Methylation sites in tris(μ-thiolato)dimolybdenum(III) complexes

Nolwenn Cabon [a], François Y. Pétillon [a],*, Philippe Schollhammer *,[a],
Jean Talarmin [a], Kenneth W. Muir *,[b]

[a] *UMR CNRS 6521, Chimie, Electrochimie Moléculaires et Chimie Analytique, Faculté des Sciences,
Université de Bretagne Occidentale, CS 93837, 29238 Brest-cedex 3, France*
[b] *Chemistry Department, University of Glasgow, Glasgow, G128QQ, UK*

Abstract

Attempts at methylating cis-$[Mo_2Cp_2(\mu\text{-}SMe)_3L_2](BF_4)$ [Cp = η^5-C_5H_5; L = CO (**1a**) CNxyl (**1b**), CNBu^t (**1c**), NCMe (**1d**)] with methyl triflate gave the corresponding thioether-bridged cations $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}SMe_2)L_2]^{2+}$ (**4^{2+}**), except in the case of **1a** which did not react at room temperature. The electronic properties of the ancillary ligands L thus have a crucial influence on the course of this reaction. The dimeric compounds $[Mo_2Cp_2(\mu\text{-}SMe)_3(CNBu^t)(CN)]$ (**2**) and $[Mo_2Cp_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1\text{-}N{=}C(CH_3)CH_2CN\}]$ (**3**), which potentially offer the alternatives of S- or N-methylation, reacted with methylating agents to give mainly the S-methylated derivatives **5** and **7**. Only in the case of the nucleophilic reactant **2** was N-methylation also observed and isomer **6** was obtained as a minor product together with **5**. New complexes have been completely characterised by multinuclear NMR, IR and elemental analysis, supplemented for **5** by X-ray diffraction study at 100 K.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Dimolybdenum complexes; Thiolato-bridged complexes; Sulfur- and nitrogen compounds; S-methylation; N-methylation; Crystal structure

1. Introduction

Alkylation reactions of thiolates and other ligands bound to transition metals have attracted renewed interest during the last decade [1]. In particular, the factors which determine where methylation occurs in anionic or neutral bis(μ-thiolato)- and tetra(μ-sulfido)-molybdenum complexes have been extensively investigated [2]. Thus, we have shown that it is possible to discriminate between two potentially reactive ligands, such as CN$^-$ and SR, in the bis(μ-thiolato) complexes $[Mo_2Cp_2(\mu\text{-}SR)_2(CO)(CN)]^-$, A$^+$ (R = Me, Pr^i, Ph or CF$_3$) by adjusting the electronic properties of the sulfur substituent to ensure methylation at a selected site [2a,2b,2c]. Selective alkylation and protonation, at either a metal centre or a sulfur lone pair, have also both been demonstrated in mono- or dinuclear thiolate complexes [3,2g]. However, it remains to be seen how methylation reactions depend on: (i) the electronic properties of ancillary ligands, L, and (ii)

the number and type (thiolate, sulfide or disulfide) of bridging S-donor ligands in $\{MoL_2(\mu\text{-}SR/\text{-}S/\text{-}SS)_n\}$ complexes. Since alkylation reactions of transition metal complexes with three bridging S-donors have not previously been explored, we now consider how the characteristics of the ancillary ligands L influence the methylation reactions of the cationic tris(μ-thiolato)-molybdenum derivatives $[Mo_2Cp_2(\mu\text{-}SMe)_3L_2](BF_4)$ (L = CO (**1a**), CNxyl (**1b**), CNBu^t (**1c**) and NCMe (**1d**) [4a,4b,4c,4d]. Also described are analogous reactions of the two neutral tris(μ-thiolato) derivatives $[Mo_2Cp_2(\mu\text{-}SMe)_3(CNBu^t)(CN)]$ (**2**) [4c] and $[Mo_2Cp_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1\text{-}N{=}C(CH_3)CH_2CN\}]$ (**3**) [5] which possess additional potential sites for attack by electrophiles.

2. Results and discussion

2.1. Reactions of $[Mo_2Cp_2(\mu\text{-}SMe)_3L_2](BF_4)$ (**1**) with methylating agents

Two different outcomes were observed when the cationic molybdenum(III) dimers **1** were treated with the hard

---

* Corresponding author.
  E-mail address: francois.petillon@univ-brest.fr (F.Y. Pétillon).

alkylating agent methyl triflate (Scheme 1). Exposure of the complexes with L = CNxyl (**1b**), CNBu^t (**1c**) or NCMe (**1d**) to a large excess of methyl triflate resulted in methylation of a thiolate ligand and formation of the dicationic thioether derivatives **4b**–**4d**. The reactions of **1c** and **1d** were fast at room temperature, reaching completion within 1 hour. However, the bis(C≡Nxyl) derivative **1b** was slower to react, requiring reaction periods of 70 h to reach completion. This contrasts with the behaviour of the dicarbonyl species **1a** which did not react at all under similar conditions; all starting material was recovered (as the triflate salt of **1a**) after stirring for 70 h.

