Cluster Complex Formation from the Sulphur-induced Disproportionation of a Mo≡Mo Triple Bond. The Structure of $[(\eta^5\text{-}C_5H_5)_3Mo_3(CO)_6S][\eta^5\text{-}C_5H_5)Mo(CO)_3]$

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Summary Elemental sulphur reacts with $Cp_2Mo_2(CO)_4$ ($Cp = \eta^5\text{-}C_5H_5$) to give the salt, $[Cp_3Mo_3(CO)_6S][CpMo(CO)_3]$, the structure of which was determined by *X*-ray crystallography.

INTEREST in reductive hydrogenation of carbon monoxide has focused attention on metal clusters[1] and on complexes of early transition metals.[2] However, carbonyl clusters of the early transition elements are extremely rare compared with the number of such complexes of the later transition metals. In view of the high reactivity of the Mo≡Mo triple bond in $Cp_2Mo_2(CO)_4$ (**1**) towards both electrophilic and nucleophilic reagents,[3] and in view of the tendency of sulphido-ligands to promote cluster formation,[4] it was of interest to investigate the reaction of elemental sulphur with (**1**).

When (**1**) is allowed to react with excess of sulphur, a variety of non-carbonyl containing sulphides, $Cp_2Mo_2S_x$, are obtained. These solids are insoluble in all common solvents and appear to be similar to those obtained from the reaction of sulphur with $Cp_2Mo_2(CO)_6$.[5] However, when one equivalent of sulphur in acetone solution was slowly added to a stirred solution of (**1**) under N_2, then no CO was evolved and a red-black solid precipitated. Recrystallization from acetone–CH_2Cl_2 afforded crystals, decomp. 200 °C, in *ca.* 50% yield. The i.r. spectrum of the product displays bands normal for η^5-C_5H_5 and ν_{CO} frequencies at 1995, 1970, 1950, 1910 (sh), 1892, 1880 (sh), 1785, and 1760, cm^{-1} (KBr disc).

The nature of the product was established by single-crystal *X*-ray diffraction† to be a salt composed of the cluster cation, $Cp_3Mo_3(CO)_6S^+$ (**2**), and the anion, $CpMo(CO)_3^-$ (**3**). The i.r. bands at 1880, 1785, and 1760 cm^{-1} may be attributed to the anion and the remainder to the cation (**2**). The cluster (**2**) appears to be the first homonuclear, molybdenum carbonyl cluster,[6] and is formed from a sulphur-mediated disproportionation of two, triply bonded dimers into a trimer and a monomer with an accompanying electron transfer.‡

$[Cp_2Mo_2(CO)_4]$ (**1**)

$[Cp_3Mo_3(CO)_6S]^+$ (**2**)

$[CpMo(CO)_3]^-$ (**3**)

$[Cp_3Mo_3S_4]^+$ (**4**)

Cp = η^5-C_5H_5

The structural parameters of the anion (**3**) are essentially identical to those previously reported.[7,8] A view of the cation (**2**), which exhibits near-C_3-symmetry, is shown in the Figure. The S-atom sits above the Mo_3 plane, and the carbonyls are divided into two sets, equatorial and axial. The latter set are bonded opposite the bridging sulphur. The equatorial carbonyls show some interaction with the adjacent Mo-atom and may be classed as barely semi-bridging (the average M–C–O_{eq} angle is 168 ± 1° *vs.* 176 ± 2° for M–C–O_{ax}).[9,10] The three Mo–Mo distances in (**2**) are 3·106(2), 3·085(2), and 3·064(2) Å (3·085 ± 0·021 Å average). The Mo–S distances are all equal and have an average length of 2·360 ± 0·004 Å. Both the Mo–Mo and Mo–S bonds are longer than those in a related cluster, $Cp_3Mo_3S_4^+$ (**4**),[11] which has *d*(Mo–Mo) = 2·812 and *d*(Mo–S) = 2·293 and 2·314 Å for doubly and triply bridging sulphur, respectively. In (**4**), each Mo^{IV} has the d^2 configuration and can form electron-pair bonds to each other. In (**2**), the Mo^{II} atoms supply more electrons than necessary to form electron-pair bonds in the Mo_3-triangle.

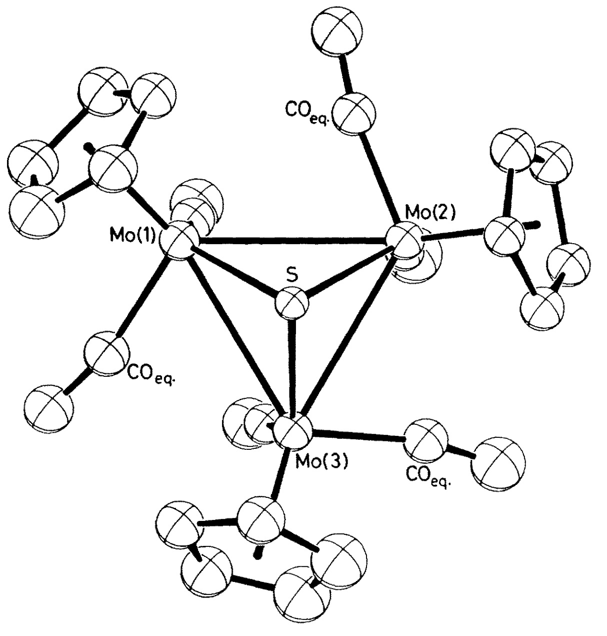

FIGURE. View down the approximate C_3-axis of the $Cp_3Mo_3(CO)_6S^+$ cation (**2**).

