Activation of Terminal Alkynes at the Sulfur-Rich Bimetallic Site $[Mo^{III}_2Cp_2(\mu\text{-}SMe)_3]^+$: Alkyne−Vinylidene Conversion and C−S and C−C Couplings Promoted by Addition of Unsaturated Substrates (RC≡CH, RN≡C, S=C=S). Crystal Structures of μ-η^1:η^2-Vinylidene, μ-η^1:η^2-Acetylide, and μ-η^1:η^3-Vinyl−Thioether Compounds

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Reactions of the bis(nitrile) compound $[Mo_2Cp_2(MeCN)_2(\mu\text{-}SMe)_3](BF_4)$ (**1**) with terminal alkynes in a 1:1 ratio in dichloromethane at room temperature led to the alkyne adduct $[Mo_2Cp_2(\mu\text{-}SMe)_3(RCCH)](BF_4)$ (**2**: R = Tol (**2a**), Ph (**2b**), $CH_3C{=}CH_2$ (**2c**), *n*Pr (**2d**), CO_2Me (**2e**), CF_3 (**2f**)). Compounds **2a**−**d** were readily deprotonated with Et_3N to give neutral acetylide derivatives $[Mo_2Cp_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CR)(\mu\text{-}SMe)_3]$ (**3**). Protonation of **3** afforded exclusively the vinylidene complexes $[Mo_2Cp_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C{=}CHR)(\mu\text{-}SMe)_3](BF_3)$ (**4**). Reaction of **1** with an excess of terminal alkyne RCCH in dichloromethane gave either the six-membered metallacycle compounds $[Mo_2Cp_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CR{=}CHCR{=}CHSMe)(\mu\text{-}SMe)_2](BF_4)$ (**5**) or the *S*-methylthiophenium derivatives $[Mo_2Cp_2(\mu\text{-}\eta^2{:}\eta^4\text{-}C_4H_2R_2SMe)(\mu\text{-}SMe)_2](BF_4)$ (**6**), depending on the nature of the R groups. Further reactions of the alkyne adducts **2** with isocyanide and carbon disulfide led to the vinyl−thioether complexes $[Mo_2Cp_2(\mu\text{-}\eta^1{:}\eta^3\text{-}CR{=}CR'\text{-}SMe)(\mu\text{-}SMe)_2(RNC)](BF_4)$ (**7**, **8**) and to their CS_2 adducts $[Mo_2Cp_2(S_2C{-}CR'{=}CRSMe)(\mu\text{-}SMe)_2](BF_4)$ (**9, 10**), which arise from regioselective C−S coupling. A mechanism is proposed for the formation of the cyclic thiometalla compounds **5**, **9**, and **10** and of the thiophenium species **6** which assigns a key intermediate role to vinyl−thioether species. The molecular structures of **3a**, **4b**, and **7a** have been established by X-ray diffraction studies.

Introduction

This study of the interaction of alkynes with the sulfur-rich dimolybdenum system $Cp_2Mo_2(\mu\text{-}SMe)_3$ was aimed at eliciting cooperative activation by the adjacent metals, leading to chemical transformations unattainable with a single metal atom.[1] Such studies also afford simple structural and chemical precedents for the behavior of less accessible natural or industrial catalyst systems.[2] Bimetallic complexes offer an attractive compromise between polymetallic activity and structural simplicity.[3] The incorporation of bridging groups inhibits fragmentation but may also affect the activity of the metal site.[4] Though sulfur-containing bridges can stabilize robust polymetallic complexes, their activity has been relatively little explored because of the notoriety of sulfur derivatives as catalyst poisons.[4b,c] In this respect, the sulfur-rich environment of the cofactors of some metalloenzymes[5] and the well-developed chemistry of thiolato-bridged diruthenium and dimolybdenum systems are noteworthy.[1c,d,4b,c]

Recently, Rakowski DuBois and co-workers reported that the thermal lability of the thioether bridge in $[Mo_2Cp_2(\mu\text{-}S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]^+$ gave rise to sub-

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(3) For example: (a) Curtis, M. D. *Polyhedron* **1987**, *6*, 759. (b) Winter, M. J. *Adv. Organomet. Chem.* **1991**, *29*, 101.

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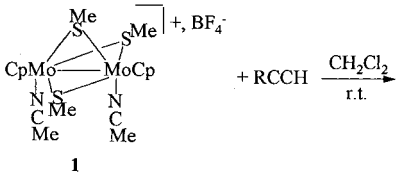
stitution and desulfurization reactions. They speculated that the active intermediate, which could be neither isolated nor characterized, was the unsaturated species $[Mo_2Cp_2(\mu\text{-}S_2CH_2)(\mu\text{-}SMe)]^+$, stabilized by coordinated solvent molecules.[6,7] We have reported stoichiometric reactions which occur at a similar tris(μ-thiolato) bimetallic site in the μ-chloro complex $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}SMe)_3]$.[8] This complex in MeCN solution afforded the stable and tractable bis(acetonitrile) species[9] $[Mo_2Cp_2(MeCN)_2(\mu\text{-}SMe)_3](BF_4)$ (**1**), which is similar to the unsaturated intermediate postulated by Rakowski DuBois. Recently, we have shown that **1** can add two terminal alkynes to its coordination sphere: formally regioselective head-to-tail and tail-to-tail linkage of the alkynes and their coupling to the sulfur atom of a thiolate bridge gave six-membered metallacycles or thiophenium derivatives.[10] These results suggest that **1** may undergo formal insertion of alkynes into a Mo−S bond. The rarity of such processes, which are known only for certain mono- and bimetallic complexes containing fluorinated alkynes[11] and for diruthenium compounds,[12] and the opportunity to develop new routes to S-heterocycles[13] have led us to investigate the reactivity of **1** toward terminal alkynes RC≡CH.

We shall show that **1** reacts with various alkynes to afford the dinuclear alkyne adducts $[Mo_2Cp_2(\mu\text{-}SMe)_3(RCCH)]^+$ (**2**), which are intermediates in the formation of thiametallacycles at the $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}^+$ site, and in which the alkyne group may also undergo an 1,2-H shift, giving rise to vinylidene species. Furthermore, addition of unsaturated molecules (e.g., isocyanides) to **2** results in the formation of vinyl−thioether derivatives with an unprecedented $\mu\text{-}\eta^1\text{:}\eta^3$-coordination. A preliminary communication of a part of this work has already appeared.[10]

Results and Discussion

1. Reaction of $[Mo_2Cp_2(MeCN)_2(\mu\text{-}SMe)_3](BF_4)$ (1) with an Equimolar Amount of Terminal Alkyne RC≡CH. A red solution of **1** in dichloromethane reacted quantitatively with 1 equiv of RCCH (R = Tol, Ph, $C(CH_3)$=CH_2, *n*Pr, CO_2Me) and with 2−3 equiv of CF_3CCH at room temperature within 30 min to give brown or green solutions. Addition of diethyl ether precipitated complexes **2a**−**f** (eq 1) as brown or green



