Organometallics **1999,** *18,* 2055−2057

Novel μ-η^2:η^2 Coordination of a Thiophenium Cation

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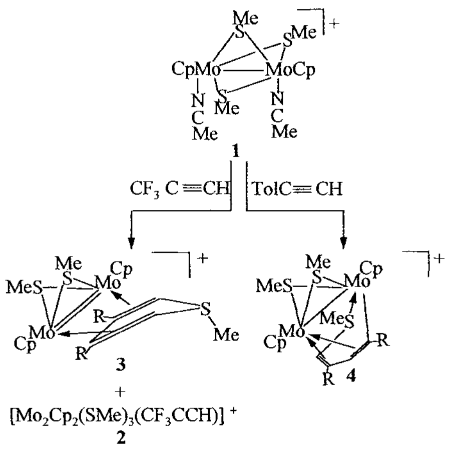
Received February 16, 1999

*Summary: Depending on the substituent (Tol or CF_3) withdrawing power, reactions of the alkyne RCCH with the bis(acetonitrile) compound $[Mo_2(C_5H_5)_2(\mu\text{-}SCH_3)_3(CH_3CN)_2](BF_4)$ (**1**) gave either the "flyover" metallacycle complex **4** or the thiophenium derivative **3**. In **3** the thiophenium ligand shows a new μ-η^2:η^2 mode of coordination. A single-crystal structure of **3**, the first complex with binding of thiophenium to a binuclear site, was obtained.*

Hydrodesulfurization catalysts contain transition metals, usually Mo and Co on an alumina support, and consequently, the various modes of thiophene (or selenophene) coordination to transition metals (η^1(S), η^2, η^4, η^5, η^4(S)-μ_2, η^4(S)-μ_3; η^2(Se)-μ_2) are currently of interest.[1] These modes of coordination can model both the adsorption of thiophene at metal sites on the surface of the catalyst and the activation of thiophene derivatives by transition metals.[1,2] Thiophenes form readily from acetylenic precursors;[1d,3] electrophilic alkynes, for example, react with transition metal thiolates to give mainly monometallic thiophenium derivatives.[4] Alkylation of the sulfur atom of thiophene ligands by either nucleophilic[5] or electrophilic[6]reagents can also give mononuclear thiophenium complexes. The suggestion[1a] that "there are few conceivable ways of bonding metals to thiophene that have not already been discovered", coupled with our present ignorance of how the catalytically active metal molybdenum binds to thiophene functionalities,[1c] prompts us to describe here our observation that the formation of a thiophenium group at a bimetallic molybdenum site can give rise to a novel μ-η^2:η^2 mode of coordination of the ligand. A similar μ-η^2:η^2 mode of coordination of the arene ligand is known in cyclohexadiene and benzene complexes.[7]

Scheme 1



Reaction of the bis(acetonitrile) compound $[Mo_2(C_5H_5)_2(\mu\text{-}SCH_3)_3(CH_3CN)_2](BF_4)$ (**1**)[8]in methylene chloride with excess trifluoropropyne at 40 °C for 24 h leads to a mixture consisting mainly of the thiophenium derivative $[Mo_2(C_5H_5)_2(\mu\text{-}SCH_3)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_4H_2(CF_3)_2SCH_3)](BF_4)$ (**3**; yield 60%) and the alkyne product **2**, formulated on the basis of ^1H NMR and elemental analysis (Scheme 1)[9] as $[Mo_2(C_5H_5)_2(SCH_3)_3(CF_3C{\equiv}CH)](BF_4)$ (yield 30%). If the reaction is performed at room temperature, the yield of **3** after 24 h is only 42%. The ring closure depends on

