ELSEVIER

Journal of Organometallic Chemistry 560 (1998) 245–251

Journal of Organo metallic Chemistry

A dimolybdenum(III) azido compound: its decomposition into amido and nitrido derivatives. Crystal structure of $[Mo_3(O)(N)Cp_3(SMe)_4]$

P. Schollhammer [a], F.Y. Pétillon [a,*], J. Talarmin [a], Kenneth W. Muir [b,*]

[a] *UMR-CNRS 6521, Chimie, Electrochimie Moléculaires et Chimie Analytique, Faculté des Sciences, Université de Bretagne Occidentale, BP 809, 29285 Brest-Cédex, France*

[b] *Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK*

Received 5 January 1998

Abstract

The thermal reaction of $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-Cl})]$ **1** with NaN_3 in THF/EtOH gives a mixture of three compounds: $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-N}_3)]$ **2**, $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-NH}_2)]$ **3** and $[Mo_3(O)(N)Cp_3(SMe)_4]$ **4**. Only the μ-azido derivative **2** is isolated if the time of thermolysis is short. Its formation in the presence of EtOH leads in turn to the products **3** and **4**. Production of **3** from **2** requires N_2 loss followed by intermolecular reduction of the bimetallic system. Complete decomposition of the complexes occurs if the time of reaction is prolonged. An X-ray diffraction study shows that **4** contains a $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-N})]$ core that is linked through a Mo=N double bond to a CpMo(O)(SMe) unit. The resulting $Mo_3(\mu_3\text{-N})$ fragment, in which the N=Mo double bond is supported by two Mo–N single bonds involving the directly bonded metal atoms, is the most striking structural feature of **4**. The triply-bridging nitrido nitrogen atom adopts a distorted trigonal planar coordination. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Di- and trimolybdenum complex; Azido ligand; Nitrido ligand; Amido ligand; Thiolato-bridged complexes; Crystal structure; Cyclopentadienyl

1. Introduction

Mononuclear derivatives of molybdenum containing diazenide, hydrazide, nitride, imide and amide ligands have been widely studied because they are involved in the reduction of N_2 to ammonia through the Chatt cycle and because transformations of these ligands at metal centres may be of relevance to biological nitrogen fixation and reduction ([1,2]a). Additional insights into catalytic or stoichiometric processes involving nitrogenous substrates can be obtained from the behaviour of N-donor ligands attached to a bimetallic site [2].

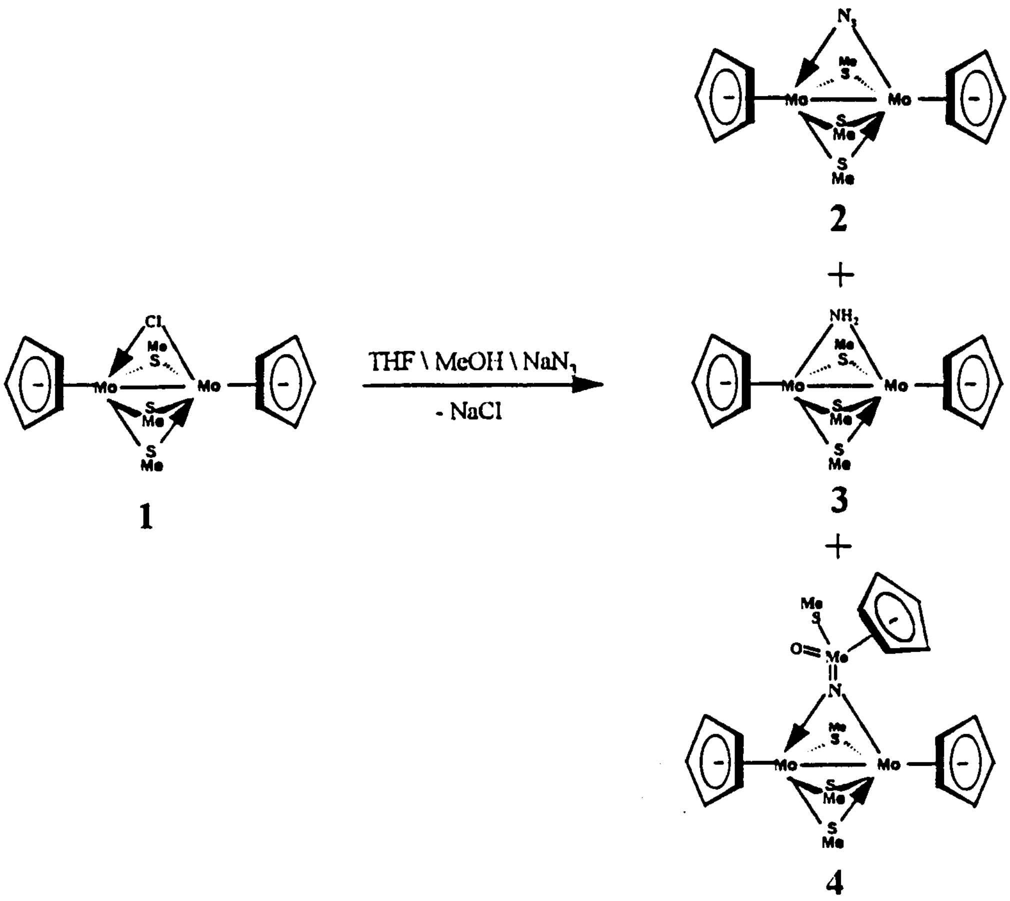
For several years we have been interested in the synthesis and reactivity of polymetallic systems that are rich in sulphur [3]. Recently we showed that the integrity of the dinuclear tris–thiolato-bridged core of the dimolybdenum(III) complex $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-Cl})]$ **1** is maintained during reactions in which the chloro bridge is opened [4] or replaced [5]. We have exploited this behaviour by reacting **1** with various hydrazines, thereby introducing into the $Mo_2(\mu\text{-SMe})_3$ bimetallic framework nitrogenous ligands, including bridging amido ([2]e) and diazenido [6] groups. These groups readily protonate, μ-NH_2 giving ammonia and RN_2— either μ-η^1-hydrazido(2-) or μ-η^2-diazene ligands. We also reported recently the electrochemical generation of an imido species from the μ-amido complex $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-NH}_2)]$ [7].