The new compounds were identified as molybdenum dimers bridged by a thioether and two thiolate ligands on the basis of their analytical, IR and NMR (^{1}H, ^{13}C, ^{19}F) data (see Section 4). The two Cp ligands are equivalent in each of the three products **4**, suggesting that methylation has occurred at a sulfur atom. The ^{1}H NMR spectra show, in addition to a single Cp resonance (relative intensity 10), two SMe$_2$ signals (intensity 3, each), and two SMe resonances (intensity 3, each). The inequivalency of the two methyl groups of the SMe$_2$ ligand is confirmed by ^{13}C{^{1}H} NMR spectroscopy. All these NMR data are consistent with location of the thioether ligand in the equatorial Mo$_2$S$_2$ plane: the two {CpMoL} cores are bridged by the three S-donor ligands as shown in Scheme 1. The ^{19}F spectra of the complexes indicate that both **4c** and **4d** have one BF$_4^-$ and one SO$_3$CF$_3^-$ as the counter ions, whereas **4b** has two SO$_3$CF$_3^-$ anions.

The facile alkylation of the isonitrile or nitrile derivatives **1b**–**1d** contrasts with the lack of reactivity of the dicarbonyl cation [Mo$_2$Cp$_2$(μ-SMe)$_3$(CO)$_2$]$^+$ (**1a$^+$**). We attribute the diminished nucleophilicity of the bridging thiolate in **1a** to enhanced S → Mo π-donation relative to that in the cations **1b**–**1d,** where the C≡NR or N≡CR groups are weaker π-acids than the CO ligands of **1a**. Clearly, the electronic properties of the ancillary ligands affect strongly the course of methylation of these related tris(μ-thiolato) compounds: weak π-acids such as CNBu^t and NCMe (and to lesser extent CNxyl) promote alkylation at the thiolate

bridge, whereas CO is sufficiently electron-withdrawing to inhibit the reaction. The ability of the trithiolates **1b**–**1d** to undergo methylation is perhaps surprising, since the overall positive charge of each complex would not be expected to favour reactions in which it behaves as a nucleophile. Indeed, we know of only one comparable example: the methylation of the thiolato bridge of the monocationic compound [Mo$_2$Cp$_2$(μ-SMe)(μ-SMe$_2$)(CO)$_2$]$^+$ (**2d**). In this case, methylation of the thiolate affords a bis(thioether) derivative, whereas the corresponding methylation reaction is not observed for the tris(thiolato) complex **1a**. This difference in susceptibility to methylation at thiolate in related dicarbonyl-molybdenum(II) and -molybdenum(III) cations may be attributable to the electronic effects of the two types of S-donor ligands. It should be observed that the mono-thioether complexes **4** are stable to further methyl addition. Finally, there is some evidence that the nucleophilicity of the sulfur atoms in the tris(thiolato)-bridged complexes **1** is restricted; for example, **1d** does not react with soft alkylating agents (e.g., CH$_3$I) though this reaction is generally observed for thiolate ligands bound to metal atoms which are in high oxidation states or are electron-deficient for other reasons [6].

The lability of the thioether ligand in complexes **4** has been demonstrated by monitoring the thermal decomposition of **4d** in CD$_3$CN by ^{1}H NMR spectroscopy. The dissociation of free dimethyl sulfide was readily detected at room temperature; the resonances of the starting complex disappeared and new resonances in the region 2.28–5.41 ppm for complex **8**, [Mo$_2$Cp$_2$(μ-SMe)$_2$(NCMe)$_4$](SO$_3$CF$_3$)(BF$_4$), and a singlet at 2.06 ppm for Me$_2$S appeared in their place.

2.2. Reactions of [Mo$_2$Cp$_2$(μ-SMe)$_3$(CNBu^t)(CN)] (2) and [Mo$_2$Cp$_2$(μ-SMe)$_3$ {μ-η^1-N=C(CH$_3$)CH$_2$CN}] (3) with methylating agents

Complexes **2** and **3** each contain three thiolate-type sulfur atoms and two types of nitrogen atom (isonitrile, cyanide, azavinylidene or nitrile) which are potential sites
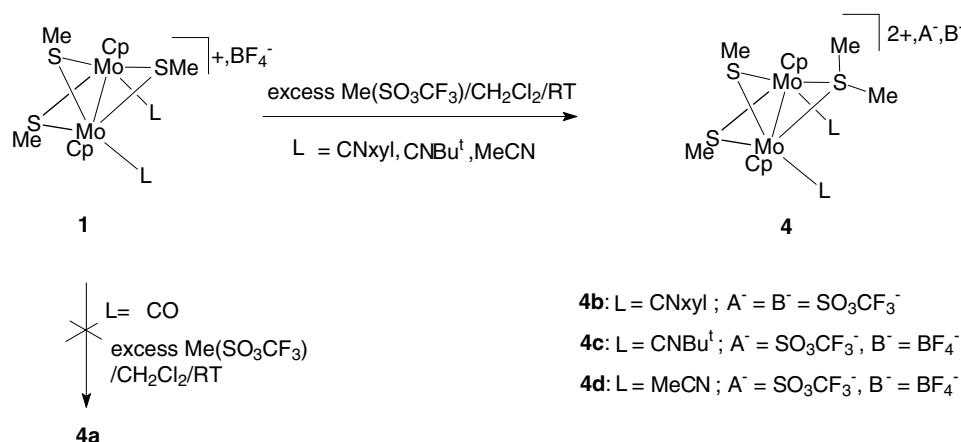
Scheme 1.

for alkylation. Accordingly, we have performed methyl additions to **2** and **3** to determine the relative nucleophilicity of their nitrogen and sulfur atoms. The reaction of **2** with 1 equiv. of (Me₃O)(BF₄) proceeded gradually, with a colour change from orange to red over a period of 1 h, and gave finally a mixture of crystals of two complexes, **5** and **6** (Scheme 2). The NMR spectra showed that only one isomer of each compound was present and that there was a 5:1 excess of **5** over **6**.

