Preliminary communication

Crystal and molecular structure of (μ-η^2,η^3-propargyl)-bis(cyclopentadienyl)tetracarbonyldimolybdenum tetrafluoroborate and (μ-η^2,η^3-1,1-dimethylpropargyl)-bis(cyclopentadienyl)tetracarbonyldimolybdenum tetrafluoroborate

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Abstract

An X-ray study of $[(\mu\text{-}\eta^2,\eta^3\text{-HC}\equiv\text{CCH}_2)\text{Cp}_2\text{Mo}_2(\text{CO})_4]^+(\text{BF}_4^-)$ (1) and $[(\mu\text{-}\eta^2,\eta^3\text{-HC}\equiv\text{CCMe}_2)\text{-}$ $\text{Cp}_2\text{Mo}_2(\text{CO})_4]^+(\text{BF}_4^-)$ (2) reveals their structures to be similar to the structure of neutral compounds of the series $(\mu\text{-}\eta^2,\eta^2\text{-RC}\equiv\text{CR})\text{Cp}_2\text{Mo}_2(\text{CO})_4$, the difference between 1 and 2 being mainly due to the markedly different Mo–C$^+$ bond lengths, which accounts for different stability and fluxional behavior of these compounds in solution.

The nature of carbocationic centre (i.e. the number of alkyl substituents at it) in metal-stabilized carbocations has long been known to exert a marked effect on the stability [1,2] and the rotation barrier around the C–C$^+$ bond [3]. However, the influence of the nature of the carbocationic centre on the molecular geometry and, in particular, on the C$^+$–metal distance has not been hitherto observed. The present paper contains preliminary results of an X-ray study of tetrafluoroborates $[(\mu\text{-}\eta^2,\eta^3\text{-}$ $\text{HC}\equiv\text{CCH}_2)\text{Cp}_2\text{Mo}_2(\text{CO})_4]^+(\text{BF}_4^-)$ (1) and $[(\mu\text{-}\eta^2,\eta^3\text{-HC}\equiv\text{CCMe}_2)\text{Cp}_2\text{Mo}_2\text{-}$ $(\text{CO})_4]^+(\text{BF}_4^-)$ (2) with either primary or tertiary alkynyl ligands †. The molecular geometry of 2 is shown in Fig. 1. Structures of cations 1 [4*] and 2 are in most respects similar to the structures of neutral compounds of the type $(\mu\text{-}\eta^2,\eta^2\text{-}$ acetylene)$\text{Cp}_2\text{Mo}_2(\text{CO})_4$ (acetylene = C_2H_2, 3; C_2Et_2, 4; C_2Ph_2, 5 [5]). In the Mo_2C_2 tetrahedral core of the cations 1 and 2 the plane C(1)–C(2)–Mo(1–2) [6*] is almost exactly normal to the Mo(1)–Mo(2) vector; the C(1)–C(2) distances are nearly equal and close to those for 3–5. The Mo–Mo distance of 2.982(2) Å in the tertiary ion 2 is equal to that in 3–5 [5]. Though this bond is somewhat longer in the primary ion 1 (3.021(1) Å) it still remains far shorter than 3.117(1) Å observed for $(\mu\text{-}\eta^2,\eta^2\text{-allene})\text{Cp}_2\text{Mo}_2(\text{CO})_4$ (6) [7]. It is noteworthy that the geometries of acetylenic complexes 3–5 and allenic complex 6 are markedly different [5,7]. The
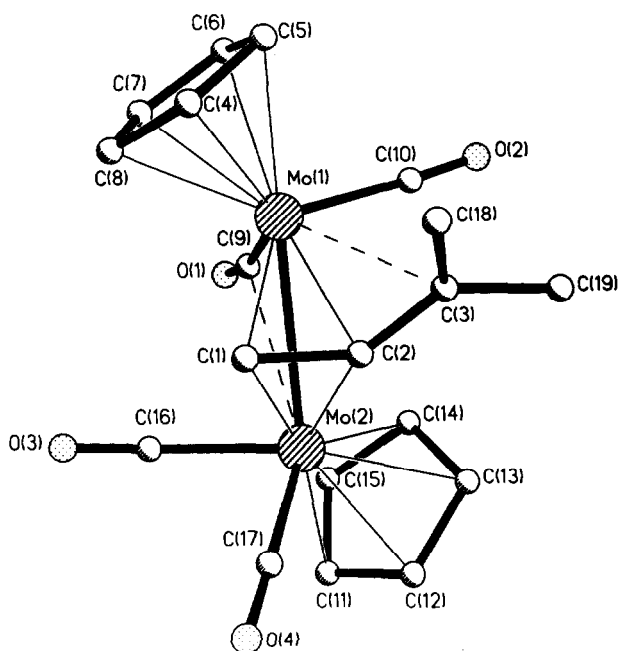
Fig. 1. The structure of cation **2**; selected interatomic distances (Å) and angles (°) (the first value refers to cation **1**, the second value refers to cation **2**). Mo(1)–Mo(2) 3.021(1), 2.982(2); Mo(1)–C(1) 2.216(5), 2.16(1); Mo(1)–C(2) 2.257(5), 2.29(1); Mo(2)–C(1) 2.153(4), 2.18(1); Mo(2)–C(2) 2.110(5), 2.12(1); C(1)–C(2) 1.353(8), 1.39(2); C(2)–C(3) 1.347(8), 1.38(2); C(9)–O(1) 1.158(7), 1.16(2); C(10)–O(2) 1.122(7), 1.14(2); C(16)–O(3) 1.104(7), 1.14(2); C(17)–O(4) 1.139(6), 1.14(2); Mo(2)–C(9) 2.884(6), 2.82(2); C(1)–C(2)–C(3) 136.4(6), 136(1); Mo(1)–C(9)–O(1) 169.1(5), 168(1).

