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

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The novel $[\text{Mo}_2\text{Cp}_2\text{Cl}_5]^-$ ion ($\text{Cp} = \text{C}_5\text{H}_5$), obtained as the salt of the bis(triphenylphosphine)iminium (PPN) cation on reacting MoCpCl_2 with PPN^+Cl^- in CH_2Cl_2 , contains two equivalent molybdenum centres at a distance of 2.413(1) Å, which are bonded to two terminal Cl atoms and one $\eta^5\text{-C}_5\text{H}_5$ 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 $\text{M}_2(\eta^5\text{-C}_5\text{H}_4\text{Pri})_2\text{Cl}_4$ ($\text{M} = \text{Mo}$: quadruply-bridged, Mo–Mo single bond; $\text{M} = \text{W}$: unbridged, W–W triple bond).

We have recently reported synthetic and structural studies on seventeen-electron $\text{Mo}^{\text{III}}\text{-Cp}$ ($\text{Cp} = \text{C}_5\text{H}_5$) derivatives of formula MoCpX_2L_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; 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-

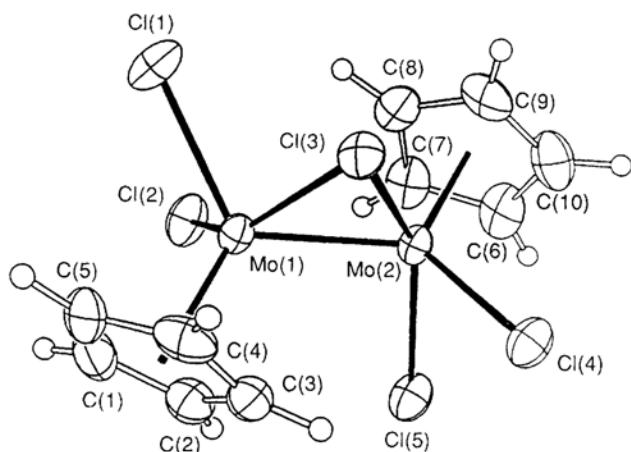


Figure 1. Structure of the anion from $\text{PPN}[\text{Mo}_2\text{Cp}_2\text{Cl}_5]\cdot\text{THF}$. Selected bond distances (Å) and angles ($^\circ$): Mo(1)–Mo(2) 2.413(1), Mo(1)–Cl(1) 2.460(3), Mo(1)–Cl(2) 2.422(2), Mo(1)–Cl(3) 2.436(2), Mo(2)–Cl(3) 2.438(2), Mo(2)–Cl(4) 2.459(2), Mo(2)–Cl(5) 2.432(3), 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.

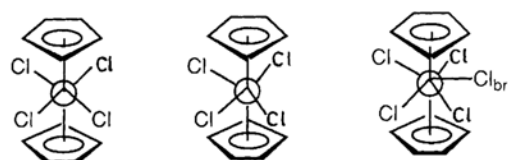
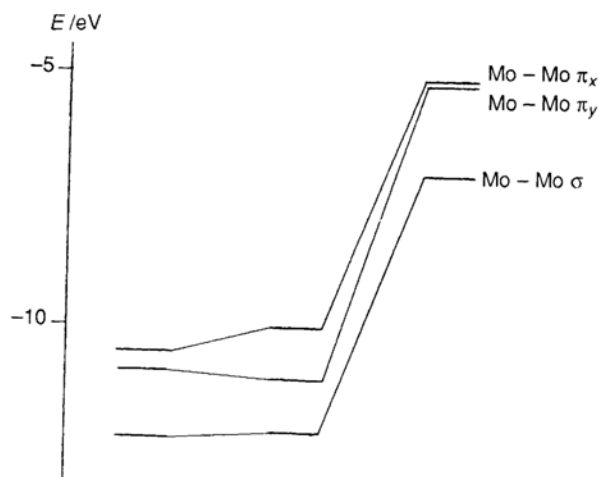
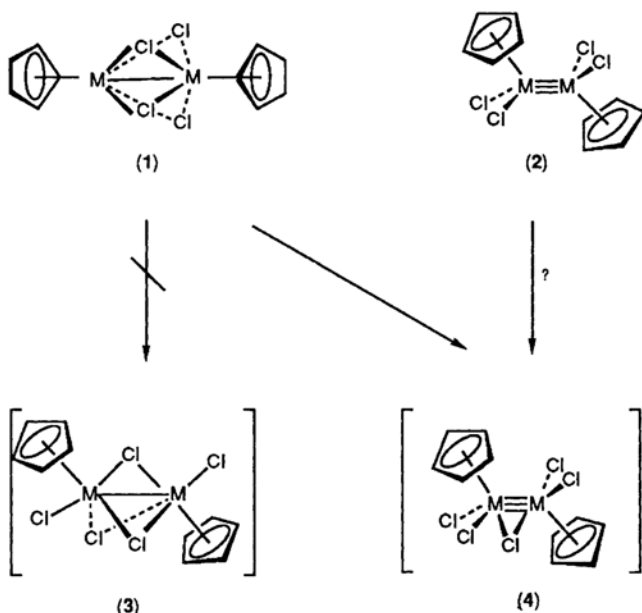


Figure 2. Frontier region of the energy level diagram for (left to right) the ideal unbridged $\text{Mo}_2\text{Cp}_2\text{Cl}_4$, the distorted isomer in which the ligands are in the same positions as in the Cl^- adduct, and the actual $[\text{Mo}_2\text{Cp}_2\text{Cl}_5]^-$ anion.