X-ray analysis establishes that the cation **5⁺** (Fig. 1) contains CpMo(CN) and CpMo(CNBuᵗ) fragments bridged almost symmetrically by one SMe₂ and two SMe ligands so that each Mo atom has a four-legged piano-stool coordination. The structure of **5⁺** differs from that of **2** [4c] by the addition of a second methyl substituent to S3, replacing μ-SMe⁻ by μ-SMe₂. In **2** the *syn* methyl groups on S1 and S3 lie on the same side of the equatorial Mo1, Mo2, S1, S3 plane as the CN and CNBuᵗ ligands. The Mo–S(μ-thioether) bond lengths in **5⁺** [2.391(1) and 2.392(1) Å] are shorter than the Mo–S(thiolate) distances [2.431(1)–2.468(1) Å] in **2** and **5⁺**. They are comparable with the Mo–S(μ-thioether) bond lengths of 2.400 and 2.405 Å in [{MoCl₂(SMe₂)}-(μ-Cl)₂(μ-SMe₂)] but longer than those in [Mo₂Cp₂-(μ-SMe₂)₂ (CO)(PMe₃)](BF₄)₂ (mean 2.341 Å) [7,2d]. The Mo–Mo distance in **5⁺** [2.833(1) Å], like that in **2** [2.804(1) Å], falls in the range 2.77–2.85 Å typical of {MoL}₂(μ-SMe)₃ complexes. Otherwise bond lengths and angles in **5⁺** are unremarkable. They agree with values in comparable structures and, indeed, particularly well with those in **2** [4c]. The spectroscopic ¹H and ¹³C{¹H}NMR) data for **5** (see Section 4) indicate that the solution structure is consistent with that observed in the solid state. In particular, an HMBC experi- riment clearly showed correlation of the methyl group at 2.56 ppm with that observed at 3.37 ppm, indicating the presence of a thioether ligand. Moreover, in the ¹H NMR spectrum, two SMe₂ resonances
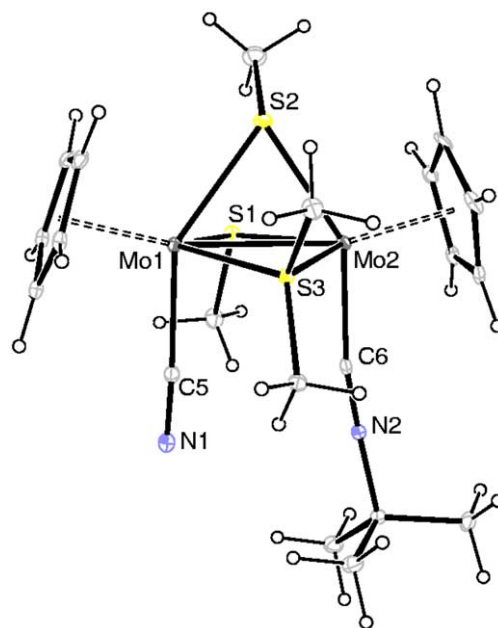

Fig. 1. Molecular structure of the cation **5⁺** showing 20% probability ellipsoids. Selected bond lengths (Å) and angles (°): Mo1–Mo2 2.833(1), Mo1–S1 2.431(1), Mo1–S2 2.465(1), Mo1–S3 2.391(1), Mo2–S1 2.468(1), Mo2–S2 2.459(1), Mo2–S3 2.392(1), Mo1–C5 2.149(4), Mo2–C6 2.093(4), C5–N1 1.151(4), C6–N2 1.154(4), N2–C7 1.464(4), 72.62(3), Mo1–C5–N1 176.7(3), Mo2–C6–N2 170.5(3), C6–N2–C7 171.2(3).

are observed, confirming that the site of methylation is at a thiolate-sulfur atom in an equatorial position. Lastly, an HMBC NMR experiment showed that long-range coupling was observed between the *t*-butyl group and the ¹³C resonance at 155.6 ppm but not that at 152.6 ppm, allowing assignment of the individual isocyanide and cyanide carbons (see Section 4).