The synthesis of azido compounds offers a route to imido derivatives. In addition, reactions involving the heterolytic cleavage of the $MN–N_2$ bond [8] might allow a nitrido ligand to be introduced into the metallic core.

---

* Corresponding authors.

PII S0022-328X(98)00516-6



Scheme 1.

We report here the reaction of the molybdenum(III) compound $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ **1** with sodium azide, leading to the azido-bridged derivative $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}N_3)]$ **2**. The reaction of **2** in solution to give the amido-bridged complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)]$ **3** and the trinuclear nitrido product $[Mo_3(O)(N)Cp_3(SMe)_4]$ **4** is also described.

2. Results and discussion

The reaction of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ **1** with one equivalent of NaN_3, in THF/ethanol (4:1) at 60°C for 1 h, gives a mixture of the three compounds: $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}N_3)]$ **2** (40% yield), $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)]$ **3** (20% yield) and $[Mo_3(O)(N)Cp_3(SMe)_4]$ **4** (20% yield) (Scheme 1). Only the μ-azido complex **2** is observed when the reaction time is shortened (10–20 min; 60–80% yields). If the reaction is allowed to continue for more than 2 h, complete decomposition occurs and no definite product is obtained. Complexes **2**–**4** were characterised by spectroscopic analyses (see Section 3). The ^{1}H-NMR spectrum of **2** is typical of a species containing a $Cp_2Mo_2(\mu\text{-}SMe)_3$ core, with resonances at δ 6.10 and 6.02 ppm due to two inequivalent cyclopentadienyl rings and three peaks due to the three bridging thiolato ligands between δ 2.44 and 2.17 ppm. The ^{13}C-NMR spectrum confirms this structure. The IR spectrum, in KBr pellets, displays a band at 2040 cm^{-1} attributable to a $\nu(N_3)$ mode. The deshielding of the resonances of the cyclopentadienyl groups, both in the ^{1}H and in ^{13}C spectra, is unusual for a bimetallic tetra-bridged complex of molybdenum(III) $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}X)]$ but can plausibly be ascribed to the electronic effect of the azido bridge on the two metal centres. The inequivalence of the two CpMo groups indicates that the azido ligand is either non-linear or unsymmetrically bonded to the two molybdenum atoms. The μ-amido compound $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)]$ **3** has been identified by comparison of its spectral data with those of an authentic sample ([2]e). The ^{1}H- and ^{13}C-NMR patterns of complex **4** indicate the presence in the molecule of three cyclopentadienyl rings and of four SMe ligands. The IR spectrum shows a band at 900 cm^{-1} characteristic of $\nu(Mo{=}O)$, and elemental analyses are consistent with the formula $C_{19}H_{27}Mo_3NOS_4$. FAB-MS also confirms the trinuclear structure proposed for **4**. The spectrum displays the characteristic multiplets which arise from the polyisotopic nature of Mo and S. It is dominated by peaks attributable to the molecular ion

