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Preliminary communication

Dealkylation of thiols by alkyne-bridged dimolybdenum complexes

Harry Adams, Neil A. Bailey, Sally R. Gay, Trevor Hamilton, Michael J. Morris *

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK

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Abstract

The reaction of $[Mo_2(CO)_4\{\mu\text{-}C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ with RSH produces the μ-vinyl complexes $[Mo_2(CO)_2\{\mu\text{-}C(CO_2Me){=}CHCO_2Me\}(\mu\text{-}SR)(\eta\text{-}C_5H_5)_2]$ when R = Et or ^{i}Pr but, for R = ^{t}Bu, dealkylation of the thiol and further hydrogenation of the alkyne occurs to give $[Mo_2(\mu\text{-}S)_2(\mu\text{-}\eta^2,\eta^1,\eta^1\text{-}cis\text{-}MeO_2CCH{=}CHCO_2Me)(\eta\text{-}C_5H_5)_2]$ in which the alkene dimethyl maleate acts as a six-electron donor ligand through its double bond and the carbonyl oxygen atoms of both CO_2Me groups. In contrast, treatment of $[Mo_2(CO)_4(\mu\text{-}C_2Me_2)(\eta\text{-}C_5H_5)_2]$ with RSH provides a convenient new route to compounds of the type $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SR)_2(\eta\text{-}C_5H_5)_2]$ when R = Et or ^{i}Pr.

Keywords: Molybdenum; Carbonyl; Thiol; Alkyne; Vinyl; Crystal structure

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1. Introduction

The chemistry of molybdenum complexes with sulphur and thiolate ligands is of considerable interest because of its relevance to the industrial hydrodesulphurization of crude oil, which is performed over a heterogeneous catalyst of molybdenum and cobalt sulphides. Although the mechanism is not known precisely, it is generally accepted that the reaction occurs at a molybdenum–sulphur site. Extensive studies, particularly by the groups headed by Rakowski Dubois and Curtis, have shown that dinuclear cyclopentadienyl molybdenum complexes with sulphur and/or thiolate ligands such as $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2(\eta\text{-}C_5H_5)_2]$ can be used to model some of the processes which may occur on the catalyst surface, and that mixed-metal clusters derived from them can act as hydrodesulphurization catalysts when supported on alumina [1].

The thermal reactions of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with thiols (RSH) are known to produce the thiolate-bridged complexes $[Mo_2(\mu\text{-}SR)_2(CO)_4(\eta\text{-}C_5H_5)_2]$, which on further heating undergo decarbonylation to $[Mo_2(\mu\text{-}SR)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ [2]. We recently reported that the introduction of a phosphido bridge into this system promotes the dealkylation of thiols; thus $[Mo_2(CO)_4(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$ reacts with RSH in refluxing toluene to give $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SR)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$ (R = ^{i}Pr or $p\text{-}C_6H_4Me$) containing sulphide and thiolate ligands as well as the phosphido bridge [3]. In this paper we show that the reactions of thiols with alkyne-bridged dimolybdenum complexes also result in dealkylation to give sulphide ligands in some cases, suggesting that such processes may be more common than previously supposed.

2. Results

The starting materials used were the transverse μ-alkyne complexes $[Mo_2(CO)_4(\mu\text{-}R^1C_2R^1)(\eta\text{-}C_5H_5)_2]$ (**1**) [4]. Initially **1a**, where $R^1 = CO_2Me$, was chosen because the strongly bound electron-withdrawing alkyne was more likely to be retained during the reaction. Treatment of **1a** with the thiols RSH (R = Et or ^{i}Pr) in refluxing toluene overnight did indeed produce the new complexes $[Mo_2(CO)_2\{\mu\text{-}C(CO_2Me){=}CHCO_2Me\}(\mu\text{-}SR)(\eta\text{-}C_5H_5)_2]$ (**2a** and **2b**), isolated as air-stable red-brown solids with good yields (**2a**, 74%; **2b**, 67%) [5]. Each complex exists as two inseparable isomers in ratios of 3 : 1 and 2 : 1 respectively; this isomerism may involve the disposition of the R group in relation to the vinyl ligand, or a *cis–trans* arrangement of the C_5H_5 rings. Spectroscopic characterization (Section 3) permit-

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* Corresponding author.