The formulation of the minor product **6** can be deduced from the spectroscopic data (see Section 4). Its ¹H NMR spectrum exhibits two signals for the two cyclopentadienyl
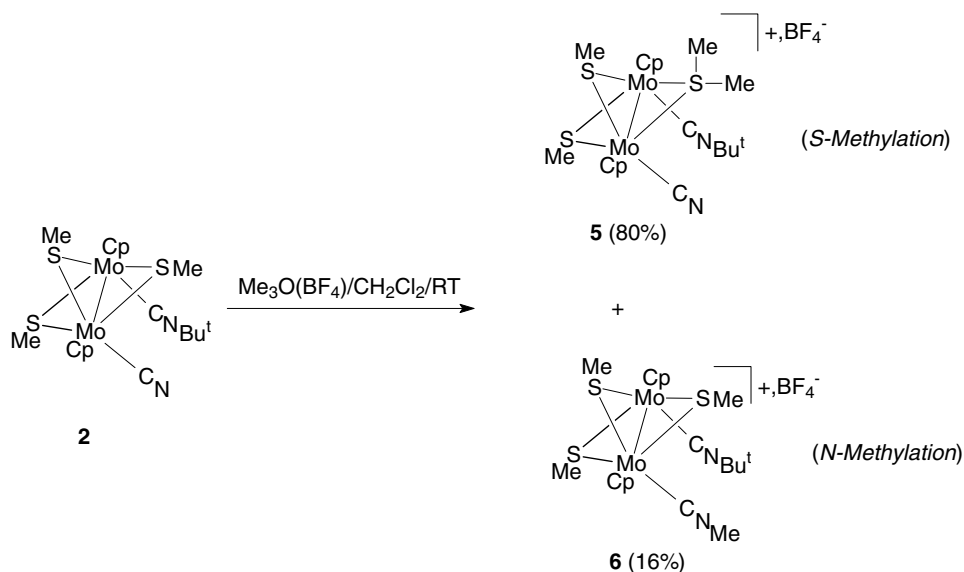
Scheme 2.
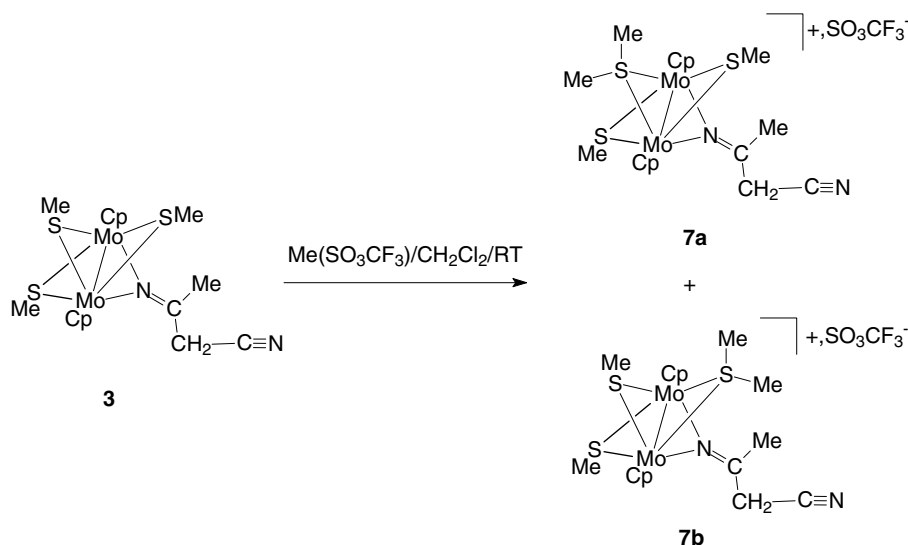
Scheme 3.

ligands, three peaks (each of intensity 3) for the three SMe bridges, and a single resonance (intensity 9) for the *t*-butyl group. In addition, a down-field signal (intensity 3) is observed in the region expected for CNMe groups (δ 3.68) [8]. This strongly suggests that methylation has occurred at the cyano-nitrogen atom and that **6** may be formulated as shown in Scheme 2.

Thus, the reaction of **2** with $(Me_3O)(BF_4)$ leads to methylation at both thiolate-S and cyano-N atoms. Since the respective products, **5** and **6**, are obtained in the ratio 5:1 it can be argued that electrophilic attack on **2** occurs preferentially at a thiolate-S atom rather than a cyano-N atom. In contrast, the reaction of Me_3O^+ with the related anionic derivative $[Mo_2Cp_2(\mu\text{-}SCF_3)_2(CO)(CN)]^-$ leads to methylation only at the cyano-N site [2c]. This difference can most probably be ascribed to deactivation of the sulfur atoms of the anionic complex by their strongly electron-withdrawing CF_3 substituents, though the presence of three thiolate bridges in **2** compared with two in the anionic complex may also be of significance.

The reaction of a dichloromethane solution of the μ-aza-vinylidene compound **3** with 1 equiv. of methyl triflate, at room temperature, led to the clean formation of a cationic complex **7** in quantitative yields, as an analytically pure solid. The NMR spectrum for **7** showed evidence for two isomers **7a** and **7b** in the ratio 1.5:1 (Scheme 3). When an acetonitrile solution of a 1.5:1 mixture of the two isomers was stirred at room temperature for 2 h **7b** isomerised into **7a**. The formation of **7** involves nucleophilic attack by a μ-thiolato ligand on the methyl triflate. Evidently the μ-thiolato ligands in **3** are more nucleophilic than the aza-vinylidene- and nitrile-N atoms. NMR, in particular, 2D HMBC^{1}H–^{13}C and ^{1}H–^{15}N experiments, showed a set of correlations of proton and carbon or nitrogen resonances in **7a** similar to those observed in the parent complex **3** for the μ-azavinylidene ligand. This implies that the μ-aza-

