μ_3-Arsenic Trimolybdenum Clusters with Oxygen and Sulphur bridging the Transition Metals

Hans-Peter Neumann and Manfred L. Ziegler*

Anorganisch-Chemisches Institut der Universität Heidelberg, D-6900 Heidelberg, West Germany

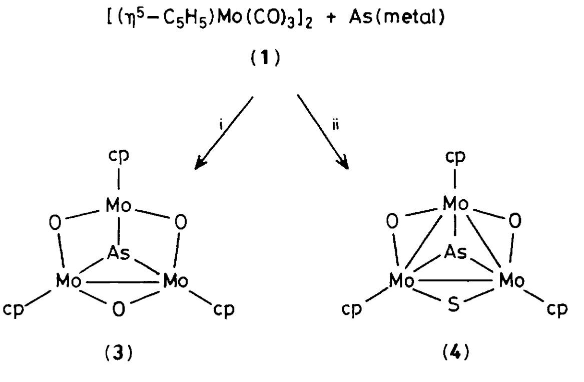
$[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (**1**) reacts with grey arsenic in boiling water-saturated toluene to produce the new trioxocluster $[\mu_3\text{-}As(\mu\text{-}O)_3\{(\eta^5\text{-}C_5H_5)Mo\}_3]$ (**3**), while reaction of As_4S_4, (**1**), and grey arsenic under the same conditions yields $[\mu_3\text{-}As(\mu\text{-}O)_2(\mu\text{-}S)\{(\eta^5\text{-}C_5H_5)Mo\}_3]$ (**4**); *X*-ray structure analyses were performed for both products.

In spite of the growing interest[1] complexes containing oxo ligands as well as cyclopentadienyl ligands are rare. In this communication we present two examples of such species. Earlier we reported the reaction of bis(tricarbonylcyclopentadienylmolybdenum)(*Mo–Mo*) (**1**) with grey arsenic to give $[\mu_3\text{-}As\{(\eta^5\text{-}C_5H_5)Mo(CO)_2\}_3]$ (**2**) and $[\mu,\eta^2\text{-}As_2\{(\eta^5\text{-}C_5H_5)Mo(CO)_2\}_2]$, and the reactivity of (**2**).[2–4] Here we present results of our studies of the reactivity of (**1**).

Refluxing a suspension of grey arsenic and (**1**) in water-saturated toluene instead of dry toluene produces the new μ_3-arsenic trimolybdenum cluster (**3**) instead of (**2**). If (**1**) and arsenic are heated together in water-saturated toluene for 24 h and then As_4S_4 is added and the mixture refluxed for a further 24 h, the cluster (**4**) is formed (Scheme 1). Depending on the reaction time and exclusion of air, yields were up to 30% (**3**) and 15% (**4**), with respect to (**1**). In both cases unreacted (**1**), $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4](Mo{\equiv}Mo)$, $[\mu,\eta^2\text{-}As_2\{(\eta^5\text{-}C_5H_5)Mo(CO)_2\}_2]$, and two as yet uncharacterized trace products were also isolated. Although As_4S_4 is a good starting material for the introduction of additional sulphur and/or arsenic atoms

$[\mu_3\text{-As}\{(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2\}_3]$

(2)



Scheme 1. cp = cyclopentadienyl. *Reagents and conditions*; i, H_2O, toluene, heat; ii, H_2O–As_4S_4, toluene, heat.

into organometallic compounds,[5] in this case only an oxygen–sulphur exchange or CO-substitution by sulphur instead of oxygen takes place. Attempts to synthesize (**4**) or a sulphido cluster analogue of (**3**) by treating (**3**) with As_4S_4 were without success; only decomposition products were obtained. Addition of S_8 or molecular oxygen to the suspension of arsenic and (**1**) in dry toluene led to $[(\eta^5\text{-C}_5\text{H}_5)\text{MoS}_x]_n$[6] or uncharacterized decomposition products, respectively. Compounds comparable to (**4**) would be the tri-μ-sulphido species $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}_3\text{S}_4]^+$,[7] $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}_3\text{S}_4]$,[8] and $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{-Mo}_2\text{MS}_4]$ (M = Mo or W).[9] Tri-μ-oxoclusters, particularly mixed μ-oxo-,μ-sulphido-clusters, such as (**3**) and (**4**) are rare. A compound similar to (**3**) can be seen in the dication $[\text{Re}_3\text{O}_6(\eta^5\text{-C}_5\text{H}_5)_3]^{2+}$.[10]