1

$$[Mo_2Cp_2(\mu SMe)_3(RCCH)]BF_4 \quad (1)$$

2

(R = Tol (**2a**), Ph (**2b**), CH_3-C=CH_2 (**2c**), *n*Pr (**2d**), CO_2Me (**2e**), CF_3 (**2f**))

solids. Under the same conditions no reaction occurred with either the more sterically hindered *t*BuC≡CH or with disubstituted alkynes RC≡CR. The complexes **2** were unambiguously formulated by spectroscopic studies as the Mo^{III}−Mo^{III} alkyne adducts $[Mo_2Cp_2(RCCH)(\mu\text{-}SMe)_3](BF_4)$, but the mode of coordination of the alkyne has not been reliably established, since monocrystals of diffraction quality could not be obtained. At room temperature the ^1H NMR spectra of **2** displayed both the resonances expected for the alkyne substituent, R, and a low-field signal (between 12 and 14 ppm) for the CH end of the alkyne, indicating coordination of an RCCH ligand to the molybdenum atoms. The single broad resonance which was observed for the two cyclopentadienyl groups suggested that a dynamic process was operative in solution at room temperature for complexes **2a**−**d**. Two cyclopentadienyl resonances were observed at room temperature for complexes **2e**,**f**, which contain alkynes with the more electron-withdrawing groups COOMe and CF_3. ^{13}C NMR spectra were recorded to get more information about the mode of coordination of the alkyne in **2**. The two resonances of the sp-hybridized carbon atoms of the alkyne R*C*C*H* display some of the largest downfield chemical shifts yet reported for M_2(alkyne) complexes (between 254 and 291 ppm),[14] lying in the carbene range but slightly lower than expected for four-electron-donor alkynes in mononuclear compounds.[15] Such data do not allow the nature of the alkyne−metal bonding to be defined without ambiguity, especially as the strong deshielding observed in **2** may partially reflect the electronic behavior of the thiolato-bridged bimetallic cation. Nevertheless, they suggest that the alkyne acts as a four-electron donor with a significant $\pi_\perp$ contribution,[15] as required by the electron-counting rules to saturate the $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}^+$ core. The alkyne coordination in **2** may not be completely described by either the classical tetrahedrane $\mu\text{-}\eta^2\text{:}\eta^2$ coordination mode (I; Chart 1)[16] or the dimetallacyclobutene $\mu\text{-}\eta^1\text{:}\eta^1$ coordination mode (II;

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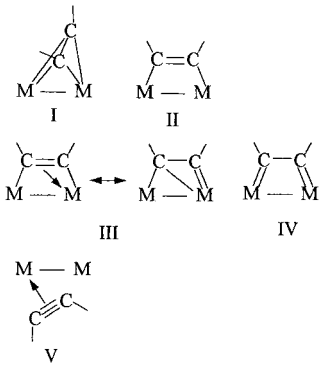
Chart 1. Suggested Limiting Form Contributions to the Structure of the Alkyne Adduct Complexes 2



Scheme 1

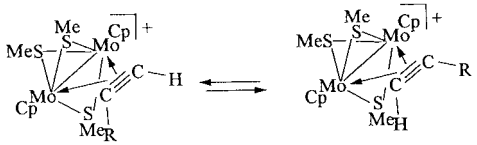
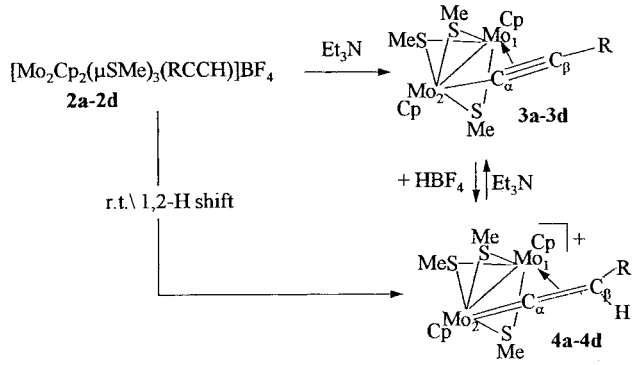


Chart 1)[17] but may also involve contributions from the μ-η^2:η^1 or μ-η^1:η^1 bis(carbene) limiting forms (III and IV; Chart 1);[18a] III resembles structures found in ynamine complexes.[18b,c] A final possibility is the unbridged four-electron-donor alkyne V (Chart 1).[15,19] The $^1J_{CH}$ value (156.5 Hz) suggests a significant C(sp) → C(sp^2) rehybridization in **2e** ($^1J_{CH}$ = 156 Hz in CH_2=CH_2 and 249 Hz in HC≡CH).[15,16] Interactions of alkynes with dinuclear complexes containing tripositive group 6 metals have been reported:[14,20] they generally give rise to adducts whose structures deviate from the ideal perpendicular bridge geometry, with an unsymmetrical $M_2(\mu$-$C_2R_2)$ unit and a C−C bond slightly twisted with respect to the M−M axis. The internal carbon chemical shifts of the alkyne bridge carbon atoms in such complexes are <200 ppm, indicating strong deshielding. Examination of the line shapes in variable-temperature ^{1}H NMR spectra of complexes **2a**,**b** revealed that only the cyclopentadienyl resonances are temperature-dependent. This suggests strongly that the alkyne vector is not perpendicular to the Mo−Mo axis in the typical $\{Mo_2Cp_2(RCCH)(\mu$-$SMe)_3\}^+$ framework;[8] consequently, the fluxional motion requires either inversion of the alkyne RC≡CH relative to the Mo−Mo axis and/or an exchange of this ligand from one molybdenum site to the other (Scheme 1). In addition, the two cyclopentadienyl signals did not coalesce on warming CD_3CN solutions of **2e**,**f**, suggesting that alkynes with strongly electron-withdrawing substituents inhibit the fluxionality. Moderate values for the energy barriers, of 46.8 kJ mol^{-1} for **2a** (R = Tol) and 50.0 ± 1 kJ mol^{-1} for **2b** (R = Ph),[21] were determined from variable-temperature ^{1}H NMR studies but are difficult to interpret without a reliable structural model for **2**.