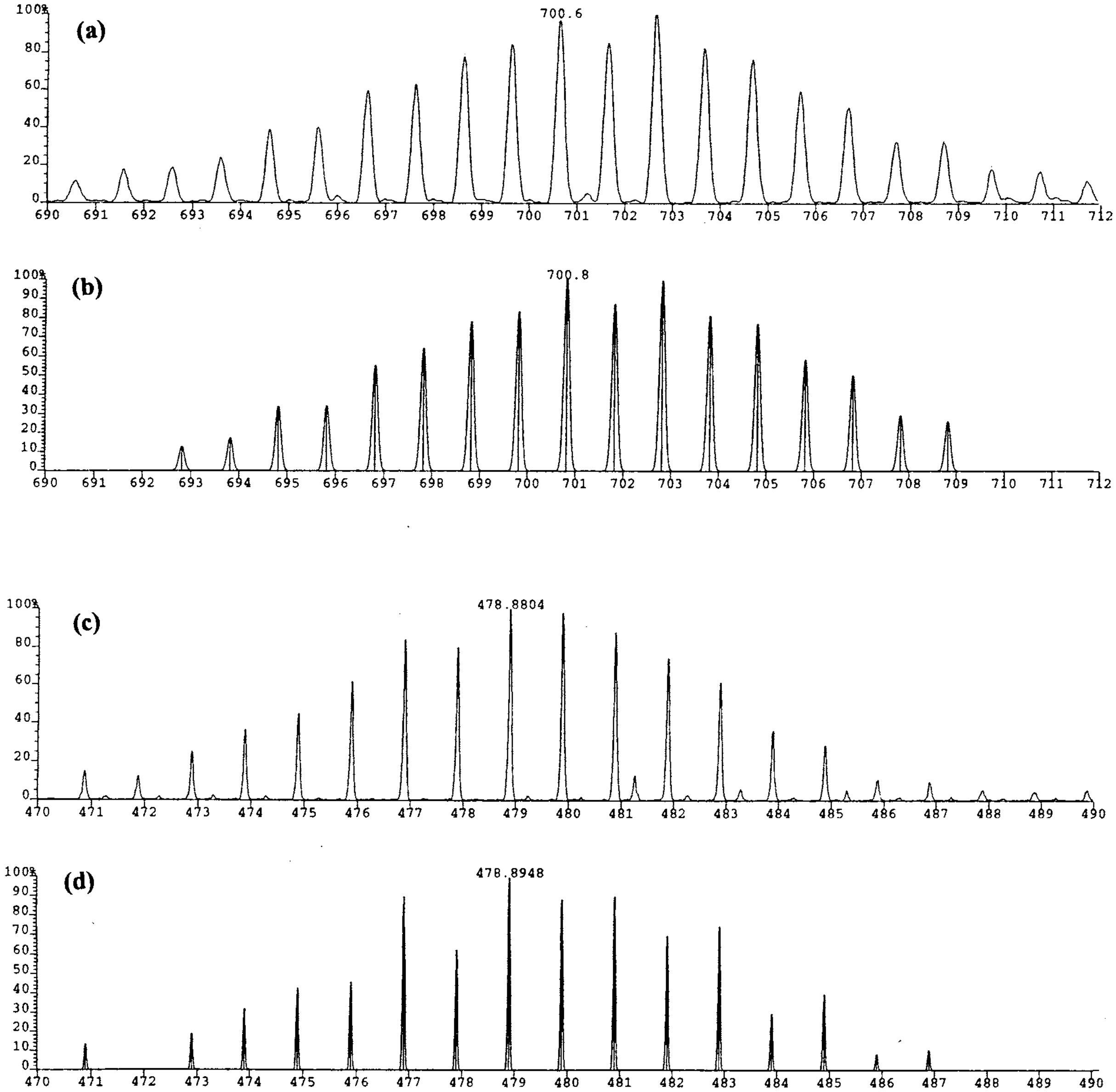


Fig. 1. (a) Measured and (b) calculated isotope patterns for the molecular ion $[Mo_3(O)(N)Cp_3(SMe)_4]^+$. (c) Measured and (d) calculated isotope patterns for $[Mo_2Cp_2(SMe)_3(\mu\text{-}NH_2)]^+$.

and to the ion $[Mo_2Cp_2(SMe)_3NH_2]^+$, the latter indicating that a $\{Mo_2Cp_2(SMe)_3N\}$ unit is present in the molecule. The observed isotope patterns for these two ions peak at m/z 701 and 479, are in good agreement with the calculated isotope distribution (Fig. 1).

The structure of **4** has also been confirmed by a single-crystal diffraction study (Fig. 2, Table 1). The molecule contains a $Mo_2Cp_2(\mu\text{-}SMe)_3$ core that has approximate local C_s symmetry and a close-to-linear Cp–Mo–Mo–Cp unit. The approximate mirror plane, defined by atoms S(2), S(3) and S(4), relates the nearly equivalent molybdenum(III) atoms Mo(2) and Mo(3). Their coordination can be described in terms of a four-legged piano stool. The Mo(2)–Mo(3) distance [2.547(1) Å] indicates the presence of the single Mo^{III}–Mo^{III} bond required by electron counting rules [9]. The $Mo_2Cp_2(\mu\text{-}SMe)_3$ core is linked via the triply bridging N(1) nitrogen atom to Mo(1). The atoms N(1), O(1), S(1) and the centroid of a Cp ring define around Mo(1), a distorted tetrahedron that is oriented so that the Mo(2)–N(1)–Mo(1)–O(1) torsion angle is $-27.9(6)°$. The unsymmetrical coordination of Mo(1) explains the NMR inequivalence of Mo(2) and Mo(3).

The usual rules suggest for Mo(1) a 16 electron configuration and oxidation state of VI, comparable with that found in the Cp*Mo(O)(N)R unit of the nitrido compound $[Cp^*Mo(NO)(R)](\mu\text{-}N)[Cp^*Mo(O)(R)]$ ($R = CH_2SiMe_3$) [10]. The Mo(1)–O(1) distance of 1.708(6) Å is close to the mean of 1.694(3) Å for

153 terminal Mo–O bonds [11]. The terminal Mo(1)–S(1) bond of 2.372(2) Å is significantly shorter than either the bridging Mo–S bonds [2.445(2)–2.480(2) Å] in the $\{Mo_2^{III}Cp_2(\mu\text{-}SMe)_3\}$ core [9] or the terminal arylthiolato Mo^{II}–S bond in the mononuclear derivative $[Mo^{II}(SPh)Cp(CO)(RNC)_2]$ [2.5040(11) Å] [12]. Somewhat surprisingly, a terminal Mo–SMe bond length does not appear to have been reported; other terminal Mo–SC_{sp^3} distances lie in the wide range 2.235–2.565 Å, with a mean for 275 such bonds of 2.405(3) Å [11]. The Mo^{VI}–S distance found here is thus slightly shorter than average, consistent with some S → Mo ($p\pi \rightarrow d\pi$) donations. Mo(1) lies 2.129(1) Å from the plane of its Cp ring, ca. 0.1 Å further than the corresponding distances [1.994(1) and 1.972(1) Å] for Mo(2) and Mo(3).

