# Cleavage of an Aryl Carbon–Sulphur Bond in Hydride–Thiolate Complexes of Molybdenum(IV); X-Ray Crystal Structure of [{Mo($SC_6H_2Pr^i_3$-2,4,6)(OMe)($PMePh_2$)}$_2$(μ-S)$_2$]

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The complexes [MoH($SC_6H_2R_3$-2,4,6)$_3$($PR'Ph_2$)] **1** (R = Me or $Pr^i$; R' = Me or Et) in THF–MeOH decompose *via* cleavage of an aryl carbon–sulphur bond to give $C_6H_3R_3$-2,4,6 and complexes [{Mo($SC_6H_2R_3$-2,4,6)(OMe)($PR'Ph_2$)}$_2$(μ-S)$_2$], **3**, one of which (R = $Pr^i$, R' = Me) has been characterized by single crystal X-ray diffraction.

Interest in molybdenum hydride complexes with sulphur ligands is high because of their relevance to hydrodesulphurisation catalysis[1–5] and to the active site of molybdenum nitrogenase.[6] There are only a few hydride complexes of molybdenum with thiolate or other sulphur donor co-ligands *e.g.* [MoH($SC_6H_2R_3$–2,4,6)($Ph_2PCH_2CH_2PPh_2$)$_2$][7–8] and [$MoH_2$($C_6H_4S_2$)($PMePh_2$)$_3$][9] and their decomposition pathways have not been investigated. Here we report an extension of our studies[10] on the series [MoH($SC_6H_2R_3$–2,4,6)$_3$($PR'Ph_2$)] **1** and [MH($SC_6H_2R_3$-2,4,6)$_3$($PMe_2Ph$)$_2$] **2** [M = Mo or W; R = Me or $Pr^i$; R' = Me or Et), which show interesting reactions with $H_2/^2H_2$ and other ligands, with retention of all thiolate ligands.

Complexes **1** readily form six-coordinate adducts with ligands such as pyridine (Scheme 1). They also catalyse $H_2/^2H_2$ exchange.[10] However, during the course of these studies we have found that complexes **1** undergo facile carbon–sulphur bond cleavage. This observation is important because, although hydrido–molybdenum intermediates have been proposed in hydrodesulphurisation chemistry on $MoS_2$ catalysts,[4,5] hitherto there has been no report of such chemistry involving molybdenum hydride complexes. It has been established that hydride transfer from [Nb($C_5H_5$)$_2H_3$] to molybdenum thiolate complexes leads to cleavage of an alkyl–sulphur bond but not an aryl–sulphur bond.[11]

Complexes **1** are prepared as in Scheme 1. The spectroscopic properties are consistent with a trigonal bipyramidal geometry with hydride *trans* to $PR'Ph_2$ (Table 1).[10] They are isolated as air-sensitive green crystals which decompose in tetrahydrofuran (THF) at 20 °C within a few hours in the

**Table 1** Spectroscopic properties of complexes **1** and **3**

| Complex | ν(Mo–H)[a]/ cm$^{-1}$ | $\delta\,^{31}P$[b] | $^2J$(PH)/ Hz | Molecular ion[c] |
|---|---|---|---|---|
| (**1**, R = $Pr^i$, R' = Me) | 1880 | −78.0 | 87.1 | 1003(1003) |
| (**1**, R = $Pr^i$, R' = Et) | 1858 | −69.0[d] | 87.0 | 1017(1017) |
| (**1**, R = Me, R' = Me) | 1940 | −78.7 | 79.0 | |
| (**3**, R = $Pr^i$, R' = Me) | | −128.9 | | |
| [MoH($SC_6H_2Pr^i_3$-2,4,6)$_3$ ($PMePh_2$)($C_5H_5N$)] | 1890 | −87.1 | 87.2 | 1082(1082) |

[a] KBr discs. [b] In benzene solution, relative to $P(OMe)_3$, doublets in the $^1H$ coupled mode. [c] FAB mass spectral data, calculated in parentheses. [d] Mo–H resonance at δ 3.28 in $^1H$ spectrum, relative to $SiMe_4$; Mo–H resonance in other hydrides obscured by ligand resonances.