vinylidene ligand remains intact when **3** is converted into **7a** and that methylation occurs at a sulfur atom to afford a thioether ligand. Moreover, the equivalency of the two methyl groups of the SMe_2 ligand in **7b** implies methylation at an axial sulfur atom. On the other hand, the ^{1}H NMR spectrum of **7a** differs from that of **7b** in that the two methyl groups of the SMe_2 ligand are inequivalent, as are the two SMe methyl groups, indicating that isomer **7a** was formed by methylation at an equatorial sulfur atom. Reaction of **3** with a methylating agent thus selectively afforded only μ-SMe_2 compounds and no trace of a methylated nitrogen adduct could be detected.

3. Conclusion

The electronic properties of terminal ligands L in $[Mo_2Cp_2(\mu\text{-}SMe)_3L_2](BF_4)$(**1**) control the nucleophilicity of the lone pairs of thiolate-S atoms and hence the formation of thioether derivatives when **1** reacts with a methylating agent. When L = CO the strong π-acidity of carbonyl diminishes the donor power of the μ-thiolato-S atoms of **1** and stops their reaction with methyl triflate, whereas this reaction occurs if L is any of the weaker π-acids $CNBu^t$, NCMe or CNxyl. Methylation of compounds **2** and **3** containing nucleophilic S and N atoms occurs preferentially at a sulfur atom.

4. Experimental

4.1. General procedures

All reactions were carried out using standard Schlenk techniques under an inert atmosphere. Solvents were deoxygenated and dried according to standard procedures. The starting materials $[Mo_2Cp_2(\mu\text{-}SMe)_3L_2](BF_4)$ (L = CO (**1a**) [4a], CNxyl (**1b**) [4b], $CNBu^t$ (**1c**) [4c], NCMe (**1d**) [4d],

$[Mo_2Cp_2(\mu\text{-SMe})_3(CNBu^t)(CN)]$ (**2**) [4c] and $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-N}{=}C(CH_3)CH_2CN]$ (**3**) [5] were prepared as described previously. Elemental analyses were obtained from either the Service de Microanalyse I.C.S.N., Gif sur Yvette (France), or the Centre de Microanalyses du CNRS, Vernaison (France). IR spectra were obtained on a Nicolet-Nexus FT IR instruments as KBr pellets. The NMR spectra (^{1}H, ^{13}C, ^{19}F, ^{15}N) were recorded at room temperature on either a Bruker AC 300 or AMX$_3$400 and DRX 500 spectrometers and were referenced to SiMe$_4$ (^{1}H, ^{13}C), CFCl$_3$ (^{19}F) and CH$_3$NO$_2$ (^{15}N). ^{1}H–^{13}C and ^{1}H–^{15}N 2D experiments were carried out on a Bruker DRX 500 spectrometer.

4.2. Reactions of [Mo₂Cp₂(μ-SMe)₃L₂(BF₄) (1) with methyl trifluoromethanesulfonate: syntheses of 4

A solution of **1** (**1a**: 168 mg, 0.28 mmol; **1b**: 110 mg, 0.135 mmol; **1c**: 190 mg, 0.262 mmol; **1d**: 105 mg, 0.166 mmol) in dichloromethane (10 ml) was stirred in the presence of a large excess of CF₃SO₃Me (**1a**: $V = 302$ μl, 2.8 mmol; **1b**: $V = 200$ μl, 1.85 mmol; **1c**: 250 μl, 2.28 mmol; **1d**: $V = 100$ μl, 0.88 mmol) at room temperature for 70, 1 and 1 h for **1b**, **1c** and **1d**, respectively, after which time the starting compound was wholly consumed. The solution was then concentrated and diethylether was added to precipitate powders, which were washed twice with cold pentane (2×10 ml) affording red-brown (**4b**: 100 mg, 72%), orange (**4c**: 205 mg, 83%) or pink-red (**4d**; 95 mg, 72%) solids. In the case of **1a**, no methylation reaction was observed and all the starting compound was recovered as the triflate salt after 24 h stirring.

4b: IR (cm^{-1}): v(CN) 2094 s, 1973 sh; v(C–F) 1263 s, 1223 m, 1151 s. ^{1}H NMR ((CD₃)₂CO): δ 7.25, 7.22, 7.20, 7.02, 7.00 (m, 6H, C–H(xyl)), 6.24 (s, 10H, Cp), 3.78 (s, 3H, S*Me*₂), 2.95 (s, 3H, S*Me*₂), 2.91 (s, 3H, S*Me*), 2.14 (s, 12H, *Me*(xyl)), 1.91 (s, 3H, S*Me*). ^{13}C{^{1}H} NMR ((CD₃)₂CO): δ 174.3 (s, xylN*C*), 137.05 (s, *C*(xyl) *ortho* or *meta*), 131.2 (s, *C*(xyl) *ipso* or *para*), 129.3 (s, *C*(xyl) *ortho* or *meta*), 128.45 (s, *C*(xyl) *ipso* or *para*), 122.2 (q, $^1J_{C-F} = 328.0$ Hz, C*F*₃SO₃$^-$), 96.2 (s, *C*₅H₅), 40.55 (s, S(*C*H₃)₂), 28.1 (s, S(*C*H₃)₂), 24.55 S(*C*H₃), 19.35 (s, *C*H₃(xyl)), 8.3 (s, S*C*H₃). ^{19}F NMR ((CD₃)₂CO): δ −74.0 (C*F*₃SO₃$^-$). Anal. Calc. for C₃₄H₄₀F₆Mo₂N₂O₆S₅: C, 39.3; H, 3.9; N, 2.7. Found: C, 38.4; H, 3.8; N, 2.6%.