Table 1
Selected bond lengths (Å) and angles (°) for **4**

Bond length (Å)			
Mo(1)–O(1)	1.708(6)	Mo(1)–N(1)	1.849(7)
Mo(1)–S(1)	2.372(2)	Mo(2)–N(1)	2.092(7)
Mo(2)–S(2)	2.478(2)	Mo(2)–S(3)	2.456(2)
Mo(2)–S(4)	2.445(2)	Mo(2)–Mo(3)	2.547(1)
Mo(3)–N(1)	2.079(7)	Mo(3)–S(2)	2.462(2)
Mo(3)–S(3)	2.480(2)	Mo(3)–S(4)	2.461(2)
Bond angles (°)			
O(1)–Mo(1)–N(1)	106.0(3)	O(1)–Mo(1)–S(1)	107.3(2)
N(1)–Mo(1)–S(1)	92.7(2)	N(1)–Mo(2)–S(4)	76.0(2)
N(1)–Mo(2)–S(3)	111.5(2)	S(4)–Mo(2)–S(3)	72.72(7)
N(1)–Mo(2)–S(2)	69.5(2)	S(4)–Mo(2)–S(2)	117.61(8)
S(3)–Mo(2)–S(2)	74.02(8)	N(1)–Mo(3)–S(4)	75.8(2)
N(1)–Mo(3)–S(2)	70.0(2)	S(4)–Mo(3)–S(2)	117.62(8)
N(1)–Mo(3)–S(3)	111.0(2)	S(4)–Mo(3)–S(3)	72.03(7)
S(2)–Mo(3)–S(3)	73.87(8)	Mo(3)–S(2)–Mo(2)	62.06(6)
Mo(2)–S(3)–Mo(3)	62.12(6)	Mo(2)–S(4)–Mo(3)	62.53(6)
Mo(1)–N(1)–Mo(3)	144.7(4)	Mo(1)–N(1)–Mo(2)	137.9(4)
Mo(3)–N(1)–Mo(2)	75.2(2)		

The distinctive structural feature of the molecule is the five-electron donor nitrogen atom N(1) of the $Mo_3(\mu\text{-}N)$ unit. It is displaced by only 0.147(6) Å from the distorted trigonal plane defined by the three molybdenum atoms. The obtuse Mo(1)–N(1)–Mo(2) and Mo(1)–N(1)–Mo(3) angles [144.7(4)° and 137.9(4)°, respectively] contrast with the acute bridging Mo(2)–N(1)–Mo(3) angle [75.2(2)°]. This mode of coordination differs from the T-shaped Mo_3N arrangement previously observed in trinuclear nitrido clusters ([8]b,[13]). The Mo(2)–N(1) and Mo(3)–N(1) distances [2.092(7) and 2.079(7) Å, respectively] are consistent with single Mo–N bonds and the Mo(1)–N distance [1.849(7) Å] with a Mo=N double bond. The angles at N(1) (sum 357.8°), the Mo–N single bond lengths and the Mo–Mo distance in **4** all agree well with corresponding values in $[Mo_2Cp_2(\mu\text{-}SMe)_3(\eta^1\text{-}\mu\text{-}N{=}NPh)]$ (bridging Mo–N–Mo angle 77.5(1)°, Mo–N (av) 2.06 Å, Mo–Mo 2.578(1) Å—[6]).