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(9) Preparation of **2** and **3**: a solution of complex **1**[8] (0.10 g, 0.16 mmol) in CH_2Cl_2 (20 mL) turned from red to green on stirring at 40 °C in the presence of excess CF_3CCH (5:1 mole ratio) for 24 h. The solvent was then reduced to 10 mL, and addition of pentane (10 mL) precipitated compound **3** as a black powder which was washed with pentane (yield: 71 mg, 60%). Evaporation to dryness of the filtrate afforded the complex **2**. **2** was washed with pentane and was obtained as a green powder (yield: 31 mg, 30%). **2**: ^1H NMR (300.13 MHz, 25 °C, CD_3COCD_3, TMS) δ 13.09 (1H, s, CF_3CCH), 6.91 (10H, s, C_5H_5), 2.26 (3H, s, SCH_3), 2.24 (3H, s, SCH_3), 2.18 (3H, s, SCH_3); ^{19}F NMR (282.29 MHz, 25 °C, CD_3COCD_3, $CFCl_3$) δ −61.2 (s, CF_3CCH), −150.4 (s, BF_4^-). Anal. Calcd for $C_{16}H_{20}BF_7Mo_2S_3$: C, 29.8; H, 3.1. Found: C, 29.9; H, 3.3. **3**: ^1H NMR (300.13 MHz, 25 °C, CD_3COCD_3, TMS) δ 5.97 (10H, s, C_5H_5), 3.38 (2H, s, $C_4(CF_3)_2H_2SCH_3^+$), 2.73 (3H, s, $C_4(CF_3)_2H_2SCH_3^+$), 2.33 (3H, s, SCH_3), 2.10 (3H, s, SCH_3); ^{19}F NMR (282.29 MHz, 25 °C, CD_3COCD_3, $CFCl_3$) δ −51.3 (s, $C_4(CF_3)_2H_2SCH_3^+$), −150.3 (s, BF_4^-). Anal. Calcd for $C_{19}H_{21}BF_{10}Mo_2S_3$: C, 30.9; H, 2.8. Found: C, 30.6; H, 3.0.

10.1021/om9900972 CCC: $18.00
Publication on Web 04/30/1999

the nature of the R group of the alkyne RC≡CH used as starting reagent. Thus, reaction of **1** with 2 equiv of p-$CH_3C_6H_4C{\equiv}CH$ in CH_2Cl_2 at room temperature for 12 h forms the flyover metallacycle complex $[Mo_2(C_5H_5)_2(\mu\text{-}SCH_3)_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CR{=}CHCR{=}CHSCH_3)](BF_4)$ (**4**; R = $C_6H_4CH_3$) (Scheme 1).[10] Thermal treatment of **4** does not lead to the formation of a thiophenium group. Preliminary results indicate that the species formulated as $[Mo_2(C_5H_5)_2(SCH_3)_3(RC{\equiv}CH)](BF_4)$ (**2**; R = $C_6H_4CH_3$, CF_3) is the precursor of **3** and **4**, as the reaction of **2** with 1 equiv of RCCH gives either **3** (R = CF_3) or **4** (R = $C_6H_4CH_3$).

Complexes **3** and **4** were characterized by NMR spectroscopy and microanalysis[9,10] and by single-crystal X-ray diffraction.[11] Recrystallization of **3** from a CH_2Cl_2–pentane solution afforded black crystals. The crystal structure of **3** contains two independent cations—one in a general position (Figure 1) and the other straddling a mirror plane—and two $[BF_4]^-$ anions, one of which also lies on a crystallographic mirror plane. The two independent cations show no significant structural differences. Each cation contains a $Mo_2(C_5H_5)_2(\mu\text{-}SCH_3)_2$ unit bridged by a four-electron-donor $\mu_2\text{-}\eta^2{:}\eta^2$-thiophenium ligand derived by fusion of one SCH_3 thiolate ligand with two head-to-head linked $F_3CC{\equiv}CH$ molecules. The Mo–Mo bond lengths (2.618(1) and 2.604(1) Å) are consistent with the bond order of 2 required by the usual electron-counting rules, being close to the mean length of 2.62 Å for 82 double bonds.[12]

