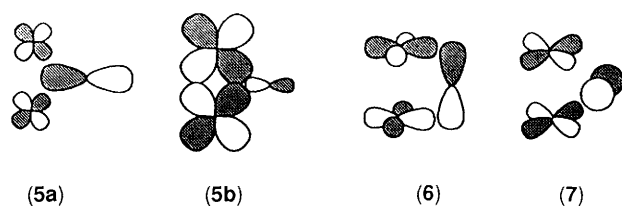**Figure 2.** Frontier region of the energy level diagram for (left to right)
the ideal unbridged Mo₂CpCl₄, the distorted isomer in which the
ligands are in the same positions as in the Cl⁻ adduct, and the actual
[Mo₂Cp₂Cl₅]⁻ anion.

in all common organic solvents, suggesting an oligomeric
formulation similar to that described for the TiCpCl₂[3] and
Ru(C₅Me₅)Cl₂[4] compounds of identical stoicheiometry.

MoCpCl₂ reacts smoothly with PPN⁺Cl⁻ [PPN⁺ =
(Ph₃P)₂N⁺] in CH₂Cl₂ to afford a brown solution from which
dark brown PPN⁺[Mo₂Cp₂Cl₅]⁻ crystallizes as a THF solvate
upon treatment with small amounts of THF and diffusion of
Et₂O.‡ Both ¹H and ¹³C NMR show a single resonance for the
cyclopentadienyl group. The structure of the product has been
established by X-ray crystallography.§ The THF solvate
molecule does not exhibit significant interactions with either
ion of the salt, and the PPN⁺ cation does not exhibit unusual
features. The anion (see Figure 1) contains two molybdenum
atoms that are bridged by a single chlorine atom and are at a
distance of 2.413(1) Å from each other. In addition, each Mo

(5a)   (5b)   (6)   (7)

atom is bonded to two terminal Cl atoms [av. Cl_t–Mo 2.443(3) Å] and to one η^5-C_5H_5 group. Although the ion does not have any crystallographically imposed symmetry, its ideal molecular symmetry is C_2, the two-fold axis passing through the bridging Cl atom and the middle of the Mo–Mo bond.

The short Mo–Mo distance clearly indicates strong metal–metal bonding. The fifteen-electron configuration of the metal allows a metal–metal triple bond to be formed. In this respect, this structure may be compared with that of $Mo_2(\eta^5$-$C_5H_4Pr^i)_2Cl_4$,[5] see structure (1) in Scheme 1 [only a single Mo–Mo bond can be formed, and the corresponding distance is 2.607(1) Å], and with that of the recently reported tungsten homologue, $W_2(\eta^5$-$C_5H_4Pr^i)_2Cl_4$,[6] structure (2) [with a triple W–W bond, formally similar to Chisholm's homoleptic dinuclear W^{III} alkoxides[7] and $W_2Cp_2(NMe_2)_4$[8]].

Fenske–Hall MO calculations[9] qualitatively agree with the bonding description shown in (4). The frontier region of the energy level diagram is shown in Figure 2. Calculations have been carried out on the ideal unbridged $Mo_2Cp_2Cl_4$ (left), on the distorted isomer where the ligands are in the same positions as in the Cl⁻ adduct (centre), and on the actual (idealized to C_2 symmetry) $[Mo_2Cp_2Cl_5]^-$ anion (right), in order to monitor the hypothetical interaction between the Mo–Mo triple bond and the bridging chloride ion in what may be described as a Lewis acid–base adduct of the two units. The three upper occupied MOs have a high contribution from metal orbitals and are, in increasing order, of σ, $\pi(yz)$, and $\pi(xz)$ type, where z is the metal–metal axis and y is the axis pointing from the centre of the metal–metal bond toward the bridging atom. The general increase in energy is caused by the introduction of a single negative charge in the system.

The main interactions of the bridging chlorine with the dimetal core are represented in (5)—(7). Structure (5) may be viewed as an interaction between a chlorine lone pair and one of the π components of the Mo–Mo triple bond. Since both of these orbitals are full, this is an overall destabilizing interaction. The in-phase combination (5a) has the major contribution from the chlorine lone pair and is found at −13.61 eV. The out-of-phase combination [(5b); mainly metal–metal π bonding] is destabilized with respect to the unbridged species, but it still represents a strong metal–metal interaction. The other two interactions (6) and (7) involve empty metal orbitals and are stabilizing in character. Since they are a basis for the same irreducible representation of the C_2 symmetry group, they mix to give rise to two new Cl–Mo_2 bonding orbitals, each containing a partial contribution from both, at −13.10 and −12.86 eV.

From a qualitative point of view, the energetic difference between structures (1) and (2) can be related to the difference between two metal–metal π bonds and four metal–chlorine (bridging) bonds (more precisely, the difference between the energetics of eight Mo–Cl_b bonds and four Mo–Cl_t bonds, corrected for any steric strain caused by the formation of the bridge system, should be considered). In the molybdenum case the Mo–Cl bonds dominate the situation, whereas in the tungsten case the strength of the two metal–metal π bonding components prevails. This is in line with the known tendency of heavier elements in a group of transition metals to form metal–metal bonds.[10] In forming the adduct with Cl⁻, the molybdenum dimer prefers to rearrange in order to maximize the metal–metal bonding, rather than assume the alternative isomeric structure with the maximum number of Mo–Cl bonds and a single Mo–Mo bond, i.e. $[CpClMo(\mu$-$Cl)_3MoClCp]^-$, structure (3). It is likely that the increased negative charge at the metals upon formation of the anionic adduct expands the metal orbitals and results in a stronger metal–metal interaction. The energetic difference between structures (1) and (2) must be very small. Since tungsten forms stronger metal–metal bonds than molybdenum, we predict that the interaction between $W_2Cp_2Cl_4$ and Cl⁻ will also result in a compound of structure (4). Structure (3) would be more favourable (most likely only for molybdenum) when electron-withdrawing substituents on the Cp ring are present, or when the Cl ligands are replaced by more electronegative groups (F, perfluorinated alkoxide, etc.).

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