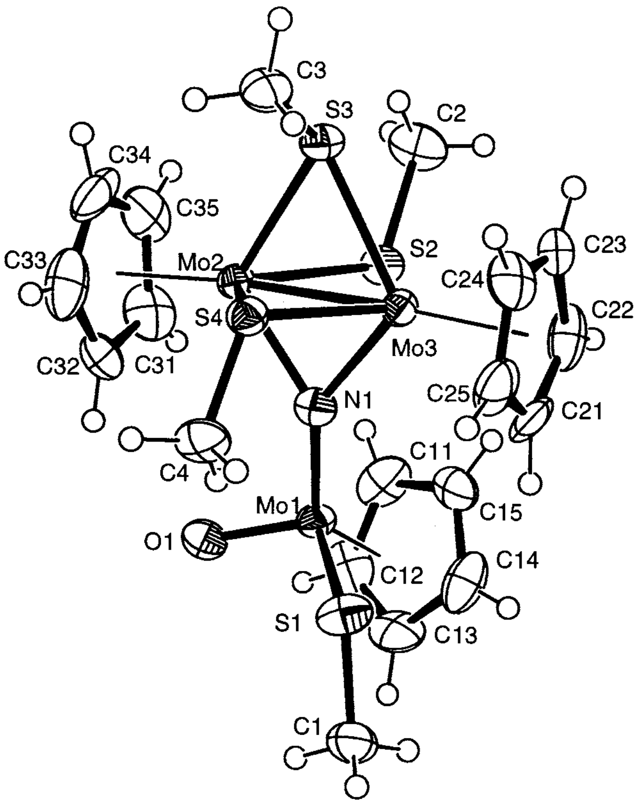
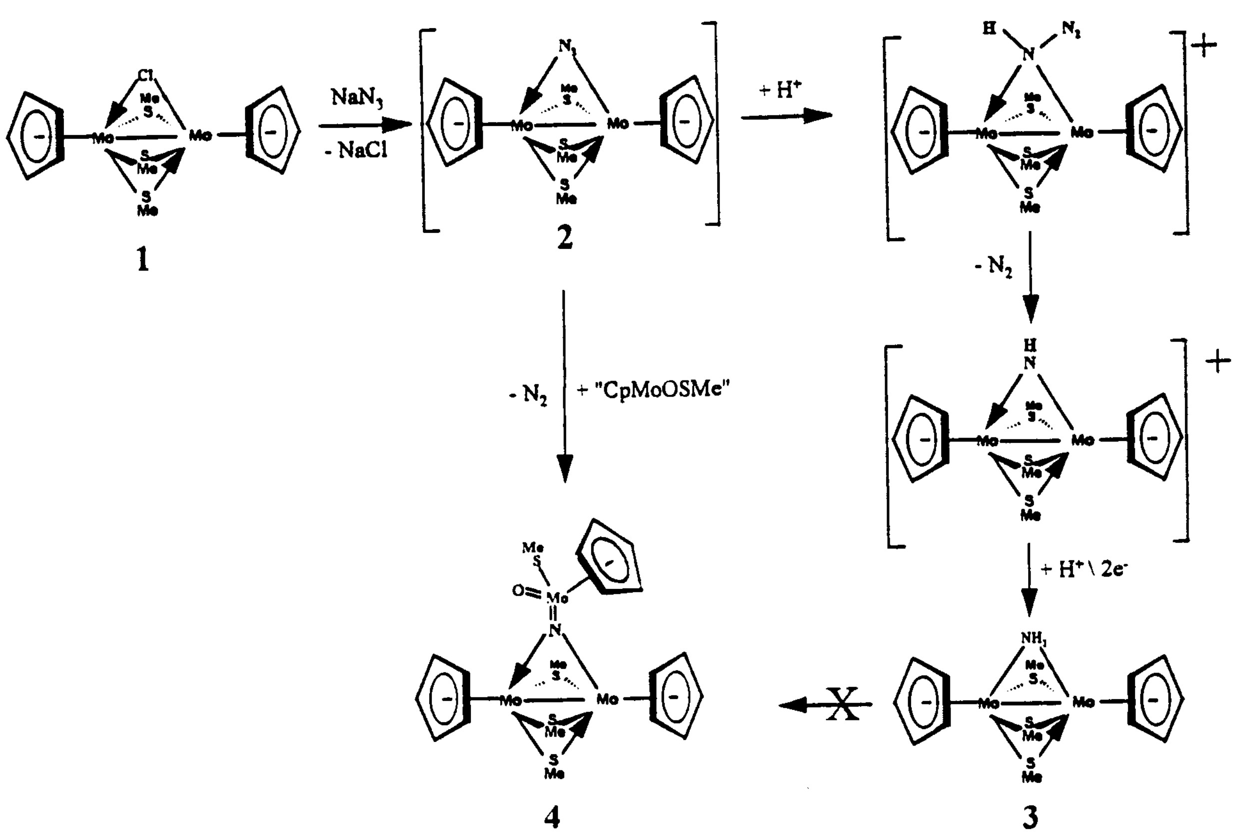


Fig. 2. A view of a molecule of **4** showing the atom numbering and 50% probability ellipsoids. Hydrogen atoms are shown as spheres of arbitrary size.

Substitution of the chloro bridge in **1** by the N_3^- ion with release of NaCl leads to the rapid initial formation of the μ-azido compound $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}N_3)]$ **2** in good yield (60–80%). Following a well-known pathway [8,14] protonation of the azide ligand (Scheme 2) then affords a μ-imido species after release of N_2. Though the proposed cationic imido intermediate has yet to be isolated, formation of such a species by two-electron oxidation of a μ-amido complex with release of a proton is known to occur, in some cases reversibly [7]. Finally, formation of **3** requires a further protonation and two-electron reduction. The requisite electrons, as proposed in another context, could come from the molybdenum atoms of other molecules [15]. Our attempts to protonate isolated samples of **2** failed to give well-defined products. The formation of **4** is more difficult to rationalise: it requires the oxidation and fragmentation of the dinuclear framework to give an oxidised mononuclear group. Formally, **4** could arise from the attachment of a {MoOCp(SMe)} fragment to the nitrogen atom of the nitrido species $\{Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}N)\}$ or by reaction of the mononuclear nitrido anion $Mo^{VI}ONCp(SMe)^-$ with $\{Mo_2^{III}Cp_2(\mu\text{-}SMe)_3\}^+$.