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ted their identification; in addition the X-ray crystal structure of **2b** was determined and will be reported in the full paper [6]. This confirmed that the dimolybdenum centre is bridged by a thiolate ligand and a vinyl group which is σ bound to one Mo atom and π bound to the other; in addition the CO_2Me group attached to the β-carbon atom of this ligand is bent round to coordinate through its carbonyl oxygen atom, creating a five-membered chelate ring. This structure is very similar to that of the analogous phosphido-bridged compound $[Mo_2(CO)_2\{\mu\text{-}C(CO_2Me){=}CHCO_2Me\}(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$, formed by the reaction of **1a** with PPh_2H under similar conditions [7].

Surprisingly the reaction of **1a** with ^tBuSH did not produce an analogous complex. In this case the major isolated product **3** (yield, 80%) was brown and showed no $\nu(CO)$ absorptions in its IR spectrum. Moreover its ^1H and ^{13}C NMR spectra (Section 3) were extremely simple, each showing only peaks due to two inequivalent C_5H_5 rings and two equivalent CO_2Me groups, together with one resonance assigned to CH (confirmed by recording the ^{13}C spectrum with an attached proton test technique). No ^tBu groups were present, and we therefore concluded that the alkyne ligand had been hydrogenated to give an alkene, and that the remaining coordination sites were occupied by sulphide ligands formed by dealkylation of the thiol.

The X-ray structure of **3** is shown in Fig. 1 and confirms these deductions. The molecule consists of two molybdenum atoms, each bearing a $\eta\text{-}C_5H_5$ ring, which are joined by a bond of length 2.887(3) Å. There are two symmetrically bridging sulphide ligands situated in a *cis* disposition (the angle between the two Mo_2S planes is 65.8°). The other bridging ligand is the *cis*-alkene dimethyl maleate which is bonded to Mo(2) by an η^2 interaction through the alkene double bond, and to Mo(1) by the carbonyl groups of both CO_2Me functionalities. The alkene therefore donates a total of six electrons to the Mo_2 unit. As far as we are aware, this represents a previously unobserved bonding mode for this ligand [8]. The observed diamagnetism implies a spin-pairing interaction between the two molybdenum atoms since both are formally Mo(III); moreover, if each metal is to achieve an 18-electron configuration, a donor bond (either directly or through the bridging ligands) is required since Mo(1) receives four electrons from the alkene ligand whereas Mo(2) receives only two.

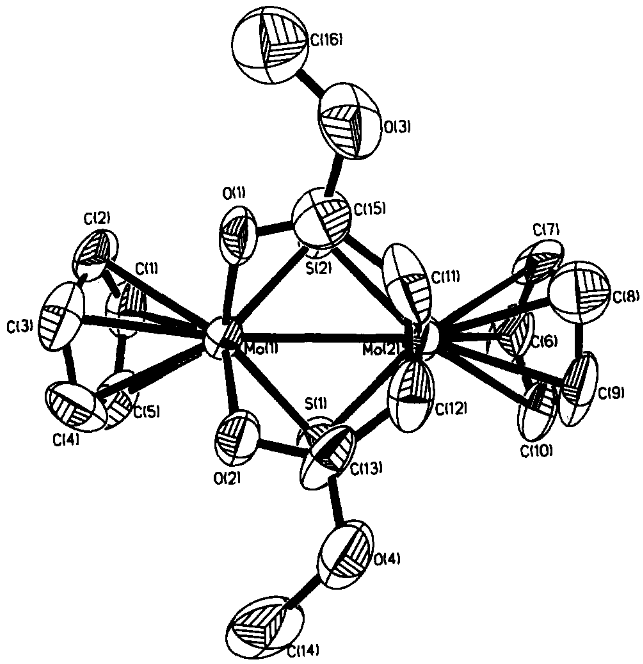
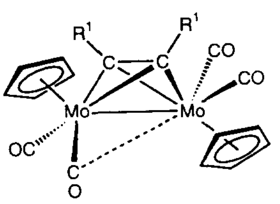