Scheme 2



2. Proton Transfer in the Alkyne Adducts $[Mo_2Cp_2(RCCH)(\mu$-$SMe)_3]^+$ (2). Compounds **2a**−**d** were readily deprotonated in the presence of Et_3N to give green solutions of the neutral acetylide derivatives $[Mo_2Cp_2(\mu$-η^1:η^2-C≡CR)(μ-$SMe)_3]$ (**3**). Addition of HBF_4 to dichloromethane solutions of **3** afforded exclusively the expected C_β-protonated vinylidene complexes $[Mo_2Cp_2(\mu$-η^1:η^2-C=CHR)(μ-$SMe)_3](BF_4)$ (**4**), which were easily deprotonated to regenerate **3** (Scheme 2). The conversion of the Mo_2(III) alkyne adducts **2** into μ-vinylidene species was revealed by ^{1}H NMR monitoring for complexes **2a**−**d**. A total of 75% of **2a** (R = tolyl) slowly transformed into **4a** within 3 days at room temperature, but over the same time solutions of **2e** and **2f** did not change. It is worth noting that, unlike *t*BuC≡CH, an excess of the terminal alkyne Me_3SiC≡CH reacted with **1** at room temperature within 1 h and afforded the μ-vinylidene complex $[Mo_2Cp_2(\mu$-η^1:η^2=C=$CH_2)(\mu$-$SMe)_3](BF_4)$ (**4e**). We assume that a 1,2-silyl shift helps to reduce steric crowding and that the product hydrolyzes under moist conditions to yield **4e**. Analogous transformations with mononuclear complexes have been reported.[22] When it is warmed in acetonitrile, **4e** regenerated the bis(acetonitrile) derivative **1**, possibly losing acetylene via the reverse vinylidene−alkyne tautomerization. These results indicate that the Mo^{III}_2 alkyne complexes isomerize to the more stable vinylidene adducts at room temperature. However, the reverse reaction, which has been reported for the conversion of the vinylidene species $[Mo_2Cp_2$-$(CO)_4(\mu$-η^1:η^2-C=CHR)] into the related Mo^I_2 alkyne derivative $[Mo_2Cp_2(CO)_4(RCCH)]$,[24] may operate at higher temperature. This alkyne−vinylidene isomer-

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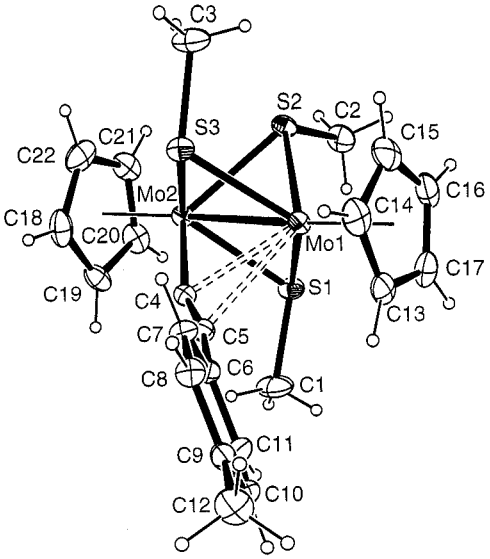


Figure 1. View of a molecule of complex **3a** showing 20% probability ellipsoids for non-hydrogen atoms.

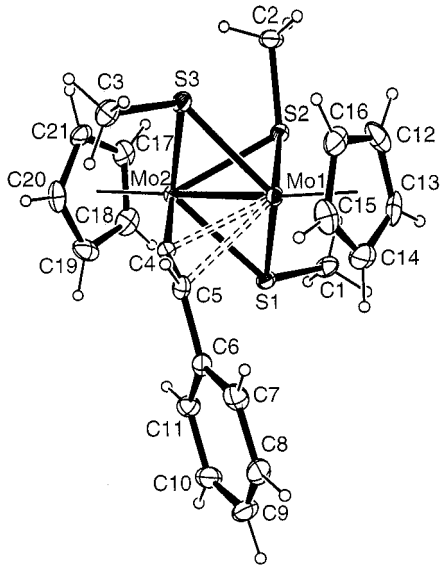


Figure 2. View of the **4b** cation showing 20% probability ellipsoids for non-hydrogen atoms.

ization at the $\{Mo_2(\mu\text{-}SMe)_3\}$ core depends on the electronic properties of the group which is borne by the alkyne as well as on those of the metallic fragment.[22,23] The 1,2-H shift does not occur when a strongly electron-withdrawing group (e.g., CO_2Me or CF_3) is present in the alkynes, whereas the tautomerization occurs readily when the alkyne contains the electron-releasing *n*-propyl group. In addition, the formation of the initial alkyne adduct **2e** upon addition of HBF_4 to **3e** (R $=CO_2Me$) shows that the electronic characteristics of the R group may control both the polarity of the acetylide μ-η^1:η^2-C≡CR bridge and the regiospecificity of the electrophilic attack, as has been previously reported for nucleophilic attack.[25]

The acetylide and vinylidene compounds were identified by NMR spectroscopy, and their structures were confirmed by X-ray analyses of crystals of **3a** (R = Tol) and **4b** (R = Ph). The ^{1}H NMR spectra of the acetylide (**3**) and vinylidene (**4**) compounds exhibited the two sets of resonances respectively expected for the $[Mo_2Cp_2(\mu\text{-}SMe)_3]$ core and for the R group. The vinylidene bridge μ-η^2:η^1-C_α=C_βHR was characterized by the observation of a ^{1}H resonance between 6 and 8 ppm, which was assigned to the =$C_\beta H$R group, and of two resonances in the ^{13}C NMR spectra, at low field in the carbene (ca. 366 ppm) and in the vinyl (ca. 115 ppm) ranges, which were assigned to C_α and C_β, respectively. A single resonance was observed for the two cyclopentadienyl groups in the acetylide and vinylidene compounds, suggesting that windshield wiper fluxionality occurs in solution at room temperature.[24] The dynamic process could be studied on the NMR time scale only for the vinylidene species: energy barriers of 34.2, 35.9, 42.3, and 61.0 ± 1 kJ mol^{-1} were determined[21] for **4a** (R = Tol), **4b** (R = Ph), **4d** (R = *n*Pr), and **4e** (R = H), respectively. Replacement of a hydrogen substituent by an alkyl or aryl group appears to lower the barrier energy for the vinylidene fluxional motion, suggesting that π-electron delocalization through a tolyl or phenyl group facilitates the motion. When R = H, the value is in the range of values determined for neutral dimolybdenum(I) vinylidene species $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2\text{:}\eta^1\text{-}C{=}CHR)]$,[24] suggesting stronger binding of the C=CH_2 moiety to the bimetallic site.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in Compounds 3a and 4b

	3a	4b		3a	4b
Mo1−Mo2	2.616(1)	2.622(1)	Mo2−S3	2.472(1)	2.481(1)
Mo1−S1	2.458(1)	2.482(1)	Mo1−C4	2.360(3)	2.268(5)
Mo1−S2	2.449(1)	2.449(1)	Mo1−C5	2.661(3)	2.589(5)
Mo1−S3	2.483(1)	2.462(1)	Mo2−C4	2.068(3)	1.894(5)
Mo2−S1	2.453(1)	2.489(1)	C4−C5	1.238(4)	1.356(6)
Mo2−S2	2.449(1)	2.445(1)	C5−C6	1.443(4)	1.470(7)
Mo1−C4−Mo2	72.1(1)	77.5(2)	C4−C5−C6	168.5(3)	124.9(5)
Mo1−C4−C5	89.8(2)	87.4(3)	C4−C5−Mo1	62.5(2)	61.3(3)
Mo2−C4−C5	160.9(3)	164.6(4)	Mo1−C5−C6	125.2(2)	117.6(3)