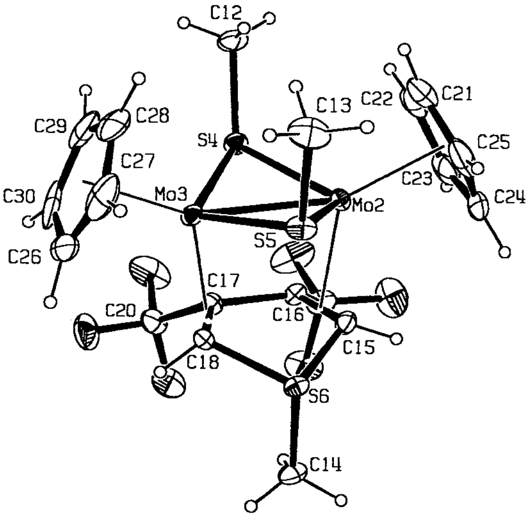

Figure 1. View of one of the two independent $[Mo_2(C_5H_5)_2(\mu\text{-}SCH_3)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_4H_2(CF_3)_2SCH_3)]^+$ cations in **3** showing 20% ellipsoids and atom labels (except for H and F atoms). Selected bond lengths (Å) and angles (deg): Mo2–C16 = 2.261(6), Mo2–C15 = 2.170(6), Mo3–C17 = 2.249(5), Mo3–C18 = 2.161(5), Mo2–S4 = 2.400(2), Mo2–S5 = 2.393(2), Mo3–S4 = 2.404(2), Mo3–S5 = 2.385(2), Mo2–Mo3 = 2.604(1), S6–C15 = 1.765(6), S6–C18 = 1.788(6), C15–C16 = 1.436(7), C16–C17 = 1.517(7), C17–C18 = 1.445(7); Mo2–S4–Mo3 = 65.7(1), Mo3–S5–Mo2 = 66.1(1), C15–S6–C18 = 90.1(3), C15–S6–C14 = 103.3(3), C18–S6–C14 = 103.5(3), C16–C15–S6 = 111.9(4), C18–C17–C16 = 110.5(4), C17–C18–S6 = 110.5(4).

The thiophenium rings adopt shallow envelope conformations in which the S atom is displaced (by 0.45 and 0.51 Å) from the virtually planar $C_\alpha C_\beta C_\beta C_\alpha$ unit away from the metal atoms. The rings are thereby folded across the $C_\alpha \cdots C_\alpha$ flap by 21 or 24°. The Mo···S(thiophenium) distances (3.386(2)–3.395(2) Å) are clearly nonbonding. The Mo–C_α bonds (2.161(5)–2.184(6) Å) are a little shorter than the Mo–C_β distances (2.249(5)–2.261(6) Å), possibly reflecting substituent (H or CF_3) electronegativity. The lengths of the S–C_α (1.769(6)–1.788(6) Å), C_α–C_β (1.436(7)–1.445(7) Å) and C_β–C_β (1.517(7)–1.519(12) Å) bonds in **3** are all greater than the corresponding distances in thiophene (1.714(1), 1.370(2), and 1.424 Å).[1a]

There are few previous structural reports of thiophenium ligands.[1d,4,5] In all cases they are attached in an η^4 fashion to $Mn(CO)_3$ and the ring has an envelope conformation, but with a larger fold (30.4–31.1°) than that found here, shorter S–C bonds (1.743(4)–1.761(3) Å), and C–C distances (C_α–C_β = 1.407(6)–1.449(5) Å; C_β–C_β = 1.376(5)–1.433(5) Å) consistent with much more delocalization than is found in **3**.[4c,5] In each cation the orientation of the thiophenium ring and the disposition of the thiophenium and thiolate methyl substituents cause the lone pairs of two sulfur atoms to point toward one another (e.g. those of S5 and S6 in Figure 1). The corresponding S···S contacts (2.948(3) and 3.007(2) Å) are at least 0.6 Å shorter than the van der Waals diameter of sulfur. The crystal packing involves C–H···F hydrogen bonds: the most significant of these links a thiophenium cation and a $[BF_4]^-$ anion (H···F