Fig. 1. Molecular structure of **3** in the crystal. Selected bond lengths are as follows: Mo(1)–Mo(2), 2.887(3) Å; Mo(1)–S(1), 2.360(5) Å; Mo(1)–S(2), 2.354(4) Å; Mo(1)–O(1), 2.192(10) Å; Mo(1)–O(2), 2.172(10) Å; Mo(2)–S(1), 2.351(5) Å; Mo(2)–S(2), 2.352(4) Å; Mo(2)–C(11), 2.266(20) Å; Mo(2)–C(12), 2.306(18) Å.

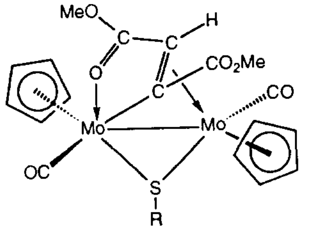
Since the CO_2Me groups clearly played an important part in the reaction, we next examined the reactions of **1b** (R^1 = Me) with thiols and found that with R = ^iPr or Et the sole products were the known purple air-stable compounds $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SR)_2(\eta\text{-}C_5H_5)_2]$ (**4a** and **4b**), which exist as two separable isomers, with total yields of around 50%. The same species were minor products (about 5%) in the reactions leading to **2a** and **2b** and have been previously made by thiol exchange from $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2(\eta\text{-}C_5H_5)_2]$ (itself prepared by hydrogenation of the polymeric sulphide $[Mo_2S_x(\eta\text{-}C_5H_5)_2]$ obtained by treating $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with sulphur) [9]. The yields from this multistep route were variable and, since **1b** is readily available with a 75% yield in one step from $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$, the present reaction provides convenient access to these compounds. However, the reaction does not work in the case of ^tBuSH; the major product is tentatively formulated as a μ-vinyl complex with a $\mu\text{-}S^tBu$ ligand. We therefore conclude that by changing the alkyne ligand it is possible to effect the dealkylation of different thiols.

3. Conclusion

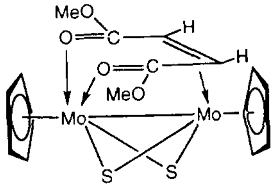
Taken together, these results suggest a pathway for the reaction in which the initial steps are the substitution of a CO ligand by the thiol and oxidative addition of the S–H bond. The alkyne is hydrogenated first to a μ-vinyl ligand and then (after addition of a second thiol) to an alkene. In the case of **1a**, these ligands are anchored to the metal through the CO_2Me group and can be isolated in **2** and **3** respectively. In the case of **1b**, the alkene is presumably released (although we have as yet made no attempt to detect it), allowing the coordination of further thiol ligands. The exact pathway of the dealkylation step remains open to question. Further experiments are



1a $R^1 = CO_2Me$
1b $R^1 = Me$



2a R = Et
2b R = ^iPr



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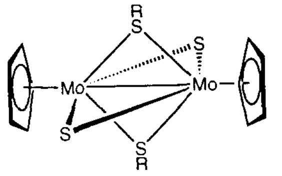

4a R = Et
4b R = ^iPr

under way with different alkyne complexes and thiols in an attempt to delineate the scope and mechanism of the reaction and determine which factors influence the dealkylation process.

4. Experimental details

Satisfactory analytical data were obtained for all new compounds. Selected spectroscopic data (IR in CH_2Cl_2; NMR in $CDCl_3$ relative to $SiMe_4$ (0.0 ppm) with coupling constants in hertz; only major isomers given for **2a** and **2b**).

