Journal of Organometallic Chemistry, 405 (1991) 207–215
Elsevier Sequoia S.A., Lausanne
JOM 21402

Dimolybdenum oxo-imido complexes: reactivity of $[(MeC_5H_4)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}NPh)]$ and crystal structure of $[(MeC_5H_4)_2Mo_2O(S)(\mu\text{-}O)(\mu\text{-}NPh)]$

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(Received August 10th, 1990)

Abstract

Reaction of hydrogen sulphide with $[(MeC_5H_4)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}NPh)]$ (**1**) results in substitution of one of the terminal oxo moieties to give $[(MeC_5H_4)_2Mo_2O(S)(\mu\text{-}O)(\mu\text{-}NPh)]$ (**2**) in high yield. The crystal structure of **2** has been determined. Whereas **1** is stable to hydrolysis in neutral media, heating **2** in wet toluene gives **1** by substitution of the terminal sulphido ligand. Addition of mineral acid to either **1** or **2** results in hydrolysis of the bridging imido moiety to give $[(MeC_5H_4)MoO(\mu\text{-}O)]_2$ (**3**) or $[(MeC_5H_4)Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)]$ (**4**) respectively. The former reaction has been investigated by ^1H NMR spectroscopy utilising trifluoroacetic acid which shows that initial protonation of **1** occurs selectively at a terminal oxo site to give $[(MeC_5H_4)_2Mo_2O(OH)(\mu\text{-}O)(\mu\text{-}NPh)][CF_3CO_2]$ (**5**). Reaction of **2** with phenylisocyanate gives $[(MeC_5H_4)_2MoS(NPh)(\mu\text{-}NPh)_2]$ (**6**) and **1** via competitive reactions involving the replacement of oxo or sulphido moieties respectively.

Introduction

The chemistry of transition metal complexes containing multiply bonded π-donor ligands continues to attract considerable attention [1]. One widely utilised synthetic route to such ligands at mononuclear centres is via the substitution of one multiply bonded ligand for another [2]. In contrast, the synthesis and interconversion of multiply bonded ligands at binuclear metal centres remains relatively unexplored [3–5]. In such systems, however, multiply bonded ligands are often able to adopt either terminal or bridging modes of coordination. While the reactivity of multiply bonded ligands at these different sites is anticipated to vary significantly, simple systems which permit a study of this phenomena are rare. We have recently described the synthesis of a number of oxo and arylimido complexes at cyclopentadienyl stabilised dimolybdenum centres [4]. This binuclear centre is capable of supporting both bridging and terminal multiply bonded moieties which do not interconvert thus allowing for an assessment of their relative reactivities. Herein we describe reactivity studies of the complex $[(MeC_5H_4)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}NPh)]$ (**1**) which contains terminal and bridging oxo moieties together with a bridging phenylimido ligand. These studies reveal that under appropriate conditions reactivity of either bridging or terminal ligands can be induced.

0022-328X/91/$03.50

Experimental

General comments All reactions were carried out under an N_2 atmosphere using predried solvents unless otherwise stated. NMR spectra were recorded on a Varian VXR 400 spectrometer. IR spectra were recorded as KBr disks on a Perkin–Elmer 983 spectrometer. Thin layer chromatography was carried out on silica (120 mesh) made up as a slurry in deionised water and activated by heating to 110 °C. Elemental analysis was performed within the chemistry department of University College. Mass spectra were carried out by the University of London Mass Spectrometry Service. The compound $[(MeC_5H_4)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}NPh)]$ **1** was prepared as previously described [4].

Reaction of $[(MeC_5H_4)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}NPh)]$ (1) with H_2S

