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Preliminary Communication

Dealkylation of thiols by a phosphido-bridged dimolybdenum complex. Crystal structure of $[Mo_2(\mu\text{-}S)_2(\mu\text{-}S^iPr)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$

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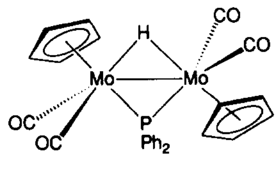
Abstract

Reaction of the phosphido, hydrido-bridged complex $[Mo_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ with thiols RSH (R = ^{i}Pr, p-C_6H_4Me) or Me_2S_2 (for R = Me) in refluxing toluene gives moderate yields of the novel quadruply-bridged species $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SR)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$; the complex with R = ^{i}Pr has been structurally characterised.

Hydrodesulfurization (abstraction of sulfur from organic compounds such as thiols, thiophenes *etc.*) is an important industrial process in the refining of crude oils [1]. The most widely-used catalysts are molybdenum and cobalt sulfide species supported on alumina, but the mechanism of the reaction has not been completely elucidated. Over the past ten years or so, dinuclear cyclopentadienylmolybdenum complexes with sulfur and/or thiolato ligands have been shown to be useful model systems for the processes occurring during hydrodesulfurization, following the important observation by Rakowski Dubois and coworkers that the various isomers of $[Mo_2S_4(\eta\text{-}L)_2]$ (L = C_5H_5, C_5H_4Me, or C_5Me_5) were capable of activating molecular hydrogen to form the bis-hydrosulfide dimers $[Mo_2S_2(SH)_2(\eta\text{-}L)_2]$ [2]. These subsequently proved active in a number of stoichiometric and catalytic reactions involving unsaturated organic molecules, displaying the propensity of the system for the making and breaking of S–H and S–C bonds [2,3]. Sulfido and thiolato-bridged dimolybdenum complexes can also serve as the starting materials for mixed metal (FeMo, CoMo, NiMo) clusters [4,5] which can themselves show catalytic activity when deposited on alumina [6].

Our interest in the chemistry of phosphido-bridged dimolybdenum complexes recently led us to explore the reactions of the phosphido, hydrido-bridged complex $[Mo_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**1**) [7] with thiols. The expectation was that this would produce the mixed phosphido, thiolato-bridged dimers $[Mo_2(\mu\text{-}SR)(\mu\text{-}PPh_2)(CO)_2(\eta\text{-}C_5H_5)_2]$ (**2**) containing a Mo=Mo double bond. This was based on two facts: (i) complex **1** reacts with additional PPh_2H to form the bis-phosphido species $[Mo_2(\mu\text{-}PPh_2)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ (**3**) [8], presumably with elimination of H_2, and (ii) the corresponding bis-thiolato species $[Mo_2(\mu\text{-}SR)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ (**4**) are known to be accessible by a number of routes, including the reaction of $[Mo_2(CO)_n(\eta\text{-}C_5H_5)_2]$ (n = 4 or 6) with RSH or RSSR [5,9]

In the event, complete reaction of $[Mo_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ with 5 equivalents of ^{i}PrSH occurred in refluxing toluene during 17 h to give two products, one green and one purple, which could be separated by column chromatography. The green complex had an IR spectrum and chromatographic properties very similar to those of **3** and **4**, which are also green, but it appears to be more sensitive than either of them, and has not yet been isolated in pure form; the characterisation data obtained, however, are con-



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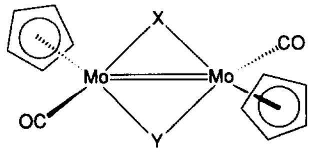
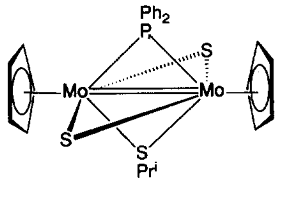


2 X = PPh$_2$, Y = SR
3 X = Y = PPh$_2$
4 X = Y = SR



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sistent with its being the mixed ligand dimer $[Mo_2(\mu\text{-}S^iPr)(\mu\text{-}PPh_2)(CO)_2(\eta\text{-}C_5H_5)_2]$.