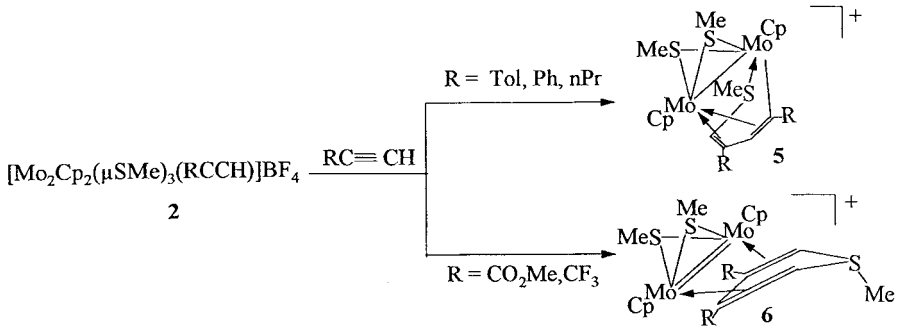
X-ray analyses of **3a** and **4b** confirm the unsymmetrical *side-on* coordination of the acetylide (Figure 1) and vinylidene (Figure 2) groups which bridge the Mo−Mo bond. The geometries of these complexes will be discussed together (Table 1), since **3a** is the deprotonated form of the tolyl analogue of **4b**. The lengths of the Mo−Mo single bonds in **3a** and **4b** are typical of values in $[Mo^{III}_2Cp_2(\mu\text{-}SR)_3]$ complexes (the mean length of 42 such bonds is 2.612 Å) and those of the μ-Mo−S bonds are unexceptional.[26] The three-electron-donor acetylide ligand in **3a** bonds terminally to Mo2 and bonds via the π-electrons of its C≡C triple bond to Mo1. The terminal Mo−C≡CR interaction involves enough back-donation from Mo2 to shorten the Mo2−C4 distance to 2.068(3) Å and lengthen the C4−C5 bond (which is also perturbed by its interaction with Mo1) to 1.238(4) Å: for comparison, in $[Mo_2(CCR)_4(PR'_3)_4]$ complexes back-donation into the terminal acetylide ligands is thought to be slight and the average Mo−C and C≡C bond lengths are 2.149 and 1.205 Å.[27] The π-interaction

(25) Mott, G. N.; Carty, A. J. *Inorg. Chem.* **1983**, *22*, 2726.

(26) (a) Allen, F. H.; Kennard, O. *Chem. Des. Automation News* **1993**, *8*, 31. Version 5.20 of the Cambridge Structural Database with 224 400 structures was used. (b) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *International Tables for Crystallography*; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C, I.U.Cr.; Table 9.6.

(27) John, K. D.; Miskowski, V. M.; Vance, M. A.; Dallinger, R. F.; Wang, L. C.; Geib, S. J.; Hopkins, M. D. *Inorg. Chem.* **1998**, *37*, 6858.

Scheme 3



between Mo1 and the C≡C bond is extremely unsymmetrical (Mo1−C4 = 2.360(3), Mo1−C5 = 2.661(3) Å) and also weak, since the mean length for 2e-donor Mo−C(η^2-C_2R_2) bonds is 2.129 Å.[26b] Protonation of an analogue of **3a** at C5 generates the four-electron-donor Mo=C=CHR vinylidene ligand present in **4b**. The Mo2−C4 distance (1.894(5) Å) now formally represents a double bond, and it is 0.17 Å shorter than the comparable distance in **3a.** Similarly, the C4−C5 bond length (1.356(6) Å) increases, as its order decreases from 3 to 2, and the Mo1−C π-bonds shorten (Mo1−C4 2.268(5), Mo1−C5 2.589(5) Å), presumably as a result of greater back-donation from Mo1. Thus, all three Mo−C distances are shorter in **4b** than **3a**. In **4b**, C5 is sp^2 hybridized and its attached aromatic ring is in conjugation with the C4−C5 double bond (C4−C5−C6−C11 = 17.3(8)°). In **3a** and **4b** the coordination of sp-hybridized C4 carbon atoms is slightly nonlinear but the Mo2−C4−C5 angles (160.9(3)° and 164.6(4)°) are within the range expected for $M_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CCR})$ and $M_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CCHR})$ groups.[23e,24] Apart from C4−C5−C6, which changes from 168.5(3) to 124.9(5)°, corresponding bond angles in **3a** and **4b** are remarkably similar (Table 1). The bridging organic ligands in **3a** and **4b** resemble those in the zerovalent $Mo_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CCR})$ and $Mo_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CCHR})$ complexes described by Froom et al., but the Mo^0−C bond lengths are in general shorter than those in **3a** and **4b** and the Mo^0−Mo^0 bond lengths of 3.10−3.12 Å are much longer.[24]

3. C−S and C−C Couplings Induced by the Addition of RCCH, RNC, and CS_2 to the Alkyne Adduct $[Mo_2Cp_2(RCCH)(\mu\text{-}SMe)_3](BF_4)$ (2). Reaction of the bis(acetonitrile) compound **1** in dichloromethane with 2 equiv or with a large excess of terminal alkyne RCCH led to brownish green solutions from which six-membered metallacycle (**5**) or *S*-methylthiophenium (**6**) derivatives were isolated, depending on the nature of the R groups. Interestingly, the same products were formed on reacting the alkyne adducts **2** with an excess (4 equiv) of RCCH (Scheme 3). In contrast, when an excess of RCCH was added to complexes **3a**−**d** or **4a**−**d**, no reaction was observed. Complexes **5** and **6** were formulated by a combination of X-ray diffraction and spectroscopic studies. Their molecular structures (see Figures 3 and 4) were reported in a preliminary communication[10] and will not therefore be described here in detail. The structure of the cation in **5a** is based on a $\{Mo_2Cp_2(\mu\text{-}SMe)_2\}$ unit which is bridged by an eight-electron-donor CR=CHCR=CHSMe ligand (R = Ph) formed by linking together one SMe bridge and two alkynes, the latter being coupled head-to-tail (Mo1−C4

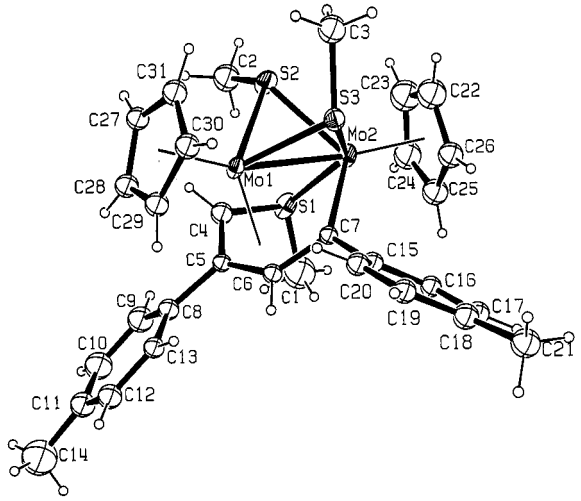


Figure 3. View of the **5a** cation showing 20% probability ellipsoids for non-hydrogen atoms.[10] As discussed in the text, Mo1 is π-bonded to the C4−C7 butadiene unit.