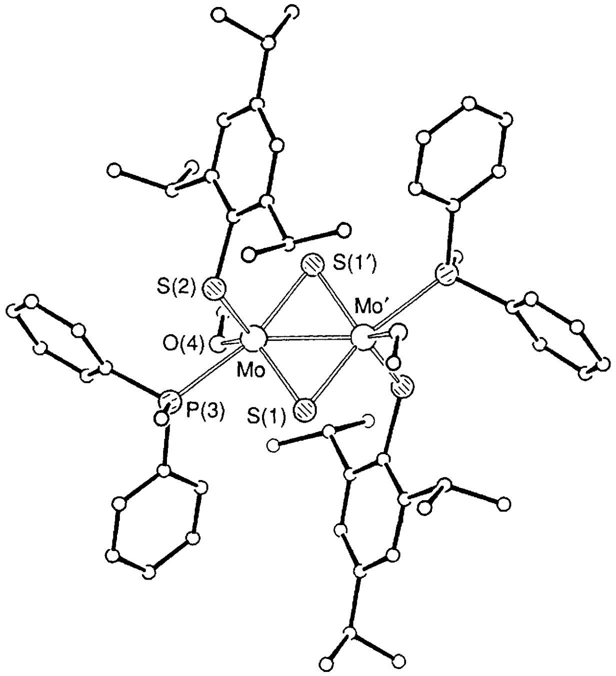
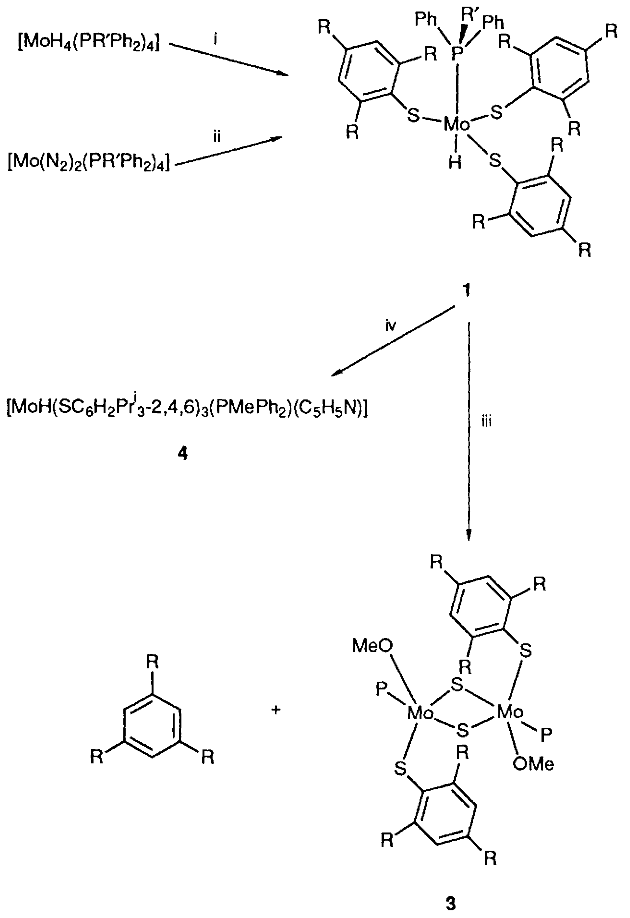


**Fig. 1** Structure of $[\{Mo(OMe)(SC_6H_2Pr^i{}_3\text{-}2,4,6)(PMePh_2)\}_2(\mu\text{-}S)_2]$. Selected distances and angles: Mo–Mo' 2.691(1); Mo–S(1) 2.231(2); Mo–S(1') 2.354(2), Mo–S(2) 2.329(2); Mo–P(3) 2.578(2); Mo–O(4) 1.902(4)Å. S(1)–Mo–S(2) 114.7(1); S(1)–Mo–P(3) 85.1(1); S(1)–Mo–O(4) 117.0(1); S(1)–Mo–S(1') 108.2(1); S(2)–Mo–P(3) 79.3(1); S(2)–Mo–O(4) 121.5(1); S(2)–Mo–S(1') 93.8(1); P(3)–Mo–O(4) 79.7(1); P(3)–Mo–S(1') 166.7(1); O(4)–Mo–S(1') 94.6(1); Mo–S(1)–Mo' 71.8(1)°.

presence of MeOH. The stability of the solutions increases with an increase of the size of R (Me<$\text{Pr}^i$) and R' (Me<Et). Because of its sensitivity, attempts to obtain a room temperature X-ray crystal structure of **1** have so far failed.

A THF–MeOH solution (**1**, R = $\text{Pr}^i$, R' = Me), when left at 20 °C, decomposes within 1 h to give green crystals of **3**. A stoichiometric amount of triisopropyl benzene was detected by GCMS analysis. When a THF/$MeO^2H$ solution was used, $C_6(^2H)H_2Pr^i{}_3$ was observed ($^2$H NMR).