A THF solution (50 cm^3) of **1** (100 mg, 0.20 mmol) was purged periodically with H_2S over a three hour period resulting in a colour change from orange to dark red. After this time the solution was purged with nitrogen to remove excess H_2S and the solvent removed under reduced pressure leaving a dark red solid. Separation of products was effected by TLC using a light petroleum (90%) and diethyl ether (10%) mixture. An orange band afforded starting material (10 mg) and a red band afforded $[(MeC_5H_4)_2Mo_2O(S)(\mu\text{-}O)(\mu\text{-}NPh)]$ (**2**) (80 mg, 77%). Crystals suitable for X-ray diffraction were grown by slow cooling of a light petroleum solution to −40 °C. Anal. Found: C, 42.58; H, 3.63; N, 2.68; S, 5.74. $Mo_2C_{18}H_{19}NO_2S$ calcd.: C, 42.77; H, 3.76; N, 2.77; S, 6.33%. ^1H NMR ($CDCl_3$): δ 1.87 (3H, s, CH_3); 1.97 (3H, s, CH_3); 4.77 (1H, q, *J* 3, C_5H_4); 5.42 (1H, q, *J* 3, C_5H_4); 5.59 (1H, q, *J* 2, C_5H_4); 5.74 (1H, q, *J* 2, C_5H_4); 5.93 (1H, q, *J* 3, C_5H_4); 6.00 (1H, q, *J* 2, C_5H_4); 6.50 (1H, q, *J* 3, C_5H_4); 6.22 (1H, q, *J* 2, C_5H_4); 7.28 (1H, tt, *J* 7, 1, C_6H_5); 7.57 (2H, tt, *J* 7, 1, C_6H_5); 7.93 (2H, td, *J* 7, 1, C_6H_5). IR 1580(w), 1487(w), 1467(m), 1442(w), 1262(s), 1078(m), 895(s), 844(s), 830(s), 817(s), 766(s), 692(s), 490(s), 478(s) cm^{-1}.

Oxidation of 2 in toluene

Heating an undried toluene solution (40 cm^3) of **2** (20 mg, 0.04 mmol) for 16 h resulted in a gradual lightening of the red solution from which **1** (14 mg, 72%) was isolated after TLC.

Acid mediated hydrolysis of 1

A drop of concentrated hydrochloric acid was added to a degassed acetone solution (20 cm^3) of **1** (20 mg, 0.04 mmol) resulting in a considerable darkening of the orange solution. After approximately 30 sec, degassed water (10 cm^3) was added to the solution resulting in a lightening. Acetone was removed under reduced pressure resulting in the precipitation of an orange solid which was filtered off and identified as the starting material (10 mg). The aqueous layer was extracted with dichloromethane (10 cm^3) which upon separation and drying gave an orange solid (10 mg, 59%) upon removal of solvent. This was identified as $[(MeC_5H_4)MoO(\mu\text{-}O)]_2$ (**3**) by comparison of IR and ^1H NMR data with that of an authentic sample.

Reaction of 1 with CF_3CO_2H

Addition of a drop of trifluoroacetic acid to a $CDCl_3$ solution of **1** in an NMR tube resulted in a rapid colour change from orange to brown. The ^1H NMR

spectrum showed the clean and complete formation of a new product formulated as $[(MeC_5H_4)_2Mo_2O(OH)(\mu\text{-}O)(\mu\text{-}NPh)][CF_3CO_2]$ (**5**). ^1H NMR ($CDCl_3$): δ 2.23 (3H, s, CH_3); 2.29 (3H, s, CH_3); 5.55 (1H, q, *J* 3, C_5H_4); 5.70 (1H, q, *J* 3, C_5H_4); 5.74 (1H, q, *J* 3, C_5H_4); 5.83 (1H, q, *J* 3, C_5H_4); 6.08 (1H, q, *J* 3, C_5H_4); 6.15 (1H, q, *J* 3, C_5H_4); 6.49 (1H, q, *J* 3, C_5H_4); 6.74 (1H, q, *J* 3, C_5H_4); 6.96 (2H, d, *J* 7, C_6H_5); 7.32 (1H, t, *J* 7, C_6H_5); 7.48 (2H, t, *J* 7, C_6H_5). Within 10 min appreciable sample decomposition had occurred.