primary ion **1** can be obtained by hydride abstraction both from (μ-η^2,η^2-HC≡CCH$_3$)Cp$_2$Mo$_2$(CO)$_4$ (**7**), and from **6** [8]. Thus, while the geometry of pro-pargyl cation is intermediate between acetylenic and allenic structures [9–11], the geometry of the coordinated propargyl cation **1** is closer to "coordinated acetylene" (structures **3–5**), than to "coordinated allene" (structure **6**). A certain similarity between the structures of **1** and **6** is likely to be associated with virtually indis-tinguishable distances C(1)–C(2) 1.353(8) and C(2)–C(3) 1.347(8) Å in cation **1** and C–C bond lengths in the allenic ligand of **6** equal to 1.44(2) and 1.41(1) Å [7].

A decrease of the C(2)–C(3) distance in cations **1** and **2** in comparison with the standard value of 1.431 Å for the C(sp)–C(sp^2) bond [12] and exceptionally strong shortening of the Mo(1)–C(3) bond down to 2.439(6) in **1** and 2.75(1) Å in **2** [13*] reveal that acetylenic ligands undergo a transformation from the usual μ-η^2,η^2-type (which is characteristic of the carbocation precursor complex) to the μ-η^2,η^3-type present in the carbocations under study. The η^3- and η^1,η^3-allylic complexes are probably the most close analogs of the compounds under consideration. Indeed, the substitution of hydrogen atoms by alkyl groups usually does result in an increase of the metal–CHAlk(allyl) or metal–CAlk$_2$(allyl) distances in mononuclear η^3-allyl complexes [14–16] and binuclear η^1,η^3-allyl complexes [17–19], but even in compounds with configurations that are strongly distorted towards η^1 this distance is never longer than 2.67 Å [20]. The Mo(1)–C(3) distance is shorter than the corresponding W–C distance (2.837 Å) in the tungsten analog of **2** [21]. The difference between the Mo(1)–C(3) distances in **1** and **2** is associated with different dihedral angles C(3)–C(2)–C(1)/C(2)–C(1)–Mo(1–2) which are equal to 82.4 in **1** and 64.5° in **2**.

The planar trigonal configuration at the C(3) atom exhibits a slight pyramidal distortion, the C(3) atom being displaced from the C(3)–H(31)–H(32) plane by 0.08(1) in **1** and from the C(3)–C(18)–C(19) plane by 0.13(1) Å in **2**.

In both cations one of the carbonyl ligands at the Mo(1) atom bonded to the cationic centre is semibridging. The angles Mo(1)–C(9)–O(1) are equal in **1** and **2**, and the same as found for corresponding parameters in **3–5** [5].

Cyclopentadienyl ligands are approximately in *anti*-conformation, the torsion angle Q(1)–Mo(1)–Mo(2)–Q(2) [22*] is decreased from 166.2 in **1** to 148.8° in **2**, while in the neutral complexes **3–5** this angle is increased from 148.4 in **3** to 164° in **5**.

In conclusion it should be noted that the structural features of "coordinated acetylene" observed in cations **1** and **2** help to understand why acetylenic (and not allenic) compounds are formed in reactions with nucleophiles [23]. The smaller Mo(1)–C(3) distance in cation **1** implies stronger bonding and, as a consequence, higher stability of **1** in comparison with **2**. The values of pK_{R^+} (in 50% aqueous acetonitrile) measured for carbinol–cation equilibrium show that the stability of cations **1** and **2** is comparable to that of cyclopropenyl cations [24], pK_{R^+} for **1** is equal to 4.82 ± 0.06, while for **2**, in agreement with structural data, pK_{R^+} does not exceed ∼ 3.1.

Both cations are stereochemically non-rigid. An intramolecular dynamic process occurring in solution [25*] leads to interconversion of Mo(1) and Mo(2), Cp(1) and Cp(2), and two pairs of carbonyl groups [5], and is accompanied by synchronous rotation of propargyl ligand around the C(1)–C(2) bond. The rotation angle is equal to the doubled dihedral angle C(3)–C(2)–C(1)/C(2)–C(1)–Mo(1–2), i.e. 164.8° for cation **1**, and 129° for cation **2**. The $\Delta G^{\ddagger}_{183}$ value (T_c = 183 K) was found to be 9.87 ± 0.3 kcal/mol for **2**, and 17.47 ± 0.64 kcal/mol for **1** [26*], which again reflects the difference in the structures of cations **1** and **2**.

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