4c: IR (cm^{-1}): v(CN) 2141 s, 2026 sh; v(C–F) 1263 s, 1226 m, 1157 s; ; v(B–F) 1110–1057 s(br). ^{1}H NMR ((CD₃)₂CO): δ 6.00 (s, 10H, Cp), 3.50 (s, 3H, S*Me*₂), 2.70 (s, 3H, S*Me*₂), 2.64 (s, 3H, S*Me*), 1.71 (s, 3H, S*Me*), 1.69. (s, 18H, Bu^t). ^{13}C{^{1}H} NMR(CD₃CN): δ 157.3 (s, Bu^{t}N*C*), 122.0 (q, $^1J_{C-F} = 322.0$ Hz, C*F*₃SO₃$^-$), 95.85 (s, *C*₅H₅), 62.5 (s, *C*Me₃), 39.1 (s, S(*C*H₃)₂), 30.0 (s, C(*C*H₃)₃), 26.9 (s, S(*C*H₃)₂), 26.5 (s, S*C*H₃), 9.55 (s, S*C*H₃), ^{19}F NMR ((CD₃)₂CO): δ −74.0 (C*F*₃SO₃$^-$), 146.0 (B*F*₄). Anal. Calc. for C₂₅H₄₀BF₇Mo₂N₂O₃S₄: C, 34.1; H, 4.6; N, 3.2. Found: C, 33.6; H, 4.5; N, 3.1%.

4d: IR (cm^{-1}): v(C≡N) 2315 w, 2274 w; v(C–F) 1263 vs, 1224 m, 1154 s; v(B–F) 1112–1048 s(br). ^{1}H NMR

((CD₃)₂CO): δ 5.97 (s, 10H, Cp), 5.61 (s, 3H, C*H*₂Cl₂), 3.07 (s, 3H, S*Me*₂), 2.83 (s, 3H, S*Me*₂), 2.70 (s, 3H, *Me*CN), 2.15 (s, 3H, S*Me*), 1.67 (s, 3H, S*Me*). ^{13}C{^{1}H} NMR ((CD₃)₂CO): δ 142.2 (s, CH₃*C*N), 122.1 (q, $^1J_{C-F} = 320.9$ Hz, C*F*₃SO₃$^-$), 97.6 (s, *C*₅H₅), 97.2 (s, *C*₅H₅), 54.7 (s, *C*H₂Cl₂), 26.3, 16.2 (s, S(*C*H₃)₂), 12.6, 12.5 (s, S*C*H₃), 4.57 (s, *C*H₃CN). ^{19}F NMR ((CD₃)₂CO): δ −74.0 (C*F*₃SO₃$^-$), 145.8 (B*F*₄$^-$). Anal. Calc. for C₁₉H₂₈BF₇Mo₂N₂O₃S₄, 1.5 CH₂Cl₂: C, 26.6; H, 3.4; N, 3.0. Found: C, 26.2; H, 3.4; N, 2.8%.

4.3. Reaction of [Mo₂Cp₂(μ-SMe)₃(CNBuᵗ)(CN)] (2) with (Me₃O)(BF₄): syntheses of [Mo₂Cp₂(μ-SMe)₂-((μ-SMe₂)(BuᵗCN)(CN)](BF₄) (5) and [Mo₂Cp₂-(μ-SMe)₃(CNBuᵗ)(CNMe)] (BF₄) (6)