Acid mediated hydrolysis of 2

An acetone solution (5 cm^3) of **2** (22 mg, 0.04 mmol) was treated with one drop of aqueous HCl resulting in a lightening of the dark red solution. Addition of water (10 cm^3) and removal of acetone under reduced pressure led to the precipitation of a red solid which was confirmed as starting material by IR. The sample was redissolved in acetone and a further drop of HCl was added. After standing for three days the acetone was removed under reduced pressure and the water layer extracted with dichloromethane (10 cm^3). TLC eluting with diethyl ether gave a red band which afforded $[(MeC_5H_4)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)]$ (**4**) (14 mg, 75%). Crystals were grown from slow evaporation of a chloroform solution. Anal. Found: C, 33.62; H, 3.45, S, 7.30, N, 0.00. $Mo_2C_{12}H_{14}O_3S$ calcd.: 33.49; H, 3.26; S, 7.44; N, 0.00%. ^1H NMR ($CDCl_3$): δ 1.97 (6H, s, CH_3); 5.41 (2H, q, *J* 3, C_5H_4); 6.16 (2H, q, *J* 3, C_5H_4); 6.18 (2H, q, *J* 3, C_5H_4); 6.20 (2H, q, *J* 3, C_5H_4). IR: 907(s), 846(w), 823(m), 803(m) cm^{-1}. *M*, 430.

Reaction of 1 with $Ph_3P{=}S$

Thermolysis of a THF solution (10 cm^3) of **1** (50 mg, 0.10 mmol) and $Ph_3P{=}S$ (30 mg, 0.11 mmol) for three days resulted in no reaction as shown by ^1H NMR spectroscopy.

Reaction of 2 with phenylisocyanate

A THF solution (10 cm^3) of **2** (30 mg, 0.06 mmol) and phenylisocyanate (0.1 cm^3) was stirred at room temperature for four days without any visible change. The solvent was removed under reduced pressure. TLC using a mixture of light petroleum (80%) and diethylether (20%) afforded four bands: orange (~ 5 mg) unidentified; orange (~ 5 mg) unidentified; red $[(MeC_5H_4)Mo_2S(NPh)(\mu\text{-}NPh)_2]$ **6** [5] (8 mg, 21%); orange **1** (10 mg, 34%).

X-Ray data collection

A red crystal of **2** of approximate dimensions 0.28 × 0.22 × 0.18 mm was mounted on a glass fibre. All geometric and intensity data were taken from the crystal using an automated four-circle diffractometer (Nicolet R3mV) equipped with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Important crystallographic parameters are presented in Table 2. The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 30 reflections taken from a rotation photograph and centred by the diffractometer. Axial photography was used to verify Laue class and unit cell dimensions. The $\bar{\omega}$–2θ technique was used to measure 3374 reflections (3251 unique) in the range $5 \leqslant 2\theta < 50°$. Three standard reflections were measured every 97 reflections, and showed no sign of loss of intensity during the data collection. The data were

corrected for Lorentz and polarisation effects and an empirical absorption correction applied. There are 2605 unique reflections with $I \geqslant 1.5\sigma(I)$. The structure was successfully solved and refined in the space group $P\bar{1}$.

Structure solution and refinement

The asymmetric unit of **2** contains one complete molecule. The positions of the molybdenum atoms were obtained by direct methods. The remaining non-hydrogen atoms were found by iterative application of least-squares refinement and difference-fourier analysis. All non-hydrogen atoms were refined anisotropically. The final least-squares refinement included 217 parameters for 2605 reflections. The last cycle gave $R = 0.063$ and $R_w = 0.062$, quality of fit 1.64 and did not shift any parameter by more than 0.001 times its estimated standard deviation.

Results and discussion

Reaction of hydrogen sulphide with $[(MeC_5H_4)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}NPh)]$ (**1**) resulted in the clean substitution of a terminal oxo moiety for a sulphido moiety resulting in the isolation of $[(MeC_5H_4)_2Mo_2O(S)(\mu\text{-}O)(\mu\text{-}NPh)]$ (**2**) in 77% yield. In the infrared spectrum bands associated with the bridging imido moiety (1262 cm^{-1}), bridging (844 cm^{-1}) and terminal (895 cm^{-1}) oxo ligation, and a terminally bound sulphido ligand (478 cm^{-1}) were all observed. In the ^1H NMR spectrum the inequivalence of the two molybdenum centres was clearly shown by the observation of two methyl resonances at δ 1.87 and 1.97 ppm while the presence of eight inequivalent cyclopentadienyl protons (Fig. 1) is indicative of two different bridging moieties. Of these second order quartets, four were of A and four of B character, the forms of which were successfully simulated (J_{AB} 3.1, $J_{AB'}$ 2.5, $J_{AA'}$ 1.8 Hz) while a series of decoupling experiments allowed the assignment of AB pairs as shown. In order to ascertain the precise geometry of **2**, an X-ray crystallographic study was undertaken the results of which are shown in Fig. 2 and Table 1.