= 2.24(2) Å, Mo1−C5 = 2.30(2) Å, Mo1−C6 = 2.40(2) Å, Mo1−C7 = 2.45(2) Å; see Figure 3). NMR spectroscopy is in accord with this structure. ^{1}H NMR spectra exhibited two resonances for the two inequivalent cyclopentadienyl ligands and the set of resonances expected for two R and three SMe groups. The chemical shifts of the SMe groups did not prove unambiguously that one of them had coupled to an alkyne. Two doublets at δ 7.12 and 5.03 ($^4J_{HH}$ = 1.4 Hz) were detected in the ^{1}H NMR spectrum of **5a** and were assigned to the two protons of the bridging ligand C(R)=C*H*C(R)=C*H*SMe. It is worth noting that similar patterns were observed for **5c**, suggesting that the same head-to-tail coupling occurs when R is an aliphatic group. The thiophenium derivatives **6** were obtained, but with diminished yields (40−50%) compared to the reactions giving the thiametallacyclic complexes **5a**,**b** (70−75%), when the reactions were conducted at room temperature. This may indicate that the pathway leading to tail-to-tail coupling of the alkyne followed by ring closure was slower than that affording complexes **5a**,**b**. Nevertheless, in the reactions of **2e** and **2f** with excess alkyne RC≡CH (R = CO_2Me, CF_3), the only products detectable by ^{1}H NMR spectroscopy were **6** and an appreciable amount of unreacted alkyne adduct **2e**,**f** (about 30% after 24 h at room temperature). We have previously noted that warming increases the yield of **6a**.[10] The principal structural feature of complex **6a** was the presence of the thiophenium ring $\{C_4H_2(CF_3)_2SCH_3\}^+$ in a shallow envelope conformation which is bound to a $\{Mo_2Cp_2(\mu\text{-}$

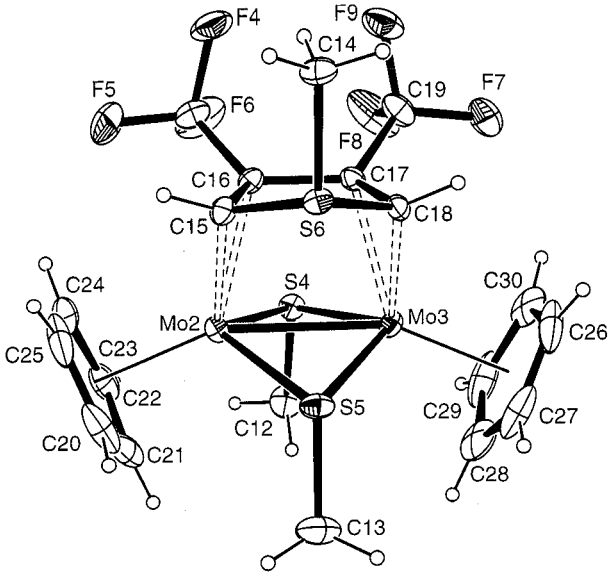
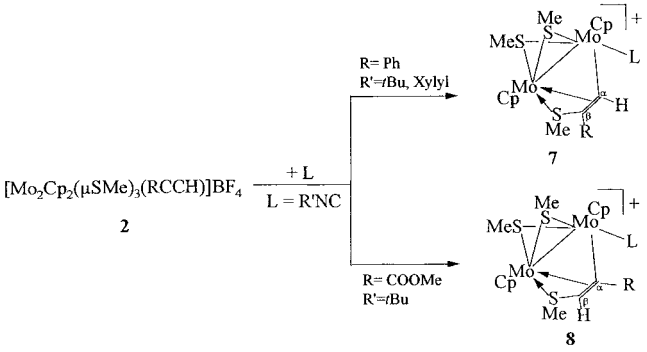


Figure 4. View of a **6a** cation showing 20% probability ellipsoids for non-hydrogen atoms.[10] In the solid there are two crystallographically independent but structurally equivalent cations. One straddles a crystallographic mirror plane; the other (shown here) has no crystallographically imposed symmetry..

Scheme 4



SMe)$_2$} bimetallic core through the C═C double bonds (Mo···S = 3.386(2)−3.395(2) Å; Mo−C$_\alpha$ = 2.161(5)−2.184(6) Å; Mo−C$_\beta$ = 2.249(5)−2.261(6) Å). The ^{1}H NMR spectrum of **6** displayed one resonance for the two Cp ligands, which is in accord with the symmetrical solid-state structure (Figure 4); a single resonance detected for two protons at about 3.3 ppm indicated the formally tail-to-tail coupling of the two alkynes.

To get additional information on the mechanistic pathway leading to complexes **5** and **6** via C−C and C−S bond formation, we investigated reactions of the alkyne adduct **2b** (R = Ph) with isocyanide substrates. **2b** reacted quantitatively in dichloromethane with 1 equiv of *t*BuNC or xylylNC to give, within 1 h, orange solutions. Orange solids, **7a**,**b**, were obtained upon addition of diethyl ether to the concentrated solution (Scheme 4). Infrared spectra of **7** showed the presence of typical ν(CN) bands at frequencies lower than those of the free ligands;[28] these data indicate that an isocyanide molecule is coordinated to a molybdenum atom in **7**. The expected set of resonances of the isocyanide

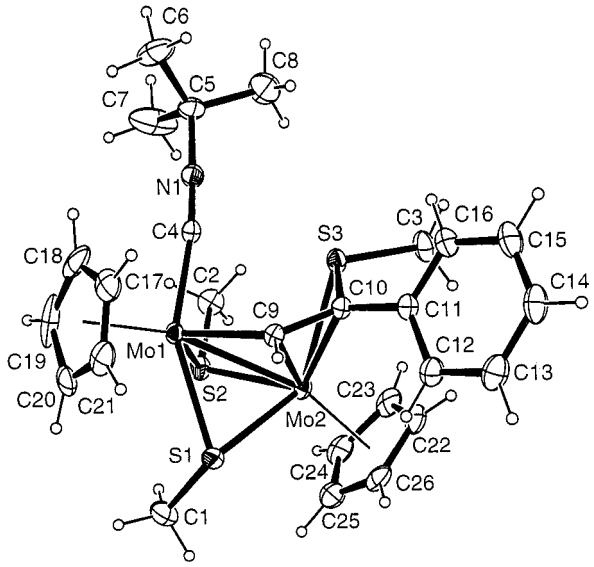


Figure 5. View of the **7a** cation showing 20% probability ellipsoids for non-hydrogen atoms.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in 7a