The ^{1}H n.m.r. spectra of (**3**) and (**4**) (60 MHz, $CDCl_3$, 23 °C) are quite simple with shift values for the cyclopentadienyl hydrogens of δ 5.83(s) for (**3**) and δ 5.63 (s, 10H) and 5.83 (s, 5H) for (**4**). The electron impact mass spectra show the typical isotopic pattern for three molybdenum atoms at *m*/*z* 606 (M^+) (**3**) and 622 (M^+) (**4**).

The structures have been determined by single *X*-ray techniques.[†] There is no crystallographic 3-fold axis present within (**3**) but there is a mirror plane passing through As, Mo(2), O(2), C(6), and C(11). The three cyclopentadienyl–molybdenum moieties are positioned at the vertices of an equilateral triangle and linked to each other by direct metal–metal bonds, a

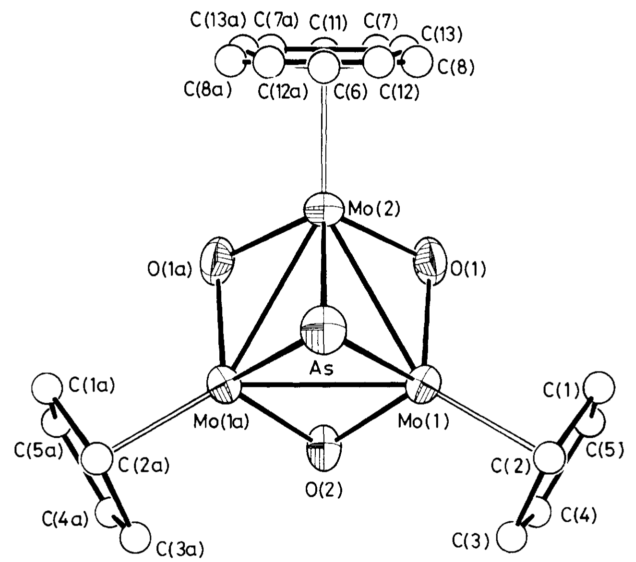


Figure 1. ORTEP plot of (**3**) showing atomic labelling scheme, and the disorder in one of the cyclopentadienyl rings. Selected bond lengths and angles: Mo(1)–Mo(2) 2.667(2), Mo(1)–Mo(1a) 2.664(2), Mo(1)–As 2.437(2), Mo(2)–As 2.467(2), Mo(1)–O(1) 1.950(9), Mo(1)–O(2) 1.933(7), Mo(2)–O(1) 1.931(7), Mo–C(cyclopentadienyl) a.v. 2.38 Å; Mo(1)–Mo(1a)–Mo(2) 60.0(0), Mo(2)–Mo(1)–Mo(1a) 59.9(1), Mo(1)–Mo(2)–O(1) 46.3(2), Mo(1)–Mo(1a)–O(2) 46.4(2), O(1)–Mo(1)–Mo(2) 86.8(3), O(2)–Mo(1)–Mo(1a) 81.1(4)°. Thermal ellipsoids correspond to 50% probability.