2a: melting point (m.p.), 227–229°C. IR: ν(CO) 1905 sh, 1877, 1667 cm^{-1}. ^{1}H NMR: δ 5.28, 5.04 (both s, C_5H_5); 3.39 (s, vinylic CH); 3.36, 3.16 (both s, CO_2Me); 2.68, 2.20 (both dq, each 1H of CH_2); 1.04 (t,J = 7 Hz, Me) ppm. ^{13}C NMR: δ 262.2, 242.9 (both s, CO); 193.3, 182.2 (both s, CO_2Me); 145.3 (s, μ-C); 94.0, 92.5 (both s, C_5H_5); 53.5, 51.0 (both s, CO_2Me); 39.1 (s, $CHCO_2Me$); 33.0 (s, CH_2); 17.7 (s, Me) ppm. Mass spectroscopy (MS): m/z 583 (M^+).

2b: m.p., 206–208°C. IR: ν(CO) 1910 sh, 1884, 1668 cm^{-1}. ^{1}H NMR: δ 5.45, 5.10 (both s, C_5H_5); 3.75 (s, CO_2Me); 3.54 (s, vinylic CH); 3.45 (s, CO_2Me); 3.18 (septet, J = 7 Hz, CH); 1.20, 0.85 (both d, J = 7 Hz, Me) ppm. ^{13}C NMR: δ 262.1, 243.1 (both s, CO); 193.2, 182.0 (both s, CO_2Me); 145.7 (s, μ-C); 94.1, 92.7 (both s, C_5H_5); 51.0, 50.5 (both s, CO_2Me); 44.5 (s, $CHCO_2Me$); 27.6 (s, Me); 27.1 (s, $CHMe_2$); 25.4 (s, Me). MS: m/z 598 (M^+).

3: m.p., 197–199°C. IR: 1552 cm^{-1}. ^{1}H NMR: δ 6.04, 6.00 (both s, C_5H_5); 3.44 (s, Me); 3.29 (s, CH) ppm. ^{13}C NMR: δ 174.7 (CO_2Me); 99.3, 97.2 (both s, C_5H_5); 52.1 (s, Me); 38.2 (s, CH). MS: m/z 530 (M^+).

4a: ^{1}H NMR: δ major isomer 6.49 (s, 10H, C_5H_5); 1.47 (q, J = 7 Hz, 4H, CH_2); 0.62 (t, J = 7 Hz, 6H, Me); minor isomer 6.44, 1.49, 0.66 (samc assignments). MS for both isomers: m/z 508 (M^+).

4b: ^{1}H NMR: δ major isomer 6.44 (s, 10H, C_5H_5); 1.71 (septet, J = 7 Hz, 2H, CH); 0.69 (d, J = 7 Hz, 12H, Me); minor isomer 6.51, 1.98, 0.68 (same assignments). MS for both isomers; m/z 536 (M^+).

Crystal data for **3**. $0.5CH_2Cl_2$: $C_{16.5}H_{19}ClMo_2O_4S_2$; $M = 572.8$; crystal dimensions, $0.8 \times 0.4 \times 0.4$ mm; monoclinic; $a = 10.028(7)$, $b = 19.367(2)$ and $c = 10.523(5)$ Å; $\beta = 90.75(5)$°; $U = 2044(2)$ Å^3, $D_c = 1.862$ g cm^{-3}, $Z = 4$; space group, $P2_1/n$; Mo Kα radiation ($\lambda = 0.710\,73$ Å), μ (Mo Kα) = 15.80 cm^{-1}; $F(000) = 1132$; data collection range, $3.5° < 2\theta < 45.0°$; 1829 independent reflections for which $|F|/\sigma(|F|) > 4.0$, corrected for absorption. The structure was solved by direct methods and refined by full matrix least-squares methods: final R, 0.0652 (R_w, 0.0797; 230 parameters). The program package Siemens SHELXTL PLUS (PC version) [10] was used. Tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

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