A mixture of **2** (100 mg, 0.175 mmol) and 1 equiv. of (Me₃O)(BF₄) (26 mg) was stirred in dichloromethane (50 ml) at room temperature for 1 h, after which time the starting compound was wholly consumed. The solvent was then removed under vacuum, and the residue was shown by ^{1}H NMR analysis to contain three compounds: **5** (80%), **6** (16%) and a minor, uncharacterised bimetallic product (4%). The residue was washed with diethylether (10 ml) and pentane (10 ml) to afford two inseparable isomers **5** and **6** as a pure red powder (91 mg, 77% overall yield). The major product **5** has been fully characterised by X-ray analysis of red crystals of this complex, which were picked from a 1:1 diethylether–dichloromethane solution of a mixture of **5** and **6** in a 5:1 ratio. IR (cm^{-1}), mixture **5–6**: v(CN) 2162 s, 2089 s. ^{1}H NMR (CDCl₃) (assignments based on ^{1}H–^{13}C HMBC experiments): δ: 5.59 (s, 5H, Cp), 5.48 (s, 5H, Cp), 3.37 (s, 3H, S*Me*₂), 2.56 s, 3H, S*Me*₂), 2.55 (s, 3H, S*Me*eq), 1.46 (s, 3H, S*Me*ax), 1.45 (s, 9H, Bu^t); **6**: δ 5.33 (s, 5H, Cp), 5.32 (s, 5H, Cp), 3.68 (s, 3H, CN*Me*), 2.39 (s, 3H, S*Me*eq), 2.34 (s, 3H, S*Me*eq), 1.48 (s, 9H, Bu^t), 1.36 (s, 3H, S*Me*ax); ^{13}C{^{1}H} NMR (CDCl₃) (assignments based on ^{1}H–^{13}C HMBC experiments), **5**: δ 155.6 (*C*NBu$^+$), 152.8 (*C*N), 93.4 (*C*₅H₅), 92.8 (*C*₅H₅), 59.5 (*C*Me₃), 35.6 (S(*C*H₃)₂), 30.4 ((S(*C*H₃)₂), 28.7 (C(*C*H₃)₃), 24.2 (S*C*H₃), 8.9 (S*C*H₃); **6**: δ 91.4 (*C*₅H₅), 91.0 (*C*₅H₅), 59.4 (*C*Me₃), 31.1 (S*C*H₃eq.), 30.6 (S*C*H₃eq.), 26.1 (C(*C*H₃)₃), 25.0 (*C*H₃NC), 9.8 (S*C*H₃ax). Anal. Calc. for C₂₀H₃₁BF₄Mo₂N₂S₃: C, 35.6; H, 4.6; N, 4.2. Found: C, 35.6; H, 4.8; N, 4.4%

4.4. Synthesis of [Mo₂Cp₂(μ-SMe)₂(μ-SMe₂){μ- N=C(CH₃)CH₂CN}](CF₃SO₃) (7)

A solution of complex **3** (100 mg, 0.18 mmol) in dichloromethane (20 ml) was stirred in the presence of 1 equiv. of CF₃SO₃CH₃ ($V = 20.5$ μl) for 1 h at room temperature. The solution was then concentrated and diethylether (10 ml) was added to precipitate an orange powder, which was washed twice with cold pentane (2×10 ml), affording **7** quantitatively as an analytically pure, orange product. Complex **7** was obtained as a mixture of two inseparable

isomers **7a** and **7b** in a 1.5:1 ratio by chromatography. Syntheses conducted at several temperatures between 0 and 40 °C showed an increasing of the yields of **7a** at the expense of those of **7b**, when the temperature increases (**7a**:**7b** ratios = 1.3 at 0 °C, and 3.0 at 40 °C). Stirring 130 mg of a mixture of the two isomers **7a** and **7b** (1.5:1 ratio) in acetonitrile for 2 h at room temperature, gave **7a** as the only product detected by ^1H NMR analysis (CD_2Cl_2). IR (cm^{-1}), mixture **7a**–**7b**: ν(CN) 2220. ^1H NMR ($CDCl_2$) (assignments based on ^1H–^{13}C and ^1H–^{15}N HMBC experiments), **7a**: 5.86 (s, 5H, Cp), 5.84 (s, 5H, Cp), 3.05 (s, 2H, CH_2CN), 2.55 (s, 6H, SMe_2), 2.09 (s, 3H, MeCN), 1.33 (s, 6H, SMe); **7b**: δ 5.85 (s, 5H, Cp), 5.83 (s, 5H, Cp), 3.08 (AB, J_{H-H} = 16.9 Hz, 2H, CH_2CN), 2.27 (s, 3H, SMe_2), 2.13 (s, 3H, SMe_2), 2.08 (s, 3H, MeCN), 1.66 (s, 3H, SMe), 1.34 (s, 3H, SMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 243 K) (assignments based on ^1H–^{13}C and ^1H–^{15}N HMBC experiments), **7a**: δ 163.1 (C=N), 116.0 ($C\equiv$N), 94.5 (C_5H_5), 32.2 (CH_2), 28.2 (CH_3C=N), 23.6 (S($CH_3)_2$), 13.1 (SCH_3). ^{15}N NMR (CD_2Cl_2, 243 K) (assignments based on ^1H–^{13}C and ^1H–^{15}N HMBC experiments), **7a**: δ −129.5 ($N\equiv$C), −33.2 (N–C); **7b**: δ −129.5 ($N\equiv$C), −33.2 (N=C). Anal. Calc. for $C_{19}H_{27}F_3Mo_2N_2O_3S_4$: C, 32.2; H, 3.8; N, 3.9. Found: C, 32.3; H, 4.0; N, 3.8%.

4.5. Transformation of *4d* in acetonitrile into [Mo₂Cp₂(μ-SMe)₂(CH₃CN)₄](BF₄)(CF₃SO₃) (8)

A solution of compound **4d** (125 mg, 0.150 mmol) in acetonitrile (5 ml) was stirred for 3 h at room temperature. The colour of the solution turned from pink-red to red-orange. The solution was then concentrated and diethylether (20 ml) was added to precipitate a red solid, affording **8** in 94% yield. Compound **8** was identified by comparison of its ^1H NMR spectrum (($CD_3)_2CO$) with that of the known bis(tetrafluoroborate) salt [9]. ^1H NMR (($CD_3)_2CO$): δ 5.41 (s, 10H, Cp), 2.80 (s, 12H, MeCN), 2.28 (s, 6H, SMe).