Complex **2** contains a dimolybdenum centre [Mo(1)–Mo(2) 2.660(1) Å] bridged symmetrically by both oxo [Mo(1)–O(1) 1.938(6); Mo(2)–O(1) 1.941(7) Å] and

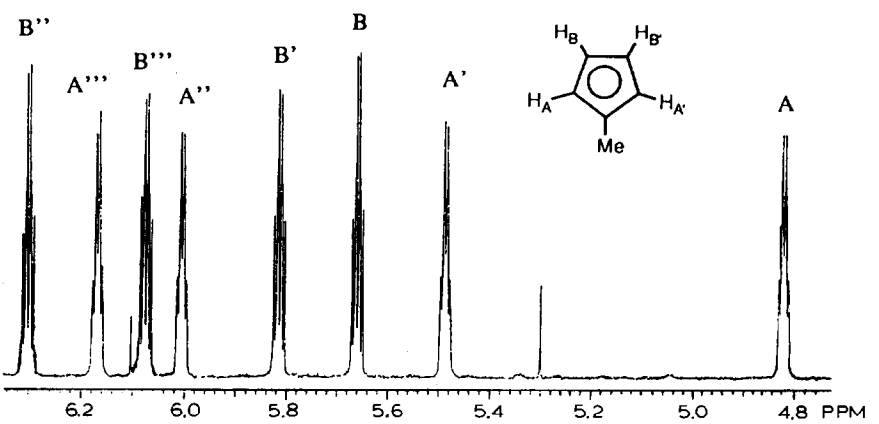


Fig. 1. Cyclopentadienyl region of the ^1H NMR spectrum of **2**.

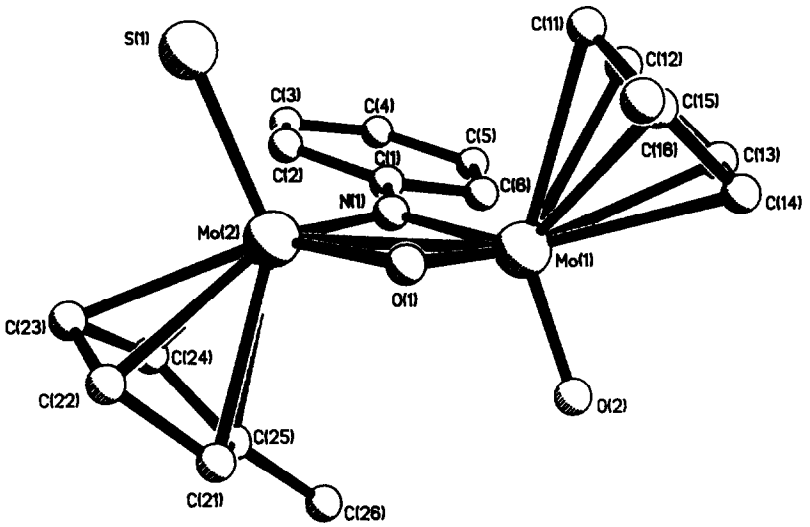


Fig. 2. The molecular structure of **2**, showing the atom-numbering scheme.

phenylimido [Mo(1)–N(1) 1.964(7); Mo(2)–N(1) 1.953(6) Å] moieties. Each molybdenum atom is bound to methylcyclopentadienyl ligands the relative orientation of which is *trans*, and are distinguished by the ligation at the further terminal site. Thus, Mo(1) carries an oxo ligand [Mo(1)–O(2) 1.715(8) Å] while Mo(2) carries the sulphido moiety [Mo(2)–S(1) 2.152(3) Å]. The central $Mo_2(\mu\text{-O})(\mu\text{-NPh})$ core is planar with the phenyl substituent being twisted slightly out of the plane. The overall geometry and constitution of **2** is similar to that found for **1** [4] and other related complexes [5–7]. Attempts to generate **2** from **1** via reaction with triphenylphoshine sulphide proved unsuccessful, **1** being quantitatively recovered.