A qualitative MO scheme, based on the frontier orbitals of the $CpMo(CO)_2$ fragment,[12] suggests that the $Cp_3Mo_3(CO)_6$ moiety forms five bonding MOs ($3a + e$) and seven anti-bonding MOs ($a + 3e$). The 3p-orbitals $(a + e)'$ of the capping sulphur atom then interact to give seven bonding ($3a + 2e$), two approximately non-bonding (e), and six anti-bonding MOs ($2a + 2e$). The electrons in the Mo_3S core then fill all bonding levels plus the non-bonding *e*-levels. Several of the bonding MOs are highly delocalized over the entire cluster so that a clean separation into Mo–Mo and Mo–S bonding is impossible.

The greater Mo–Mo and Mo–S distances in (**2**) *vis-a-vis* (**4**) could be explained by assuming the 'non-bonding' *e*-levels are actually slightly anti-bonding, leading to Mo–Mo and Mo–S bond orders less than unity in (**2**). However, the Mo–Mo distances in (**2**) are commensurate with Mo–Mo single bond lengths in a variety of Cp_2Mo_2 compounds.[9,13] The Mo atoms in (**2**) have the 18-electron count whereas those in (**4**) have only 16 electrons and are co-ordinatively unsaturated. Hence, S → Mo π-donation, known to cause

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† The structure was solved by the Patterson method and subsequent difference maps. The current *R*-value is 0·051 based on refinement with all atoms anisotropic except nine C-atoms using 2542 reflections with $I > 3\sigma(I)$. *Crystal data:* $C_{29}H_{20}Mo_4O_9S$, triclinic, space group $P\bar{1}$, $M = 928$, $a = 13{\cdot}564(4)$, $b = 14{\cdot}361(4)$, $c = 7{\cdot}857(3)$ Å, $\alpha = 93{\cdot}79(3)$, $\beta = 95{\cdot}29(3)$, $\gamma = 99{\cdot}25(2)$, $U = 1499(1)$ Å^3; $D_c = 2{\cdot}06$, $D_m = 2{\cdot}1$ g cm^{-3}; $Z[Cp_4Mo_4(CO)_9S] = 2$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ There are nine CO groups per 4 Mo-atoms in the product, but only 8 CO per 4 Mo in the starting dimers. Thus, a carbonyl-poor fraction must also be produced. This fraction has been isolated, but not identified.

both M–M and M–S bond contraction,[14] is postulated to be a more important bonding feature in (**4**)

The potential of utilizing the unsaturated Mo≡Mo triple bond in (**1**) to form carbonyl clusters has been realized Recent results, to be reported elsewhere, also show that Mo_3, Mo_4, and Mo_6 clusters are formed from the reaction of (**1**) and hydridic reducing agents [15]

This work was supported by the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation

(*Received*, 8*th July* 1980, *Com* 742)

[1] E L Muetterties, *Bull Soc Chim Belg*, 1974 **84** 959, E L Muetterties, T N Rhodin, E Band, C F Brucker, and W R Pretzer, *Chem Rev*, 1979, **79**, 91, A K Smith and J M Basset, *J Mol Catal*, 1977, **2**, 229, G Henrici-Olive and S Olive, *Angew Chem*, *Int Ed Engl*, 1976, **15** 136, W Parshall *J Mol Catal*, 1978 **4**, 1, R G Bergman, *Acc Chem Res*, 1980, **13**, 113

[2] J C Huffmann, J G Stone, W C Krusell ,and K G Caulton, *J Am Chem Soc*, 1977, **99**, 5829, L I Shoer and J Schwarz, *ibid*, p 5831, K S Wong, W R Scheidt, and J A Labinger, *Inorg Chem*, 1979, **18**, 136

[3] M D Curtis and R J Klingler *J Organomet Chem* 1978, **161**, 23

[4] H Vahrenkamp, *Angew Chem*, *Int Ed Engl* 1975 **14**, 322

[5] M R Dubois, D L Dubois, M C Vanderveer, and R C Haltiwanger, Paper No 131, Abstracts, Division of Inorganic Chemistry, American Chemical Society, 179th Nat Meeting 1980 See also M R Dubois, R C Haltiwanger, D J Miller, and G Glatzmeier, *J Am Chem Soc*, 1979, **101**, 5245

[6] P J Vergamini, H Vaherkamp, and L F Dahl, *J Am Chem Soc*, 1971, **93**, 6236, have reported a mixed metal cluster incorporating the $CpMo(CO)_2$ group

[7] D L Crotty, E R Corey, I J Anderson, M D Glick, and J P Oliver, *Inorg Chem*, 1977, **16**, 920

[8] M A Adams, K Folting, J C Huffman and K G Caulton *Inorg Chem*, 1979, **18**, 3020

[9] M D Curtis, K R Han, and W M Butler, *Inorg Chem*, 1980, **19**, 2096, R J Klingler, W M Butler, and M D Curtis, *J Am Chem Soc*, 1978, **100**, 5034

[10] F A Cotton, L Kruczynski, and B A Frenz *J Organomet Chem*, 1978, **160**, 93

[11] P J Vergamini, H Vahrenkamp, and L F Dahl, *J Am Chem Soc*, 1971, **93**, 6327

[12] E D Jemmis, A R Pinhas, and R Hoffmann, *J Am Chem Soc*, 1980, **102**, 2576

[13] R D Adams, D M Collins, and F A Cotton, *Inorg Chem*, 1974, **13**, 1086, M H Chisholm, F A Cotton, M W Extine, and L A Rankel, *J Am Chem Soc*, 1978, **100**, 807

[14] E I Stiefel, *Progr Inorg Chem*, 1977, **22**, 3, B Spivak and Z Dori, *Coord Chem Rev*, 1975, **17**, 99

[15] M D Curtis and K R Han, unpublished results