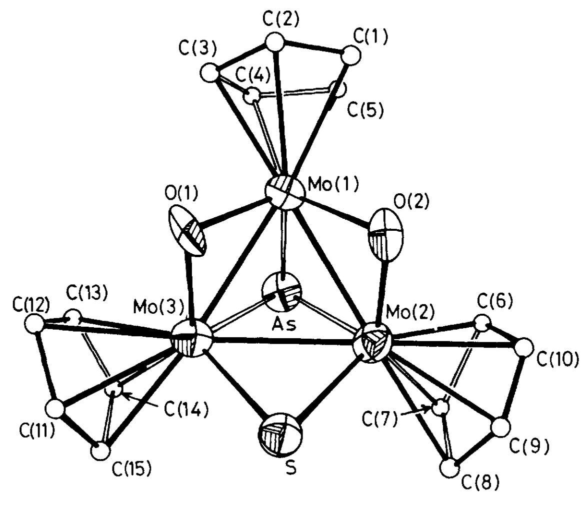


Figure 2. ORTEP plot of (**4**) showing atomic labelling scheme. Selected bond lengths and angles: Mo(1)–Mo(2) 2.687(4), Mo(1)–Mo(3) 2.666(5), Mo(2)–Mo(3) 2.809(5), Mo(1)–O(1) 1.88(2), Mo(1)–O(1) 1.91(2), Mo(2)–O(2) 1.94(2), Mo(1)–S 2.28(1), Mo(3)–O(1) 1.93(2), Mo(1)–S 2.29(2), Mo–As av. 2.47(1), Mo–C(cyclopentadienyl) av. 2.34 Å; Mo(1)–Mo(3)–Mo(2) 63.3(1), Mo(2)–Mo(3)–Mo(1) 58.0(1), Mo(3)–Mo(2)–Mo(1) 58.7(1), O(1)–Mo(3)–Mo(1) 88.7(8), O(2)–Mo(2)–Mo(1) 88.3(8), S–Mo(3)–Mo(2) 75.6(3), Mo(1)–O(1)–Mo(3) 44.9(6), Mo(3)–S–Mo(2) 52.0(2)°. Thermal ellipsoids correspond to 50% probability.

[†] *Crystal data* for (**3**)·MeOH: $C_{15}H_{15}AsMo_3O_3\cdot MeOH$, *M* = 606.1, monoclinic, space group $P2_1/m$, *a* = 9.239(2), *b* = 10.803(3), *c* = 9.685(2) Å, β = 109.32(1)°, *U* = 911 Å^3, *Z* = 2, D_c = 2.21 g cm^{-3}, *F*(000) = 603.67 electrons, μ(Mo-K_α) = 37.97cm^{-1}, λ = 0.71073 Å. The structure was solved by heavy atom (Patterson and Fourier) methods and refined using blocked-cascade least-squares, with all non-hydrogen atoms (except the carbon atoms of the disordered cyclopentadienyl ring) anisotropic. Hydrogens were fixed in idealised positions and refined isotropically. 1015 Unique, observed [$I > 2\sigma(I)$] reflections collected at 293 K on a Siemens-Stoe AED-II diffractometer, gave *R* = 0.047, R_w = 0.037.

For (**4**): $C_{15}H_{15}AsMo_3O_2S$, *M* = 622.2, rhombohedral, space group *Pbca*, *a* = 16.58(1), *b* = 16.56(1), *c* = 12.35(1) Å, *U* = 3390 Å^3, *Z* = 8, D_c = 2.43 g cm^{-3}, *F*(000) = 2368 electrons, μ(Mo-K_α) = 42 cm^{-1}, λ = 0.71073 Å. Structure solution and refinement as for (**3**), with carbons and hydrogens isotropic, all others anisotropic. 820 Unique, observed [$I > 2\sigma(I)$] reflections collected at 293 K on a Siemens-Stoe AED-II diffractometer gave *R* = 0.071, R_w = 0.052.

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.

triply bridging arsenic atom, and three doubly bridging oxygen atoms. Despite the triply bridging ligand not being the same as the doubly bridging ligands, the resulting molecule has to be considered as isostructural to the $[(\eta^5\text{-}C_5H_5)_3Mo_3S_4]^+$ cation[7] and $[(\eta^5\text{-}C_5H_5)Mn_3(NO)_4]$.[11] The Mo–Mo distances of 266 pm are markedly shorter than the average basal distance in (**2**) (311.6 pm), but they can still be considered to be Mo–Mo single bonds [*d*(Mo–Mo) in elemental Mo 272, *d*(Mo=Mo) 242 pm].[12] The Mo–As distances are *ca.* 247 pm [8 pm shorter than in (**2**)] and the Mo–O distances are *ca.* 195 pm.