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(10) Preparation of **4**: a red solution of complex **1** (0.20 g., 0.32 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature with 2 equiv of $C_6H_4CH_3CCH$ (v = 40.1 μL), for 12 h. The mixture became brownish. The solvent was then reduced under vacuum, and addition of pentane precipitated compound **4** as a green powder which was washed with pentane (yield: 183 mg, 73%): ^1H NMR (300.13 MHz, 25 °C, CD_3COCD_3, TMS) δ 7.80 (2H, d, J = 8.5 Hz), 7.36 (2H, d, J = 8.5 Hz), 7.02 (2H, d, J = 8.5 Hz), and 6.58 (2H, d, J = 8.5 Hz) (2 × $C_6H_4CH_3$), 7.12 and 5.03 (2 × 1H, 2 × d, J = 1.4 Hz, $-CH{=}CRCH{=}CR-$, 5.56 (5H, s, C_5H_5), 5.39 (5H, s, C_5H_5), 2.45, 2.42, 2.28, 2.24, 1.86 (5 × 3H, 5 s, 2 × $C_6H_4CH_3$ and 3 × SCH_3). Anal. Calcd for $C_{31}H_{35}BF_4Mo_2S_3$: C, 47.6; H, 4.5. Found: C, 47.3; H, 4.4.

(11) Crystal data for **3**: $C_{19}H_{21}BF_{10}Mo_2S_3$, M_r = 738.23; crystal dimensions 0.31 × 0.11 × 0.09 mm, monoclinic, space group $P2_1/m$, a = 9.616(1) Å, b = 28.167(4) Å, c = 13.821(2) Å, β = 105.36(1)°, V = 3609.7(8) Å^3, Z = 6, ρ_{calcd} = 2.038 g cm^{-3}. All X-ray measurements were made at 20 °C on an Enraf-Nonius CAD4 diffractometer with Mo Kα X-radiation, λ = 0.710 73 Å. Intensities for 7998 unique reflections with 2.4 < θ < 27° were obtained from 10 311 measurements based on ω-scans corrected for Lp and absorption effects (ψ-scans, T_{max} = 0.763, T_{min} = 0.724; μ(Mo Kα) = 1.39 mm^{-1}). $R(F)$ = 0.045 for 4693 observed ($I > 2\sigma(I)$) reflections; $R(F)$ = 0.104 and $R(wF^2)$ = 0.105 for all 7998 reflections used in the refinement on F^2 of 507 parameters. $|\Delta\rho|$ < 0.94 e Å^{-3}. H atoms rode on the parent C atoms, but methyl group orientations and x, y, z, and U_{iso} parameters of thiophenium ring H atoms were refined. Programs used: SHELXS97 (Patterson) and SHELXL97 (Sheldrick, G. M. University of Göttingen, Göttingen, Germany, 1997) and WINGX (Farrugia, L. J. University of Glasgow, Glasgow, Great Britain, 1996). Crystal data for **4**: $C_{31}H_{35}BF_4Mo_2S_3$, M_r = 782.46; crystal dimensions 0.30 × 0.28 × 0.13 mm, monoclinic, space group $P2_1$, a = 10.451(2) Å, b = 16.117(2) Å, c = 11.001(3) Å, β = 101.19(2)°, V = 1817.7(6) Å^3, Z = 2, ρ_{calcd} = 1.430 g cm^{-3}, μ (Mo Kα) = 0.901 mm^{-1}. Intensities for 3712 unique reflections (including 399 Friedel pairs) with 2.8 < θ < 25° were obtained from 4310 measurements corrected for Lp and absorption effects (ψ-scans, T_{max} = 0.892, T_{min} = 0.774). $R(F)$ = 0.080 for 1853 observed ($I > 2\sigma(I)$) reflections; $R(F)$ = 0.17 and $R(wF^2)$ = 0.22 for all 3712 reflections after refining 153 parameters. $|\Delta\rho|$ < 1.2 e Å^{-3}. The experimental and computational methods were the same as those used for **3,** but data collection was stopped after the standard intensities had fallen by more than 25%, presumably because of solvent loss. In the unit cell there are two equivalent voids, each of ca. 190 Å^3, capable of containing disordered solvent. After many unsuccessful attempts to model the solvent by conventional methods, it was refined by back-transformation of the electron density map (van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194) and was then found to account for about 5% of $F(000)$. U_{ij} values were refined only for Mo and S atoms, and the riding model was used for H atoms.

(12) Found by searching the current version (190 307 entries) of the Cambridge Structural Database (see http://www.ccdc.cam.ac.uk/) using locally mounted versions of the programs QUEST and VISTA.