Spectroscopic data[†] for the air-stable purple complex **5** showed the absence of CO ligands, the retention of the phosphido bridge, and the incorporation of one S^iPr ligand per Mo_2 unit. Since no Mo=O groups were visible in the solid-state IR spectrum it was thought likely that the remaining coordination sites were occupied by sulfido ligands, but whether these were terminal Mo=S groups or μ-S ligands was not clear. One notable feature of the ^1H NMR spectrum was the low field shift of the equivalent C_5H_5 ligands (δ 6.40), similar to those observed for $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SR)_2(\eta\text{-}C_5H_4Me)_2]$ (R = H, alkyl) [2].

A suitable crystal of **5** was subjected to an X-ray diffraction study, which revealed the structure shown in Fig. 1 [10*]. The two cyclopentadienyl molybdenum fragments are bridged virtually symmetrically by two sulfido ligands and the thiolato and phosphido bridges, with the latter two in a *trans* disposition. Both the Mo_2S_2 and Mo_2SP units are essentially planar, and they intersect virtually perpendicularly. The Mo–Mo distance of 2.623(2) Å is compatible with a metal–metal double bond, though a recent theoretical analysis of $[Mo_2(\mu\text{-}X)_4(\eta\text{-}C_5H_5)_2]$ systems (X = halide) suggests that the true bonding picture is predominantly metal-ligand based, since in a d^2–d^2 dimer such as **5** the metal–metal bond would have a $\sigma^2\delta^{*2}$ configuration [11]. The closest comparable structure in the literature is that of centrosymmetric $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SMe)_2(\eta\text{-}C_5H_4Me)_2]$[Mo–Mo 2.582(1), Mo–S 2.352(2), Mo–SR 2.478(2) Å] [2]; the C_5Me_5 analogue has also been structurally characterised and displays a very similar geometry [12]. Several other closely related quadruply-bridged compounds have been prepared [3,13], but in virtually every case all the bridging groups have been sulfur donors; complex **5** represents the first example in which there is a phosphido group [14*].

Reaction of **1** with *p*-thiocresol or with Me_2S_2 under similar conditions produces the analogous complexes of type **5** with $\mu\text{-}SC_6H_4\text{-}4\text{-}Me$ or μ-SMe ligands, which have been characterised spectroscopically. In each case, as with **5**, observation of two doublets for

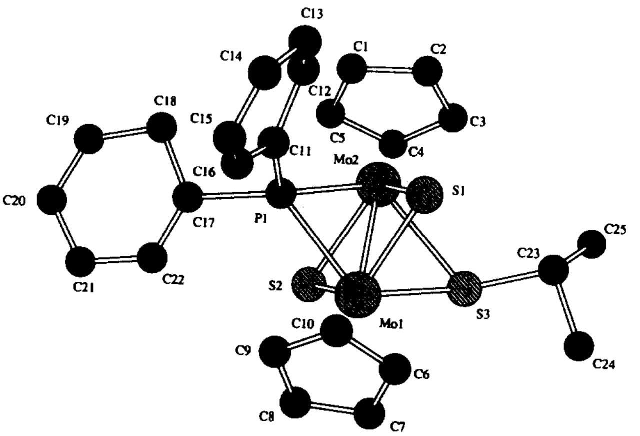

Fig. 1. Molecular structure of **5** in the crystal. Only the higher occupancy C_5H_5 positions and one orientation of the ^iPr group are shown. Selected bond lengths in Å: Mo(1)–Mo(2) 2.623(2); Mo(1)–S(1) 2.352(2); Mo(1)–S(2) 2.368(3); Mo(1)–S(3) 2.498(3); Mo(1)–P(1) 2.409; Mo(2)–S(1) 2.323(2); Mo(2)–S(2) 2.359(3); Mo(2)–S(3) 2.485(4); Mo(2)–P(1) 2.400(3). Selected bond angles (°): Mo(1)–S(1)–Mo(2) 68.2(1); Mo(1)–S(2)–Mo(2) 67.4(1); Mo(1)–S(3)–Mo(2) 63.5(1); Mo(1)–P(1)–Mo(2) 66.1(1).

the *ipso*-carbon atoms of the inequivalent phenyl groups of the $\mu\text{-}PPh_2$ ligand in the ^{13}C NMR spectrum indicates that sulfur inversion at the bridging thiolato ligand must be slow on the NMR timescale.