The X-ray crystal structure of **3** has been determined and is shown in Fig. 1.† The dinuclear, sulphur-bridged complex



**Scheme 1** *Reagents and conditions*: i, R' = Me, 3 equiv. $HSC_6H_2R_3$-2,4,6, R = Me or $\text{Pr}^i$, THF, 0 °C, 2 h; R' = Et, 3 equiv. $HSC_6H_2Pr^i{}_3$-2,4,6, toluene, 20 °C, 7 min; ii, R' = Me, 3 equiv. $HSC_6H_2R_3$-2,4,6, R = Me or $\text{Pr}^i$, THF, 0 °C, 2 h; iii, THF–MeOH, 20 °C, 1 h; iv, R' = Me, R = $\text{Pr}^i$ and excess of $C_5H_5N$, THF, 0 °C, *ca.* 30 min.

*Identification procedures:* green crystals of compounds (**1**, R' = Me) were obtained from THF–MeOH and of (**1**, R' = Et), from toluene–MeOH and were characterized by microanalysis and spectroscopic properties shown in Table 1; green crystals of compound **3** were obtained from MeOH, characterized as for compounds **1** with, in addition, the X-ray crystal structure determination (see text); other crystals characterized by microanalysis and properties as in Table 1. Substituents on P atoms in **3** have been omitted for clarity.

$[\{Mo(OMe)(SC_6H_2Pr^i{}_3\text{-}2,4,6)(PMePh_2)\}_2(\mu\text{-}S)_2]$ crystallizes with a precise centre of symmetry between the two molybdenum atoms. The Mo–Mo distance of 2.691(1) Å and the Mo–S–Mo angle of 71.8(1)° indicate a significant degree of metal-metal bonding. The structure is very similar to that of $[\{Mo(SBu^t)_2(PMe_2Ph)\}_2(\mu\text{-}S)_2]$[Mo-Mo 2.741(1) Å] which forms under very similar circumstances[12] [eqn. (1)]:

$$2\ cis\text{-}[Mo(N_2)_2(PMe_2Ph)_4] + 8\ HSBu^t \rightarrow [\{Mo(SBu^t)_2(PMe_2Ph)\}_2(\mu\text{-}S)_2] + \text{other products} \quad (1)$$

Two main mechanisms for the formation of **3** can be envisaged. The first involves intramolecular migration of the hydride to the sulphur-bound carbon of an aryl group, possibly *via* a coordinated thiol intermediate. Such a mechanism has been proposed for systems based on tungsten.[16,17] The second is an intermolecular attack of a hydride from one Mo on the sulphur-bound carbon at a second Mo.

The mechanism must account for the following observa-

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† *Crystal data:* $[\{Mo(OMe)(SC_6H_2Pr^i{}_3\text{-}2,4,6)(PMePh_2)\}_2(\mu\text{-}S)_2]$, $C_{58}H_{78}Mo_2O_2P_2S_4$, $M$ = 11189.3, triclinic, space group $I\bar{1}$ (equiv. to no. 2), $Z$ = 2, $a$ = 10.922(1), $b$ = 20.209(1), $c$ = 13.661(1) Å, $\alpha$ = 82.829(6), $\beta$ = 89.928(6), $\gamma$ = 97.148(6)°, $U$ = 2968 Å$^3$, $D_c$ = 1.33 g cm$^{-3}$, $F(000)$ = 1240. $\mu$(Mo-K$\alpha$) = 6.4 cm$^{-1}$, $\lambda$(Mo-K$\bar{\alpha}$) = 0.71069 Å. Enraf-Nonius CAD4 diffractometer with monochromated radiation, cell parameters refined from settings (in four orientations) of 24 strong reflections with $\theta$ *ca.* 10.5°, and diffraction intensities measured to $\theta_{max}$ = 20°. Corrections applied for Lorentz-polarization effects, crystal deterioration, absorption and to ensure no negative net intensities.

2756 unique data entered into SHELX[13] program system. The Mo positions found from Patterson synthesis. All non-hydrogen atoms found in subsequent electron density maps or difference Fourier synthesis. Full-matrix least-squares refinement was concluded with $R$ = 0.066, $R_w$ = 0.047 for all data, weighted $w = 1.14/\sigma^2(F)$. All non-hydrogen atoms refined anisotropically. Hydrogen atoms in ideal positions with freely-refined isotropic thermal parameters. Scattering factors for neutral atoms taken from reference (14) and all computer programs listed in reference (15) were run on a MicroVAX II computer in the Nitrogen Fixation Laboratory.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

tions. Five coordination appears to be necessary, since the six-coordinate complexes **2** and **4** (Scheme 1) are stable in THF–MeOH. Methanol appears to be essential for the cleavage reaction because in its absence we have not observed production of $C_6H_3Pr^i{}_3$-2,4,6 from **6** in dry THF after several days at 20 °C.

Mechanistic work is in progress but on balance we favour the mechanism which involves intermolecular attack of hydride on the S–C bond. If this is correct, then these reactions can be thought of as models for steps in hydrodesulphurisation by $MoS_2$ catalysts involving hydride and thiolate groups on Mo.

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