In similar systems, we have previously noted a pronounced reactivity difference towards hydrolysis of imido ligands occupying either terminal or bridging sites. Thus, in the tetraimido complex $[(MeC_5H_4)Mo(NPh)(\mu\text{-NPh})]_2$ both terminal imido ligands undergo rapid hydrolysis whereas the bridging ligands are indefinitely stable towards hydrolysis even in acidic media [5]. Both **1** and **2** are indefinitely stable to hydrolysis in $CHCl_3$ at room temperature. Heating a wet toluene solution of **2**, however, resulted in the slow formation of **1**, a result of the substitution of the terminal sulphido moiety for an oxo ligand. A similar hydrolysis of a terminal sulphido ligand at a molybdenum(V) centre has been reported [6]. In contrast, in

Table 1

Selected bond angles (Å) and angles (°) for **2**

Mo(1)–Mo(2)	2.660(1)	Mo(1)–Mo(2)–N(1)	47.0(2)
Mo(1)–O(1)	1.938(6)	Mo(1)–Mo(2)–O(1)	46.7(2)
Mo(1)–O(2)	1.715(8)	Mo(1)–Mo(2)–S(1)	116.0(1)
Mo(1)–N(1)	1.964(7)	Mo(2)–Mo(1)–O(2)	112.1(3)
Mo(2)–N(1)	1.953(6)	O(1)–Mo(1)–N(1)	93.6(3)
Mo(2)–S(1)	2.152(3)	O(1)–Mo(2)–N(1)	93.9(3)
Mo(2)–O(1)	1.941(7)		

Table 2

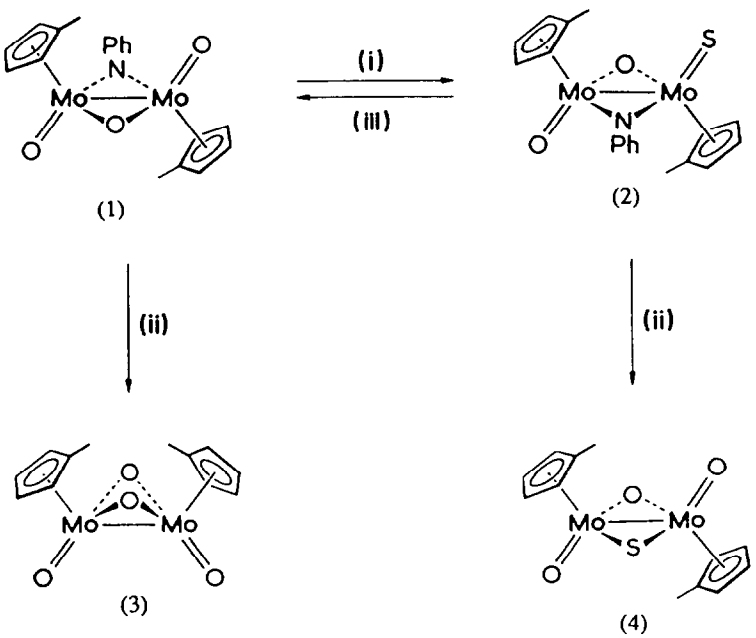
Crystallographic data for **2**

Formula	$C_{18}H_{19}NO_2SMo_2$
Fw	505.32
a, Å	7.592(2)
b, Å	9.8905(3)
c, Å	14.291(3)
α, deg	71.32(2)
β, deg	75.86(2)
γ, deg	67.84(2)
U, Å^3	924.11
Z	2
$F(000)$	500
d_{calc}, g/cm^3	1.82
Cryst. size, mm	0.28×0.22×0.18
μ(Mo-K_α), cm^{-1}	14.44
Data collection instrument	Nicolet R3mV
Radiation	Mo-K_α (λ = 0.71073 Å)
Orient. reflections: no.; range	30; $7 \leqslant 2\theta \leqslant 25$
Temp., °C	19
No. of unique data	3251
Total with $F_o^2 \geqslant 1.5\sigma(I)$	2605
No. of parameters	217
R [a]	0.063
R_w [b]	0.062
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.000967F^2$
Largest shift/esd, final cycle	0.001
Largest peak, e/Å^3	0.89

[a] $R = \Sigma[\,|F_o| - |F_c|\,]/\Sigma|F_o|$. [b] $R_w = \Sigma[\,|(F_o - F_c)| \cdot w^{1/2}]/\Sigma[F_o w^{1/2}]$.