Scheme 2. Protonation of the azide ligand [8,14].

In conclusion, we have synthesised a μ-azido complex that decomposes, in protic solvents such as EtOH, into dinuclear amido and trinuclear derivatives. The trinuclear species contains a novel μ_3-nitrido ligand bridging molybdenum atoms in intermediate (III) and high (VI) formal oxidation states. Its formation indicates that linking a metallic framework to the nitrogen atom of the dinuclear $\{Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}N)\}$ core may be a feasible route to heterotrimetallic Mo_2M nitrido clusters.

3. Experimental

3.1. General procedures

The reactions were performed under nitrogen using standard Schlenk techniques, and solvents were deoxygenated and dried by standard methods.

IR spectra were obtained with a Perkin-Elmer 1430, and NMR spectra were recorded on a Bruker AC300 spectrophotometer. Shifts are relative to tetramethylsilane as an internal reference for ^{1}H and ^{13}C-NMR. The MS spectra were measured on a high resolution MS/MS Zab Spec TOF VG analytical at CRMPO (Rennes). Chemical analyses were performed by the Centre de Microanalyses du CNRS, Vernaison. Standard methods were used for preparation of $[Cp_2Mo_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ ([3]a).

3.2. Thermal reaction $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ **1** with NaN_3

A solution of NaN_3 (0.026 g, 0.4 mmol) in EtOH (10 ml) was added to a solution of **1** (0.2 g, 0.4 mmol) in THF (40 ml). The mixture was stirred at 60°C for 1h, changing from green to red/orange during this time. NaCl (0.020–0.023 g) precipitated from the solution and was separated by filtration. The solvents were evaporated to dryness. Complex **3** was extracted with pentane (3 × 15 ml). Evaporation of the extract and washing with cold pentane (2 ml) afforded a brown powder of **3** (0.038 g, 20% yield). The residue was dissolved in dichloromethane:pentane (1:1) and the solution was kept at -15°C overnight. Compound **4** precipitated. Filtration and evaporation of the filtrate afforded **2**, which was washed with pentane and obtained as a brown powder (0.117 g, 40% yield). **4** was dissolved in dichloromethane and purified by chromatography on a silica gel column, being eluted with CH_2Cl_2:THF (100:1) as a purple band. It was washed with pentane and obtained as a purple solid (0.06 g, 22% yield).

2: ^{1}H-NMR ($CDCl_3$): δ (ppm) 6.10 (s, 5H, Cp), 6.02 (s, 5H, Cp), 2.44 (s, 3H, SMe), 2.26 (s, 3H, SMe), 2.17 (s, 3H, SMe). ^{13}C-NMR ($CDCl_3$): δ (ppm) 105.2 (Cp), 104.1 (Cp), 29.5 (SMe), 26.4 (SMe), 20.0 (SMe). IR (KBr, cm^{-1}): 2040 $\nu(N_3)$. Anal. Calc. for $Mo_2C_{13}H_{19}N_3S_3$: C, 30.9; H, 3.8; N, 8.3. Found: C, 30.6; H, 3.8; N, 7.7.

3 ([2]e): ^{1}H-NMR ($CDCl_3$): δ (ppm) 5.29 (s, 10H, Cp), 1.54 (s, 3H, SMe), 1.53 (s, 3H, SMe), 1.37 (s, 3H, SMe). ^{13}C-NMR ($CDCl_3$): δ (ppm) 91.2 (Cp), 12.5 (Cp), 12.2 (SMe), 9.6 (SMe). IR (KBr, cm^{-1}): 3380 and 3280 ν(NH).

4: ^{1}H-NMR ($CDCl_3$): δ (ppm) 6.07 (s, 5H, Cp), 5.72 (s, 5H, Cp), 5.71 (s, 5H, Cp), 2.61 (s, 3H, SMe), 1.59 (s, 3H, SMe), 1.57 (s, 3H, SMe), 1.47 (s, 3H, SMe). ^{13}C-NMR ($CDCl_3$): δ (ppm) 104.3 (Cp), 98.9 (Cp), 95.1 (Cp), 22.4 (SMe), 20.5 (SMe), 10.8 (SMe), 8.9 (SMe). IR (KBr, cm^{-1}): 900 ν(MoO). Anal. Calc. for $Mo_3C_{19}H_{27}NOS_4$: C, 32.5; H, 3.9; N, 2.0. Found: C, 32.6; H, 3.9; N, 2.0.

3.3. *X-ray analysis of* $[Mo_3(O)(N)Cp_3(SMe)_4]$ ***4***

Measurements were made at 23°C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatised Mo–K_α radiation, $\lambda = 0.71073$ Å, using a crystal of dimensions $0.40 \times 0.10 \times 0.05$ mm^3.

Crystal data: $C_{19}H_{27}Mo_3NOS_4$, $M = 701.48$, triclinic, space group $P\bar{1}$, $a = 8.1878(12)$, $b = 10.633(2)$, $c = 13.558(2)$ Å, $\alpha = 84.818(13)$, $\beta = 84.846(10)$, $\gamma = 83.596(14)$°, $V = 1164.4(3)$ Å^3, $Z = 2$, $D_{calc} = 2.001$ g cm^{-3}, μ(Mo–K_α) $= 1.961$ mm^{-1}.