The dealkylation of the thiol reagents to form μ-S ligands is a novel observation for such Mo_2 systems; previously reported reactions of thiols with $[Mo_2(CO)_n(\eta\text{-}C_5H_5)_2]$ (n = 4 or 6) have only given complexes with intact thiolato ligands, never ones with sulfido groups [5,9,13,15*]. The dealkylation of thiolato ligands at mononuclear Mo centres has been reported by Morris in $[MoH(SAr)_3(PRPh_2)]$ (Ar = $2,4,6\text{-}C_6H_2Me_3$ or $2,4,6\text{-}C_6H_2{}^iPr_3$, R = Me, Et) [16] and by Boorman on reaction of $[NbH_3(\eta\text{-}C_5H_5)_2]$ with molybdenum thiolato complexes [17]; in each case the presence of the hydride ligand has been deemed significant. Perhaps surprisingly then, prolonged treatment of **3** with ^iPrSH in refluxing toluene also gives a low yield of **5** (11% after 10 days, with most of **3** recovered unchanged). It is possible that both of these reactions proceed *via* the mixed ligand dimer **2**, and experiments are under way to confirm this pathway.

Acknowledgements

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[†] Spectroscopic data for **5** (NMR in $CDCl_3$; shifts relative to TMS = δ0.0 ppm for ^1H and ^{13}C, and to H_3PO_4 = 0.0 ppm for ^{31}P, coupling constants in Hz): Yield 16%. M.p. 258–259°C. ^1H NMR: δ 7.05–6.80 (m, 10H, Ph); 6.40 (s, 10H, C_5H_5); 2.05 (septet, J 7.0, 1H, CH); 0.80 (d, J 7.0, 6H, Me). ^{13}C NMR: δ 143.0 (d, J 34, PC_{ipso}); 141.4 (d, J 28, PC_{ipso}); 134.5–126.8 (m, Ph); 96.2 (s, C_5H_5); 33.4 (s, CH); 26.4 (s, Me). ^{31}P NMR: 27.2 ppm. Anal. Found: C, 45.90; H, 4.12. $C_{25}H_{27}Mo_2PS_3$ calc.: C, 46.44; H, 4.18%. FAB MS: m/z 648 $(M+2H)^+$.

[*] Reference number with asterisk indicates a note in the list of references.

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10. Crystal data for **5**: $C_{25}H_{27}Mo_2PS_3$; $M = 946.53$; crystal dimensions 0.85 × 0.30 × 0.25 mm. Trigonal (rhombohedral setting), $a = 15.524(9)$ Å, $\alpha = 84.55(5)°$, $U = 3694(4)$ Å^3; $D_c = 1.744$ g cm^{-3}, $Z = 6$. Space group $R3c(C_{3v}^6$, No. 161). Mo Kα radiation ($\lambda = 0.71069$ Å), μ(Mo Kα) = 13.16 cm^{-1}, $F(000) = 1943.34$. Data collection range $3.5 < 2\theta < 45°$, 2267 independent reflections for which $|F|/\sigma(|F|) > 3.0$, corrected for absorption. The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least squares methods. Both cyclopentadienyl ligands were rotationally disordered with occupancies 0.77:0.23 and 0.81:0.19. After occupancy and orientational optimization, the lower occupancy fragment was fixed in position. The isopropyl group was also disordered 0.50:0.50 in two orientations on the bridging sulphur: after optimization, each fragment was refined with constrained geometry. Final R 0.0271 (R_w 0.0266, 252 parameters). Program package SHELXTL [18] implemented on the Data General DG30 computer, which was used for structure solution and refinement. Supplementary material concerning the crystal structure can be obtained from the authors.
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