acidic media rapid hydrolysis of the bridging imido moiety was observed for both **1** and **2**, the sulphido moiety of the latter remaining intact under these conditions. Thus, addition of aqueous hydrochloric acid to an acetone solution of **1** results in an appreciable darkening of the solution consistent with the formation of a protonated species. Rapid neutralisation led to the partial recovery of **1** (40%) together with the formation of the known complex $[(MeC_5H_4)MoO(\mu\text{-}O)]_2$ (**3**) (59%) [8] formed via hydrolysis of the bridging imido ligand. This behaviour is in marked contrast to that exhibited by the related complex $[(MeC_5H_4)MoO(\mu\text{-}NPh)]_2$ which undergoes numerous protonation–deprotonation cycles by aqueous acid with no sign of hydrolysis [5].

Complex **2** exhibits similar behaviour to **1** in acid media. Thus, while addition of hydrochloric acid to an acetone solution of **2** followed by neutralisation is reversible over short time periods, prolonged exposure results in the hydrolysis of the bridging imido moiety and the isolation of $[(MeC_5H_4)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)]$ (**4**) in 75% yield as a dark red solid. Complex **4** was characterised by analytical and spectroscopic techniques. The absence of any resonances associated with a phenylimido moiety in either the IR or ^{1}H NMR spectra indicates that hydrolysis has occurred which was confirmed by mass spectral data. That the sulphido group now adopts a bridging position is surmised from the lack of absorptions attributed to a terminal sulphido moiety in the IR spectrum (adsorptions due to bridging sulphido ligands generally



Scheme 1. (i) H_2S, THF; (ii) aqueous HCl, acetone; (iii) H_2O, toluene, 110 °C.

occur below 200 cm^{-1} and are thus inaccessible), while the observation of a single methyl resonance and four cyclopentadienyl resonances in the ^1H NMR spectrum indicate that the molecule possesses a centre of symmetry but no mirror plane. Complex **1** which also contains these symmetry elements exhibits similar characteristics in its ^1H NMR spectrum. A number of complexes closely related to **4** are known which display similar geometric properties to **2**, that is a planar metallacore geometry and a *trans*-disposition of cyclopentadienyl rings [6,7]. The transfer of the sulphido moiety from a terminal to a bridging site during the hydrolysis of **2** is interesting since we have not previously encountered the mobility of multiply bonded ligands in these systems, and may result from the thermodynamic preference of this ligand to occupy a bridging site. Thus, in the related bisoxo-bissulphido complex $[(C_5Me_5)MoO(\mu\text{-}S)]_2$ [6] both sulphido ligands occupy bridging sites while in a related series of complexes namely, $[(Et_2NCS_2)MoX(\mu\text{-}X)]_2$ ($X_4 = O_3S$, O_2S_2, OS_3) the sulphido moieties always occupy bridging sites [9]. Although there appears to be a thermodynamic preference for the sulphido moiety to occupy a bridging site, the isolation of **2** in which sulphur occupies a terminal site while the molecule contains a bridging oxo ligand suggests a strong kinetic stability.

In order to further investigate these processes and to determine the initial site of protonation a ^1H NMR study of the reaction of **1** with trifluoroacetic acid was carried out (Fig. 3). Upon addition of an excess of trifluoroacetic acid to a $CDCl_3$ of **1** an immediate darkening of the solution was observed with the clean formation of a new complex formulated as $[(MeC_5H_4)_2Mo_2O(OH)(\mu\text{-}O)(\mu\text{-}NPh)][CF_3CO_2]$ (**5**). This formulation is based on the observation of two methyl resonances and eight cyclopentadienyl resonances which indicate that the molecule contains neither a plane of symmetry or an inversion centre, the loss of the latter being consistent with protonation on a terminal oxo moiety. Support for this hypothesis comes from the