Cell dimensions are based on the setting angles of 22 reflections with $5.8 < \theta(\text{Mo–K}_\alpha) < 22.0$°. The intensities of 5348 reflections with $2.4 < \theta(\text{Mo–K}_\alpha) < 26$°, $-11 \leq h \leq 11$, $-15 \leq k \leq 2$ and $-19 \leq l \leq 19$ were estimated from $\omega/2\theta$ scans and corrected for Lp effects, 4.6% decomposition and for absorption using experimental Ψ-scans (empirical transmission factors 0.590–0.826 [16]). Averaging gave 4572 unique reflections ($R_{int} = 0.063$); of these 86 with $I < -3\sigma(I)$ were excluded from refinement calculations and 2524 were deemed observed $[I > 2\sigma(I)]$. The structure was solved by Patterson [17] and Fourier methods and refined to convergence ($\Delta\sigma < 0.01$ for 230 parameters, Table 2) on F^2 with $w = [\sigma^2(F^2) + (0.0197P)^2]^{-1}$ where $P = (F^2_{obs} + 2F^2_{calc})/3$. Final agreement indices were $R[I > 2\sigma(I)] = 0.045$ and wR_2 (all data) $= 0.116$ and in the final difference map $|\Delta\rho| < 0.93$ eÅ^{-3}. Anisotropic U_{ij} were refined for all non-hydrogen atoms. The Cp rings were refined as rigid groups with riding H atoms [C–H = 0.93 Å; U (H) $= 1.2U_{eq}$(C)]. One orientation parameter was refined for each methyl group [C–H = 0.96 Å; U (H) $= 1.5U_{eq}$(C)]. Scattering factors and anomalous dispersion corrections were those incorporated in the least-squares refinement program SHELXL-93 [18] and the WINGX package [19] was used for other calculations.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **4**

	x	y	z	U_{eq}
Mo(1)	2408(1)	584(1)	2599(1)	30(1)
Mo(2)	2936(1)	−2637(1)	3847(1)	27(1)
Mo(3)	2149(1)	−2787(1)	2090(1)	26(1)
S(1)	−310(3)	982(2)	2087(2)	45(1)
S(2)	5026(3)	−2613(2)	2407(2)	34(1)
S(3)	3024(3)	−4710(2)	3168(2)	33(1)
S(4)	115(3)	−2934(2)	3536(2)	31(1)
O(1)	2364(8)	1108(6)	3756(4)	45(2)
N(1)	2287(8)	−1147(6)	2792(5)	30(2)
C(1)	−759(12)	2687(9)	1783(7)	49(3)
C(2)	6452(10)	−4056(9)	2258(8)	51(3)
C(3)	1437(11)	−5664(8)	3732(7)	43(2)
C(4)	−1201(10)	−1503(9)	3736(7)	45(2)
C(11)	5249(7)	751(7)	2002(5)	55(3)
C(12)	4641(9)	2008(7)	2218(5)	55(3)
C(13)	3417(9)	2462(5)	1557(6)	55(3)
C(14)	3269(8)	1486(7)	932(4)	55(3)
C(15)	4401(9)	428(5)	1207(5)	47(3)
C(21)	1335(10)	−1688(5)	579(5)	52(3)
C(22)	2778(7)	−2519(7)	359(4)	50(3)
C(23)	2406(8)	−3782(6)	636(5)	43(2)
C(24)	734(8)	−3731(6)	1027(4)	46(2)
C(25)	73(7)	−2437(7)	992(5)	51(3)
C(31)	4377(9)	−1616(8)	4816(5)	57(3)
C(32)	2690(9)	−1336(6)	5144(5)	54(3)
C(33)	2077(9)	−2486(9)	5551(5)	64(3)
C(34)	3385(14)	−3477(6)	5473(5)	80(4)
C(35)	4806(10)	−2939(9)	5019(6)	73(4)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

4. Supporting information available

Tables of atomic parameters, a complete geometry listing, and observed and calculated structure factors are available from the authors. The structure will be deposited in the Cambridge Structural Database.

Acknowledgements

We are grateful to Dr P. Guenot (CRMPO, Rennes) for recording the mass spectra. We thank the CRNS (France), EPSRC (UK) and the Universities of Brest and Glasgow for support.

References

[1] (a) C.J. Pickett, J. Bioinorg. Chem. 1 (1996) 601. (b) R.L. Richards, Coord. Chem. Rev. 154 (1996) 83. (c) R.A. Henderson, J. Chem. Soc. Dalton Trans. (1995) 503. (d) R.E. Eady, G.J. Leigh, J. Chem. Soc. Dalton Trans. (1994) 2739.

[2] (a) M. Hidai, Y. Mizobe, Chem. Rev. 95 (1995) 5970. (b) G.J. Leigh, J.S de Souza, Coord. Chem. Rev. 154 (1996) 71. (c) T.A. Bazhenova, A.E. Shilov, Coord. Chem. Rev. 144 (1996) 69. (d)

S. Gambarotta, J. Organomet. Chem. 500 (1995) 117. (e) P. Schollhammer, F.Y. Pétillon, S. Poder-Guillou, J.Y. Saillard, J. Talarmin, K.W. Muir, Chem. Commun. (1996) 2633. (f) D. Sellmann, New J. Chem. 21 (1997) 681.