Mo1−Mo2	2.825(1)	N1−C4	1.151(5)
Mo1−C4	2.104(4)	N1−C5	1.470(6)
Mo1−C9	2.128(4)	Mo1−S1	2.463(1)
Mo2−C9	2.293(4)	Mo1−S2	2.441(1)
Mo2−C10	2.308(4)	Mo2−S1	2.431(1)
C9−C10	1.399(6)	Mo2−S2	2.434(1)
S3−C10	1.782(4)	Mo2−S3	2.540(1)
S3−C3	1.811(5)		
N1−C4−Mo1	172.7(4)	S3−C10−Mo2	75.6(2)
C4−N1−C5	175.0(5)	Mo1−C9−Mo2	79.3(1)
C11−C10−Mo2	131.0(3)	C11−C10−S3	122.2(3)
C10−S3−C3	107.1(2)	C9−C10−Mo2	71.7(2)
C10−C9−Mo1	130.1(3)	C10−C9−Mo2	72.9(2)
C3−S3−Mo2	113.2(2)	C9−C10−S3	114.0(3)
C10−S3−Mo2	61.6(1)		

ligands were detected in the ^{1}H and ^{13}C NMR spectra. In particular, the signals of the *C*N groups were observed at 166.3 ppm (**7a**) and 187.1 ppm (**7b**), in accord with a terminal bonding mode of the isocyanide (Mo−CN−R). The chemical shifts of the unsaturated carbon atoms of the alkyne fall in the sp^2-hybridized carbon range (160−100 ppm). The ^{13}C chemical shifts for the σ-bonded (C$_\alpha$) and the non-σ-bonded (C$_\beta$) carbon atoms of the μ-vinyl appear at about 152−150 and 112 ppm, respectively, which are in accord with carbene-like character for C$_\alpha$ and sp^3 hybridization at C$_\beta$.[29] X-ray analysis of **7a** revealed a C−S bond between the carbon atom bearing the R group of the alkyne ligand and the sulfur atom of one SMe group (S3−C10 = 1.782(4) Å). The structure of **7a** (Figure 5 and Table 2) can be regarded as that of a μ-η^1:η^3 vinyl−thioether complex in which the vinylic C9−C10 unit is σ-bonded to Mo1 (Mo1−C9 = 2.128(4) Å) and π-bonded to Mo2 (Mo2−C9 = 2.293(4) Å, Mo2−C10 = 2.308(4) Å) and the S3 atom is σ-bonded to Mo2 (Mo2−S3 = 2.540(1) Å). The Mo(1)−Mo(2) length (2.825(1) Å) in **7a** is in accord with the electron-counting rules, which require an order of 1 for the Mo(1)−Mo(2) bond, and with the presence of the less sterically constraining MeSCR═CH− bridging group.

(28) Pétillon, F. Y.; Schollhammer, P.; Talarmin, J. *J. Organomet. Chem.* **1991**, *411*, 159.

(29) Schollhammer, P.; Pétillon, F. Y.; Poder-Guillou, S.; Talarmin, J.; Muir, K. W.; Yufit, D. S. *J. Organomet. Chem.* **1996**, *513*, 181.

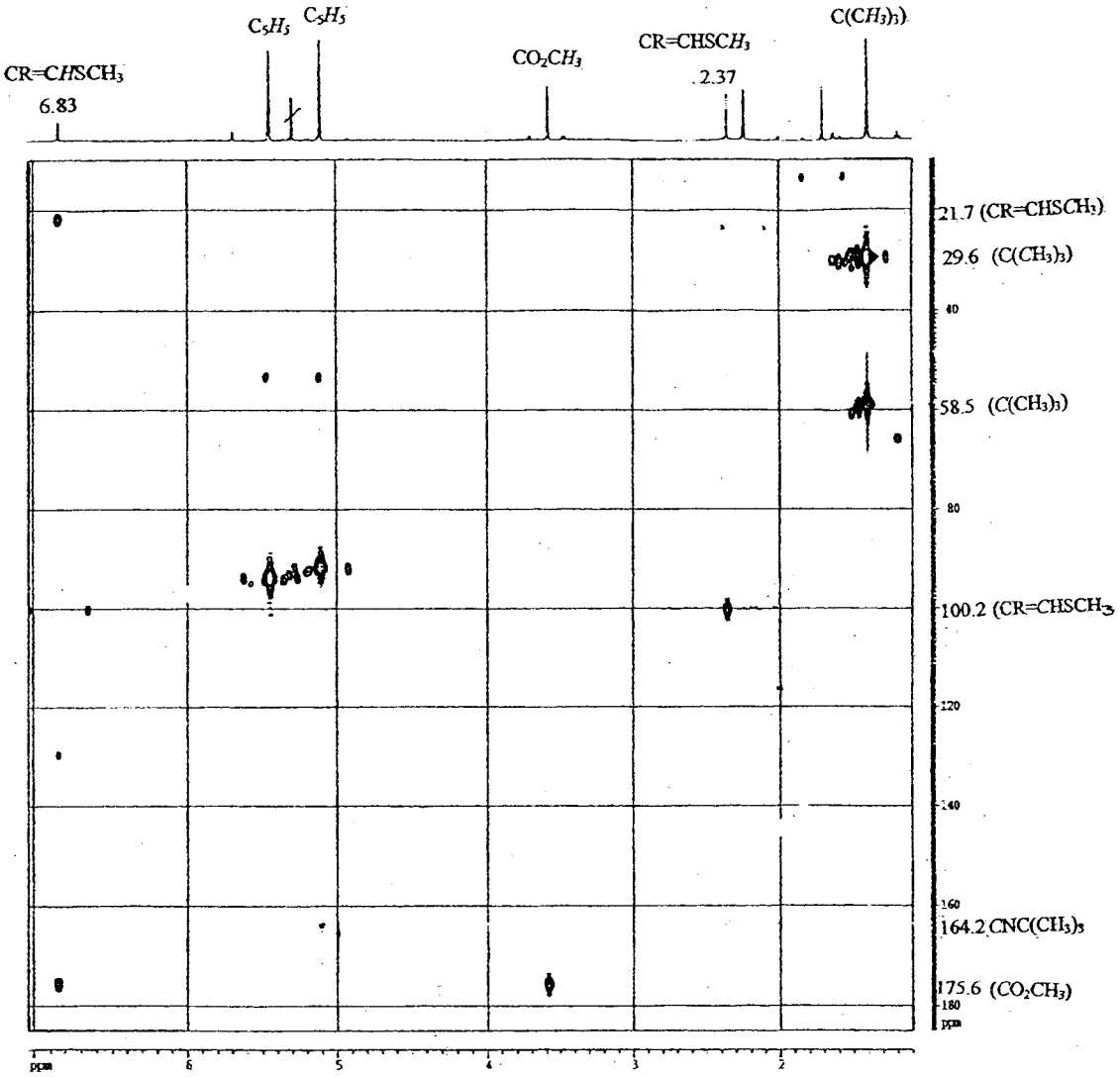


Figure 6. $^1H-^{13}C$ 2D HMBC spectrum of **8** (298 K, $CDCl_3$).