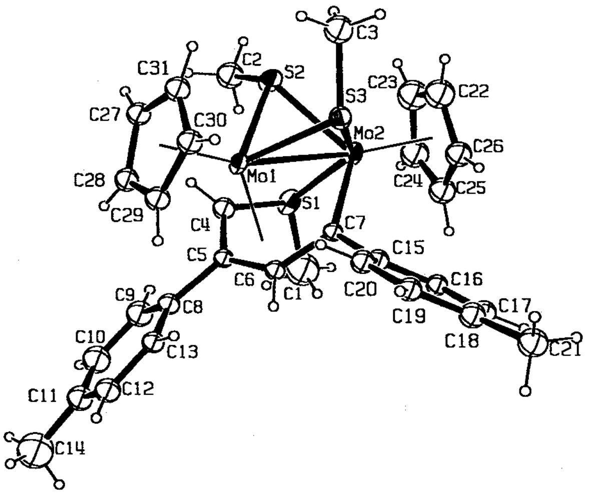

Figure 2. View of the $[Mo_2(C_5H_5)_2(\mu\text{-}SCH_3)_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CR{=}CHCR{=}CHSCH_3)]^+$ ($R = C_6H_4CH_3$) cation in **4** showing 20% vibrational ellipsoids. H atoms are represented by spheres of arbitrary radius. Selected bond lengths (Å): Mo1−C4 = 2.24(2), Mo1−C5 = 2.30(2), Mo1−C6 = 2.40(2), Mo1−C7 = 2.45(2), Mo1−S2 = 2.415(6), Mo1−S3 = 2.502(6), Mo1−Mo2 = 2.761(2), Mo1⋯S1 = 3.328(6), Mo2−C7 = 2.13(2), Mo2−S2 = 2.384(6), Mo2−S1 = 2.446(7), Mo2−S3 = 2.449(6).

= 2.33(5) Å, C−H⋯F = 165(5)°). Some cyclopentadienyl and fluorine atoms show highly anisotropic displacement parameters, and there is one abnormal interionic contact (C28⋯C28^i = 2.97(1) Å; i denotes the symmetry transformation x, $^1/_2 - y$, z) which may indicate disorder of a cyclopentadienyl ring.

Black-green crystals of **4** were obtained by slow diffusion of diethyl ether in a dichloromethane solution of the complex. The X-ray analysis of **4** is of low accuracy because the crystals decomposed during data collection, but the results establish that the structure of the cation (Figure 2) is based on a $Mo_2(C_5H_5)_2(\mu\text{-}SCH_3)_2$ unit bridged by an eight-electron-donor $^-C(R){=}CHC(R){=}CHSMe$ ligand formed by coupling two alkynes and one SMe bridge. The C(R)═CHC(R)═CH head-to-tail linking of the alkynes is in accord with the ^{1}H NMR spectrum, which displays two doublets ($^4J_{HH} = 1.4$ Hz) at 7.12 and 5.03 ppm attributed to the two protons of the bridging ligand C(R)═C*H*C(R)═C*H*SMe. The C4−C5−C6−C7−Mo2 chain is nearly planar, and the Mo1 atom is bonded to all four atoms of the C_4 chain (Mo1−C4 = 2.24(2) Å, Mo1−C5 = 2.30(2) Å, Mo1−C6 = 2.40(2) Å, Mo1−C7 = 2.45(2) Å).

The mechanisms of formation of compounds **3** and **4** could involve metallacycle intermediates and may be similar to those proposed for polynuclear phosphole complexes of cobalt[13] and for mononuclear derivatives of tungsten or molybdenum containing ligands with a "C_4SR" backbone.[14] Metallacycles resulting from the coupling of the two alkyne molcules at the bimetallic centers in transition-metal thiolate dimers are known.[15]

The uncommon mode of coordination of the thiophenium group in compound **3** can be proposed as a very simple model for activation of a thiophenic functionality at a molybdenum surface.[1] In compound **3**, which has been structurally characterized, we have the first binding of thiophenium to a binuclear site. Further transformations of this thiophenium substrate are under investigation.

Acknowledgment. We thank the CNRS, EPSRC, Glasgow University, and Brest University for financial support.

Supporting Information Available: Tables of atomic parameters and all distances and angles for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for **3** and **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 112645/CCDC 112646. Copies can be obtained free of charge on application to CCDC, 12 Union Rd., Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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