[3] (a) M.B. Gomez de Lima, J.E. Guerchais, R. Mercier, F.Y. Pétillon, Organometallics 5 (1986) 1952. (b) P. Schollhammer, F.Y. Pétillon, R. Pichon, S. Poder-Guillou, J. Talarmin, K.W. Muir, L. Manojlovic-Muir, Organometallics 14 (1995) 2277. (c) S. Poder-Guillou, P. Schollhammer, F.Y. Pétillon, J. Talarmin, K.W. Muir, P. Baguley, Inorg. Chim. Acta 257 (1997) 153. (d) P. Schollhammer, F.Y. Pétillon, S. Poder-Guillou, J. Talarmin, K.W. Muir, D.S. Yufit, J. Organomet. Chem. 513 (1996) 181. (e) S. Poder-Guillou, P. Schollhammer, F.Y. Pétillon, J. Talarmin, New J. Chem. 21 (1997) 477.

[4] F. Barrière, Y. Le Mest, F.Y. Pétillon, S. Poder-Guillou, P. Schollhammer, J. Talarmin, J. Chem. Soc. Dalton Trans. (1996) 3967.

[5] P. Schollhammer, E. Guénin, S. Poder-Guillou, F.Y. Pétillon, J. Talarmin, K.W. Muir, P. Baguley, J. Organomet. Chem. 539 (1997) 193.

[6] P. Schollhammer, E. Guénin, F.Y. Pétillon, J. Talarmin, K.W. Muir, D.S. Yufit, Organometallics, in press.

[7] F.Y. Pétillon, P. Schollhammer, J. Talarmin, J. Chem. Soc. Dalton Trans. (1997) 4019.

[8] (a) K. Denicke, J. Strahle, Angew. Chem. Int. Ed. Engl. 31 (1992) 955. (b) Z. Dori, R.F. Ziolo, Chem. Rev. 73 (1973) 274. (c) Y.J. Kim, D.-H. Kim, J.Y. Lee, S.W. Lee, J. Organomet. Chem. 538 (1997) 189 and references cited therein. (d) D. Seyferth, R. Taube, J. Organomet. Chem. 229 (1982) C19. (e) J. Chatt, J.R. Dilworth, J. Chem. Soc. Chem. Comm. (1975) 983. (f) P.C. Bevan, J. Chatt, J.R. Dilworth, R.A. Henderson, G.J. Leigh, J. Chem. Soc. Dalton Trans. (1982) 821. (f) P.T. Bishop, J.R. Dilworth, J.P. Hutchinson, J.A. Zubieta, Transition Met. Chem. 15 (1990) 177.

[9] See ([2]e, [5], [6]) for other examples of compounds with bimetallic $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}$ cores.

[10] J.D. Debad, P. Legzdins, R. Reina, M.A. Young, R.J. Batchelor, F.W.B. Einstein, Organometallics 13 (1994) 4315.

[11] (a) Cambridge Structural Database (October, 1997 version). F.H. Allen, O. Kennard, Chemical Design Automation News, 8 (1993) 1; 31–37. (b) Searches were performed at the Daresbury National Laboratory, Warrington, UK. D.A. Fletcher, R.F. McMeeking, D. Parkin, J. Chem. Inf. Comput. Sci. 36 (1996) 746. (c) See also International Tables for Crystallography, Vol. C, International Union of Crystallography, Kluwer, Dordrecht, 1992, pp. 714–778.

[12] L.C. McDermott, K.W. Muir, F.Y. Pétillon, S. Poder-Guillou, P. Schollhammer, Acta Cryst. C52 (1996) 74.

[13] (a) W.L. Gladfelter, Adv. Organomet. Chem. 24 (1984) 41. (b) N.D. Feasey, S.A.R. Knox, A.G. Orpen, J. Chem. Soc. Chem. Comm. (1982) 75. (c) D. Fenske, T. Godemeyer, K. Dehnicke, Z. Naturforsch. 43B (1988) 12. (d) M.H. Chisholm, K. Folting, J.C. Huffman, J. Leonelli, N.S. Marchant, C.A. Smith, L.C.E. Taylor, J. Am. Chem. Soc. 107 (1985) 3722.

[14] L.A.P. Kane-Maguire, F. Basolo, R.G. Pearson, J. Am. Chem. Soc. 91 (1969) 4609.

[15] P. Legzdins, D.T. Martin, C.R. Nurse, B. Wassink, Organometallics 2 (1983) 1238.

[16] A.C.T. North, D.C. Philips, F.S. Matthews, Acta Cryst. A24 (1968) 351.

[17] (a) G.M. Sheldrick, SHELXS. A program for the solution of crystal structures, University of Göttingen, Germany, 1985. (b) A.C.T. North, D.C. Philips, F.S. Matthews, Acta Cryst. A45 (1990) 467.

[18] G.M. Sheldrick, SHELXL93. A program for the refinement of crystal structures, University of Göttingen, Germany, 1993.

[19] L.J. Farrugia, WINGX. A program system for X-ray analysis, University of Glasgow, UK, 1996.