The Mo1−C9 distance is comparable with that observed in the μ-σ:η^2-vinyl dimolybdenum(II) complex [Mo_2Cp-(μ-SPh)(μ-σ:η^2-C(CH_3)=CH(CH_3))][29] (2.121(8) Å), whereas the Mo2−C9 and Mo2−C10 π bonds in **7a** are slightly shorter than those in the μ-σ:η^2-vinyl Mo^{II}_2 complex (2.359(8) and 2.397(7) Å), perhaps reflecting the difference in the oxidation states of the molybdenum atoms. The C9−C10 double bond (1.399(6) Å) appears to be lengthened by its coordination to Mo2. Structural features of the terminal tBuNC ligand are unexceptional.[30] The μ-η^1:η^3 structure of the five-membered dimolybdenacycle in **7a** differs from the μ-η^2:η^2 arrangement found in most related complexes, where the vinyl−thioether forms part of a thiametallacyclobutene system which is linked to the second metal atom through the vinylic double bond.[12b−c,31] The μ-η^1:η^1 coordination of the −C(CF_3)=CHSMe unit in the eight-membered dimolybdenacycle complex [Mo_2Cp_2\{μ-η^1:η^1-C(CF_3)=CHSMe\}$_2$] shows how the vinyl−thioether ligand can tailor its electron donation to the demands of the metal atoms.[11g] To our knowledge, **7a** provides the first crystallographic example of a μ-η^1:η^3-CR^1=CR^2-SR^3 ligand, though μ-η^1:η^3-bonding has been proposed to explain the isomerism in [$Fe_2(CO)_4$\{μ-C(CF_3)=C(CF_3)-SMe\}].[32]

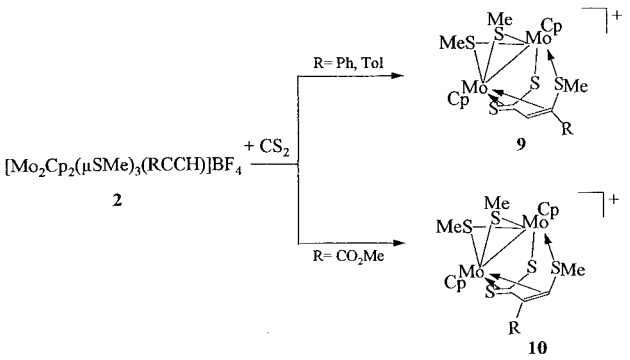
To find if the regioselectivity of the C−S coupling depends on the nature of the alkyne substituent, as has been previously observed for the coupling of SMe with two alkynes (see above), a solution of the complex **2e** in CH_2Cl_2 was treated with 1 equiv of *t*BuNC. A compound **8** in which the isocyanide was coordinated to one molybdenum atom (Scheme 4) was formed. The $^1H-^{13}C$ HMQC and $^1H-^{13}C$ HMBC 2D NMR spectra allowed full assignment of ^{13}C chemical shifts and indicated unambiguously that in **8** the sulfur atom of one SMe group was bonded to the carbon of the alkyne bearing the hydrogen atom (Figure 6). The correlation peaks between the methyl protons at 2.37 ppm and the carbon at 100.2 ppm ($^3J_{CH}$) and those between the proton of the CH group at 6.83 ppm, the methanethiolate carbon at 21.7 ppm ($^3J_{CH}$), the carbon bearing the CO_2Me group at 129.6 ppm ($^2J_{CH}$), and the carbon of the CO_2Me group at 175.6 ppm ($^3J_{CH}$), are in accord with a MeSCH=CR−

(30) McDermott, L. C.; Muir, K. W.; Pétillon, F. Y.; Poder-Guillou, S.; Schollhammer, P. *Acta Crystallogr.* **1996**, *C52*, 74.

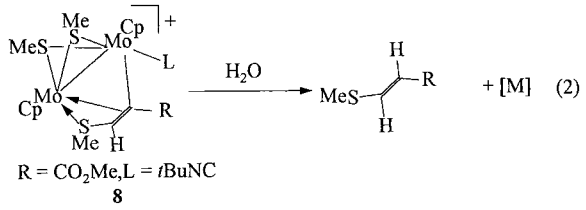
(31) (a) King, J. D.; Mays, M. J.; Pateman, G. E.; Raithby, P. R.; Rennie, M. A.; Solan, G. A.; Choi, N.; Conole, G.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1999**, 4447. (b) Rumin, R.; Guennou, K.; Pétillon, F. Y.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1997**, 1381.

(32) Rumin, R.; Pétillon, F.; Manojlovic-Muir, L.; Muir, K. W. *Organometallics* **1990**, *9*, 944.

Scheme 5



backbone. Very weak correlations were also detected between the $C(CH_3)_3$ signal at 1.41 ppm and both the C_5H_5 signal at 5.11 ppm and the carbon signal of the isocyanide at 164.2 ppm ($^4J_{CH}$ and $^3J_{CH}$). When **8** was left overnight in $CDCl_3$, quantitative evolution of an organic product was observed. It was identified by its ^1H NMR spectrum and $^1H-^{13}C$ HMBC 2D NMR experiments as the *E* isomer of the vinyl−thioether $MeSCH{=}CHCO_2Me$, formally the product of anti-Markownikoff addition of HSMe to the alkyne. The residual organometallic species was not identified (eq 2).



(2)

Investigations of the reactivity of the alkyne adducts with carbon disulfide again indicated that the regioselective formation of products with new C−S and C−C bonds was controlled by the R substituent of the alkyne. An excess of CS_2 was added to dichloromethane solutions of complexes **2a**,**b**,**e** (Scheme 5). The solutions turned brownish red within 2 h and afforded compounds **9** and **10**, which were identified by NMR spectroscopy, since diffraction-quality crystals could not be obtained. ^1H NMR spectra of **9** and **10** displayed two broad resonances, which were assigned to the cyclopentadienyl ligands. These resonances coalesced upon warming, showing that the complexes were fluxional. Energy