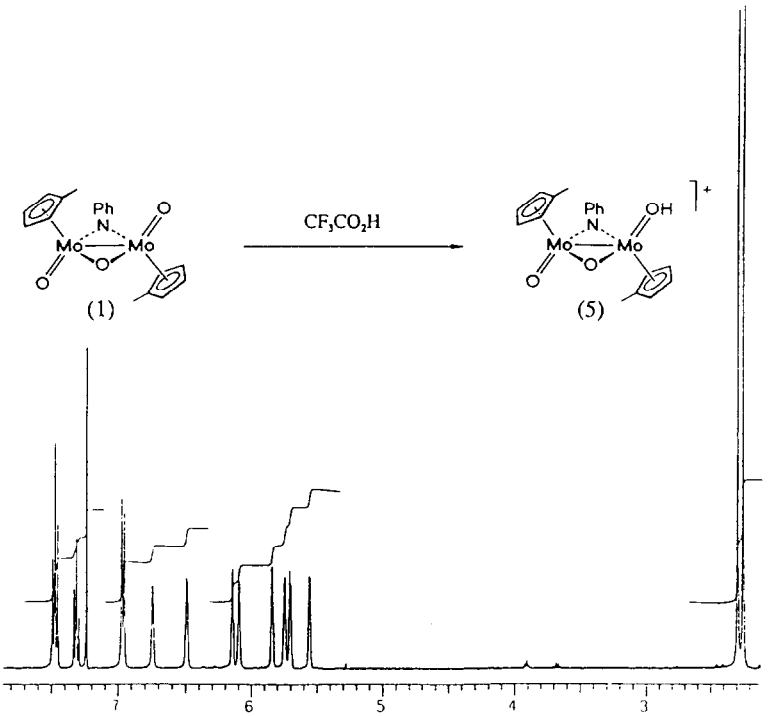
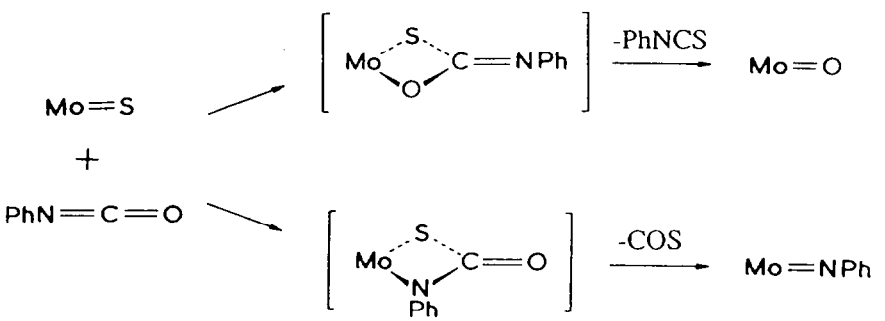


Fig. 3. ^{1}H NMR spectrum of **5**.

observation of simple and sharp resonances attributed to the phenylimido ligand in the aromatic region of the spectrum. Attempts to isolate **5** have to date proved unsuccessful since even after 10 min, appreciable decomposition is observed. Thus it appears that initial protonation of **1** takes place at a terminal oxo ligand, the hydrolysis reaction being induced by later attack of water at the electropositive metal centre.

We [5] and others [10] have previously utilised Wittig-like $(2+2)\pi$ additions of arylisocyanates to organometallic oxides in order to substitute oxo for arylimido moieties. Addition of excess phenylisocyanate to a THF solution of **2** led to the formation of a number of products including that expected for the substitution of



Scheme 2.

both oxo moieties for phenylisocyanate ligands, namely $[(MeC_5H_4)_2Mo_2(NPh)S(\mu\text{-}NPh)_2]$ (**6**) [5]. Surprisingly, however, the major product of this reaction was **1** (34%) formed via substitution of the terminal sulphido moiety for an oxo ligand, a result which indicates the occurrence of competitive substitution pathways as shown in Scheme 2. To our knowledge this behaviour has not previously been observed.

Conclusions

Under the appropriate conditions the selective reactivity of either terminal or bridging multiply bonded ligands can be induced at the dimolybdenum centre. This is exemplified by the reactivity of $[(MeC_5H_4)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}NPh)]$ (**1**) towards H_2S and mineral acid, resulting in the selective substitution of a terminal oxo and bridging phenylimido ligand respectively. The latter reaction is particularly interesting since while the hydrolysis of terminal imido ligands is known to occur at a number of metal centres [1,4,5], the replacement of a bridging imido for an oxo moiety has not previously been reported.

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