4.6. Crystal data for *5*

All measurements were made on a Nonius KappaCCD diffractometer with Mo Kα radiation, λ = 0.71073 Å. Standard procedures were used to solve and refine each structure [10]. Non-hydrogen atoms were refined with anisotropic displacement tensors. H-atoms were located using stereochemical considerations for Cp groups and difference maps for methyl groups. They subsequently rode on their parent C atoms. The orientation of each methyl was freely refined.

[$C_{20}H_{31}Mo_2N_2S_3$](BF₄) · CH_2Cl_2, M = 759.26, T = 100 K, triclinic, a = 8.8413(3) Å, b = 11.0381(4) Å, c = 15.5759(5) Å, α = 71.955(2)°, β = 80.720(2)°, γ = 83.592(1)°, V = 1423.3(1) Å^3, space group $P\bar{1}$, Z = 2, D_c = 1.772 Mg/m^3, μ(Mo Kα) = 1.33 mm^{-1}, 19,070 measured reflections, 6461 independent, [R_{int} = 0.061], $R(F)$ = 0.0673, $wR(F^2)$ = 0.0735 (all data), $|\Delta\rho|$ < 0.83 e Å^{-3}.

5. Deposited material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as CCDC 279845. Copies can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ [Fax: international +44(0)-1223/336-033; E-mail: deposit@ccdc.com.ac.uk]. Tables of crystallographic data, atomic parameters and geometric parameters are available as Supplementary data.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem. 2005.09.042.

References

[1] A.J.L. Pombeiro, V.Y. Kukushkin, in: J.A. McCleverty, T.J. Mayer (Eds.), Comprehensive Coordination Chemistry II, vol. 1, Elsevier, Oxford, 2004, p. 585.
[2] (a) M.-L. Abasq, F.Y. Pétillon, J. Talarmin, J. Chem. Soc., Chem. Commun. (1994) 2191;
(b) M.-L. Abasq, F.Y. Pétillon, P. Schollhammer, J. Talarmin, New. J. Chem. 20 (1996) 1221;
(c) M.-L. Abasq, D.L. Hughes, F.Y. Pétillon, R. Pichon, C.J. Pickett, J. Talarmin, J. Chem. Soc., Dalton Trans. (1997) 2279;
(d) N. Kuhn, E. Zauder, R. Boese, D. Bläser, J. Chem. Soc., Dalton Trans. (1988) 2171;
(e) H. Brunner, H. Kauermann, W. Meir, J. Wachter, J. Organomet. Chem. 263 (1984) 183;
(f) C.J. Casewit, R.C. Haltiwanger, J. Noordik, M. Rakowski DuBois, Organometallics 4 (1985) 119;
(g) P. Bernatis, R.C. Haltiwanger, M. Rakowski DuBois, Organometallics 11 (1992) 2435;
(h) L.L. Lopez, J. Gabay, R.C. Haltiwanger, K. Green, J. Allshouse, C.J. Casewit, M. Rakowski DuBois, Organometallics 12 (1993) 4764;
(i) J. Gabay, S. Dietz, P. Bernatis, M. Rakowski DuBois, Organometallics 12 (1993) 3630;
(j) J. Allshouse, B.B. Kaul, M. Rakowski DuBois, Organometallics 13 (1994) 28.
[3] M.Y. Darensbourg, W.-F. Liaw, C.G. Riordan, J. Am. Chem. Soc. 111 (1989) 8051.
[4] (a) M.B. Gomes de Lima, J.E. Guerchais, R. Mercier, F.Y. Pétillon, Organometallics 5 (1986) 1952;
(b) N. Cabon, F.Y. Pétillon, P.Y. Orain, P. Schollhammer, J. Talarmin, K.W. Muir, J. Organomet. Chem., 690 (2005) 4583;
(c) N. Cabon, E. Paugam, F.Y. Pétillon, P. Schollhammer, J. Talarmin, K.W. Muir, Organometallics 22 (2003) 4187;
(d) 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, M. Pichon, K.W. Muir, F.Y. Pétillon, R. Pichon, J. Talarmin, Eur. J. Inorg. Chem. (1999) 221.

[6] M.T. Ashby, J.H. Enemark, D.L. Lichtenberger, Inorg. Chem. 27 (1988) 191.

[7] P.M. Boorman, K.J. Moynihan, R.T. Oakley, J. Chem. Soc., Chem. Commun. (1982) 899.

[8] H. Adams, N.A. Bailey, C. Bannister, M.A. Faers, P. Fedorko, V.A. Osborn, M.J. Winter, J. Chem. Soc., Dalton Trans. (1987) 341.

[9] P. Schollhammer, F.Y. Pétillon, J. Talarmin, K.W. Muir, Inorg. Chim. Acta 284 (1999) 107.

[10] (a) G.M. Sheldrick, SHELX97, University of Göttingen, Germany, 1998;

(b) L.J. Farrugia, WINGX – A Windows Program for Crystal Structure Analysis, J. Appl. Cryst. 32 (1999) 837.