Scheme 1

line powder. The molybdenum product is easily separated from ZnCl_2 since the latter remains dissolved in tetrahydrofuran (THF), and a thorough washing affords analytically pure material in high yields.[†] The MoCpCl_2 compound is insoluble

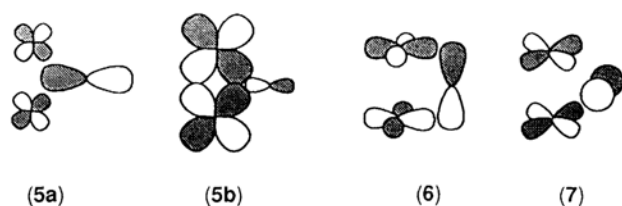
[†] MoCpCl_2 (2.21 g, 7.31 mmol) and Zn powder (0.48 g, 7.3 mmol) were suspended in THF (50 ml). The mixture was stirred at room temperature for ca. 20 h, during which time a pale brown precipitate replaced the partially dissolved red MoCpCl_2 , while the metallic zinc was completely consumed. The product was filtered, washed thoroughly with THF to remove the soluble ZnCl_2 by-product, and dried *in vacuo*. Yield 1.46 g (86%). Satisfactory elemental analyses (C, H) were obtained for $\text{C}_5\text{H}_5\text{Cl}_2\text{Mo}$.

in all common organic solvents, suggesting an oligomeric formulation similar to that described for the TiCpCl_2 ³ and $\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}_2$ ⁴ compounds of identical stoichiometry.

MoCpCl_2 reacts smoothly with PPN^+Cl^- [$\text{PPN}^+ = (\text{Ph}_3\text{P})_2\text{N}^+$] in CH_2Cl_2 to afford a brown solution from which dark brown $\text{PPN}^+[\text{Mo}_2\text{Cp}_2\text{Cl}_5]^-$ crystallizes as a THF solvate upon treatment with small amounts of THF and diffusion of Et_2O .[‡] Both ^1H and ^{13}C 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

[‡] Selected data for $\text{C}_{50}\text{H}_{48}\text{Cl}_5\text{Mo}_2\text{NP}_2\text{O}$: satisfactory elemental analyses (C, H, Cl) were obtained; ^1H NMR ($[\text{D}_6]\text{acetone}$) δ 7.71–7.55 (m, 30H, PPN^+), 5.95 (s, 10H, Cp), 3.61 (m, 4H, THF), 1.78 (m, 4H, THF); ^{13}C NMR ($[\text{D}_6]\text{acetone}$) δ 106.2 (Cp); IR (Nujol mull, cm^{-1}) 3110w, 3100w, 1590w, 1435s, 1415w, 1315s, 1305s, 1295s, 1285s, 1270s, 1180w, 1165w, 1115s, 1060m, 1020m, 995m, 840m, 820m, 800m, 755m, 720s, 695s, 545s, 535s, 495m.

[§] Crystal data for $\text{PPN}^+[\text{Mo}_2\text{Cp}_2\text{Cl}_5]^- \cdot \text{THF}$: $\text{C}_{50}\text{H}_{48}\text{Cl}_5\text{Mo}_2\text{NOP}_2$, monoclinic, space group $P2_1/c$, $a = 15.978(3)$, $b = 8.939(2)$, $c = 34.137(8)$ Å, $\beta = 94.61(3)^\circ$, $U = 4860(2)$ Å³, $Z = 4$, $D_c = 1.432$ g cm^{-3} , $\mu(\text{Mo}-\text{K}\alpha) = 8.83$ cm^{-1} . Of 9321 data collected (Nicolet R3m, $T = 293\text{K}$, $4 \leq 2\theta \leq 50^\circ$), 8557 were independent and 5106 were observed [$F_o \geq 5\sigma(F_o)$]. With all non-hydrogen atoms anisotropic, hydrogen atoms idealized isotropic contributions and phenyl rings constrained to planar, hexagonal geometry: $R = 5.09\%$, $R_w = 5.75\%$, $\text{GOF} = 1.310$, $\Delta(\rho)_{\text{max}} = 0.64$ e Å⁻³, and $N_o/N_v = 10.7$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



atom is bonded to two terminal Cl atoms [av. Cl–Mo 2.443(3) Å] and to one η^5 -C₅H₅ group. Although the ion does not have any crystallographically imposed symmetry, its ideal molecular symmetry is C₂, 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 Mo₂(η^5 -C₅H₄Pr)₂Cl₄,⁵ 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, W₂(η^5 -C₅H₄Pr)₂Cl₄,⁶ structure (2) [with a triple W–W bond, formally similar to Chisholm's homoleptic dinuclear W^{III} alkoxides⁷ and W₂Cp₂(NMe₂)₄].⁸

Fenske–Hall MO calculations⁹ 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 Mo₂Cp₂Cl₄ (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 C₂ symmetry) [Mo₂Cp₂Cl₅][–] 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 C₂ symmetry group, they mix to give rise to two new Cl–Mo₂ 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(μ -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 W₂Cp₂Cl₄ 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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