If one oxygen atom is substituted by a sulphur atom, the resulting steric consequences for the molecule are theoretically trivial, but still significant enough to be demonstrated by *X*-ray structure analysis. Owing to the larger atomic radius of sulphur, the distance between the Mo atoms bridged by sulphur is increased to 280 pm. Thus the triangle formed by the three Mo atoms is no longer equilateral but isosceles, with interior angles of 58, 58, and 63°. The arsenic atom is shifted towards the Mo(2)–Mo(3) axis, *i.e.* it is no longer situated above the epicentre of the base. The Mo–S distance of 228 pm is in agreement with values in other compounds containing μ-sulphur investigated previously.[7,13]

In both (**3**) and (**4**) the cyclopentadienyl rings are bent towards the arsenic atom, whilst the group VI elements are located beyond the Mo triangle. Contrary to Dahl,[7] we regard the group VI elements as four-electron donors. If this is the case, the closed shell configuration or '18-electron rule' is fulfilled for each molybdenum atom.

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Received, 26th October 1987; Com. 1559

References

1 W. A. Herrmann, *J. Organomet. Chem.*, 1986, **300**, 111.

2 K. Blechschmitt, H. Pfisterer, T. Zahn, and M. L. Ziegler, *Angew. Chem.*, 1985, **97**, 73; *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 66.

3 K. Blechschmitt, T. Zahn, and M. L. Ziegler, *Angew. Chem.*, 1985, **97**, 686; *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 702.

4 $[\mu,\eta^2\text{-}As_2\{(\eta^5\text{-}C_5H_5)Mo(CO)_2\}_2]$ has been prepared before: P. J. Sullivan and A. L. Rheingold, *Organometallics*, 1982, **1**, 1547.

5 H. Brunner, H. Kauermann, B. Nuber, J. Wachter, and M. L. Ziegler, *Angew. Chem.*, 1986, **98**, 551; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 557; G. A. Zunk, T. B. Rauchfuss, S. R. Wilson, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1984, **106**, 7621; H. Brunner, H. Kauermann, U. Klement, J. Wachter, T. Zahn, and M. L. Ziegler, *Angew. Chem.*, 1985, **97**, 122; *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 132; I. Bernal, H. Brunner, W. Meier, H. Pfisterer, J. Wachter, and M. L. Ziegler, *Angew. Chem.*, 1984, **96**, 428; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 438.

6 M. R. DuBois, R. C. Haltiwanger, D. J. Miller, and G. Glatzmeier, *J. Am. Chem. Soc.*, 1979, **101**, 5245.

7 P. J. Vergamini, H. Vahrenkamp, and L. F. Dahl, *J. Am. Chem. Soc.*, 1971, **93**, 6327.

8 W. Beck, W. Danzer, and G. Thiel, *Angew. Chem.*, 1973, **85**, 625; *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 582.

9 H. Brunner, H. Kauermann, and J. Wachter, *J. Organomet. Chem.*, 1984, **265**, 189.

10 W. A. Herrmann, R. Serrano, M. L. Ziegler, H. Pfisterer, and B. Nuber, *Angew. Chem.*, 1985, **97**, 50; *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 50.

11 R. C. Elder, F. A. Cotton, and R. A. Schunn, *J. Am. Chem. Soc.*, 1967, **89**, 3645.

12 Ch. Elschenbroich and A. Salzer, 'Organometallchemie,' ed. B. G. Teubner, Stuttgart, 1986.

13 M. Rakowski DuBois, D. L. DuBois, M. C. Van Der Veer, and R. C. Haltiwanger, *Inorg. Chem.*, 1981, **20**, 3064.