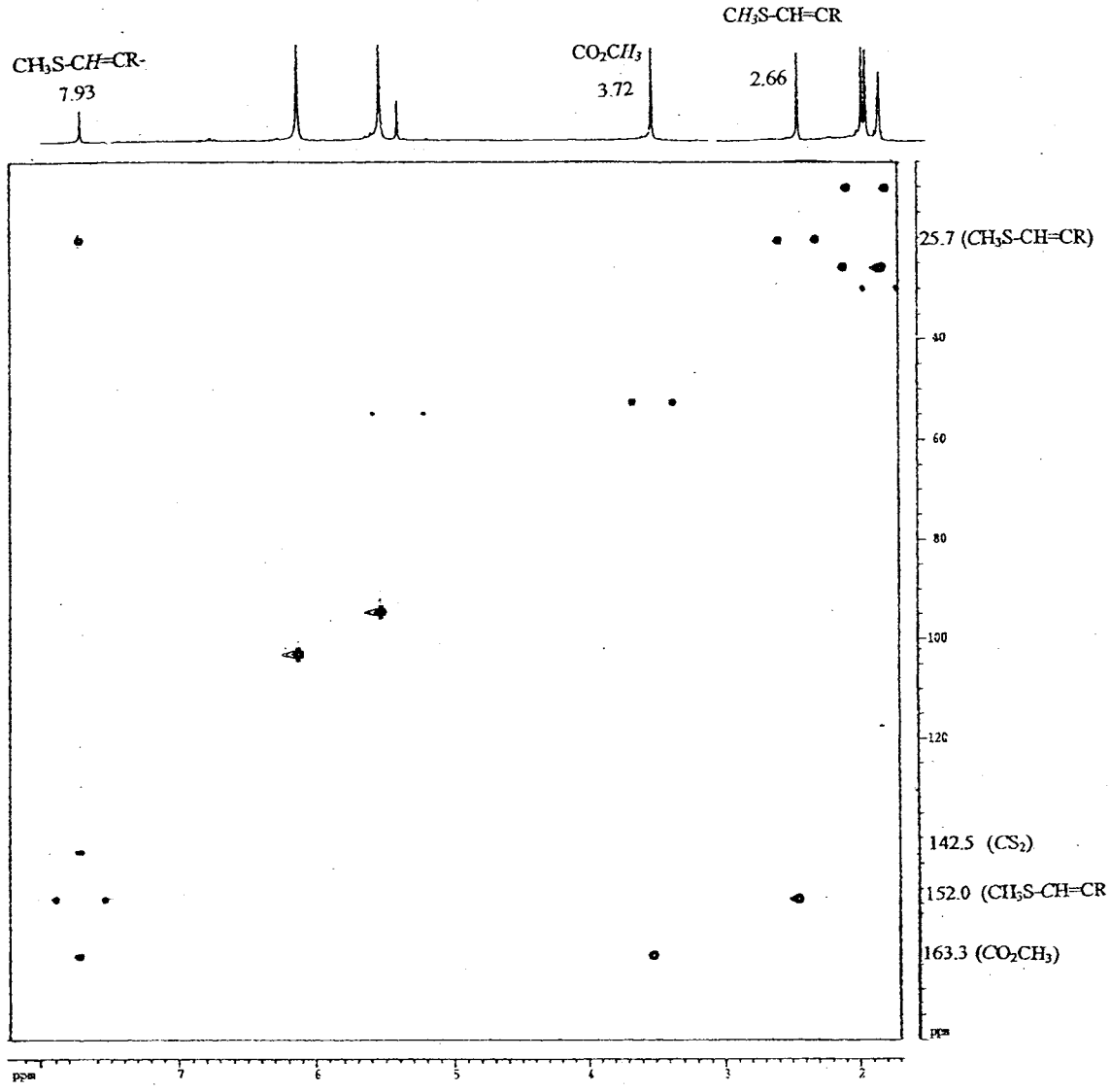
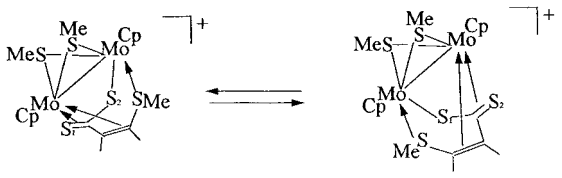


Figure 7. $^1H-^{13}C$ 2D HMBC spectrum of **10** (298 K, CD_3COCD_3).

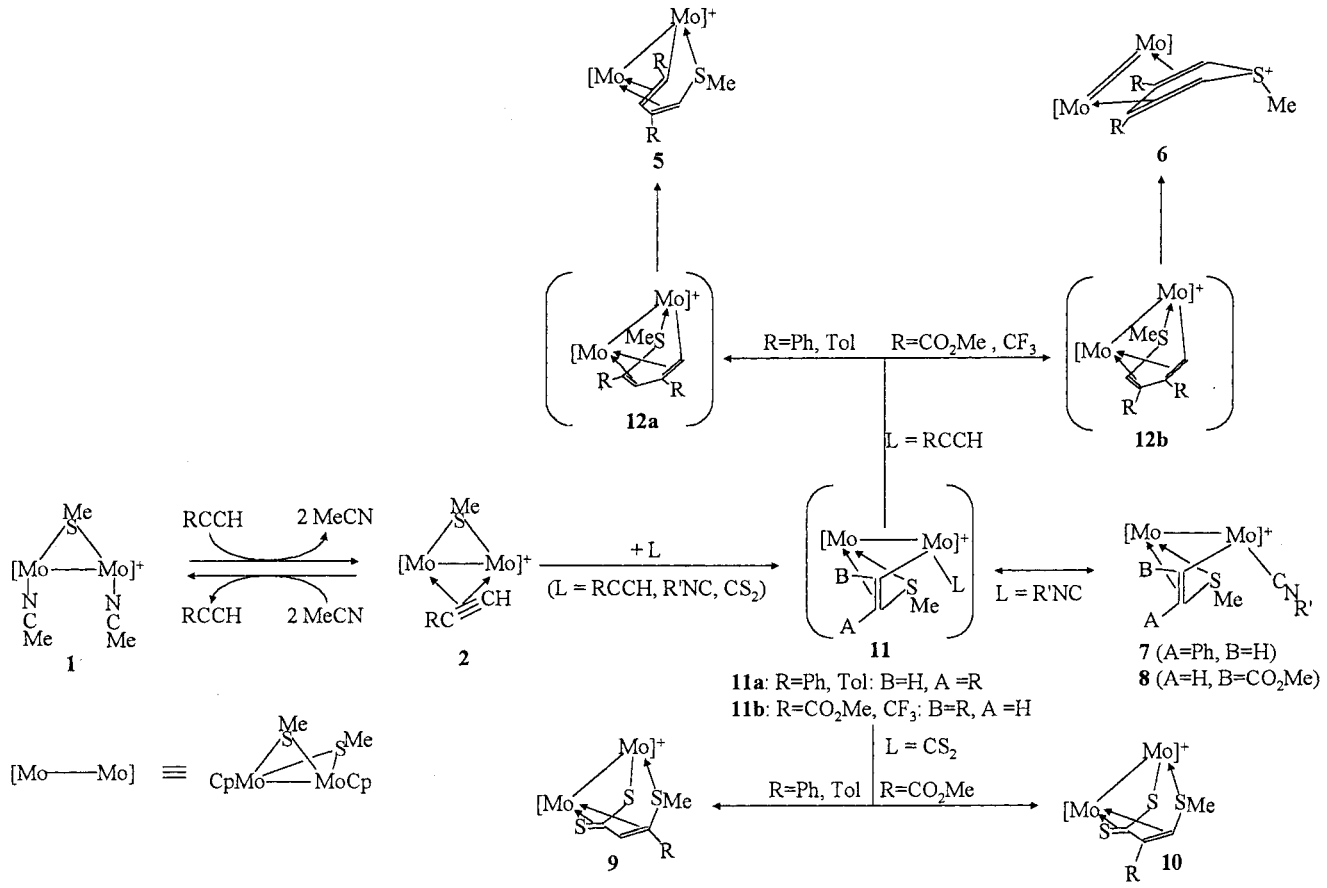
Scheme 6



barrier values of 63.1, 63.8, and 66.3 ± 1 kJ.mol^{-1} were determined for **9a**,**b** and **10**, respectively.[21] The signals of the CH groups were detected at about 6 ppm. Two-dimensional heteronuclear $^{1}H-^{13}C$ inverse-correlation experiments were carried out to characterize **9a** and **10**. Full assignment of the ^{13}C chemical shifts was achieved by means of $^{1}H-^{13}C$ HMQC and $^{1}H-^{13}C$ HMBC 2D NMR experiments, which revealed that one carbon atom of the alkyne binds to the sulfur atom of a SMe group and the other to the carbon of CS_2 and, in addition, that the regioselectivity of the C−S coupling depends on the nature of the alkyne substituent. The $^{1}H-^{13}C$ HMBC 2D NMR spectra of **9a** (Figure 7) and **10** are in accord with the respective formation of MeS−C(tol)=CHCS$_2^-$ and MeSCH=C(CO_2Me)CS_2. No correlation peak between the CH signal and any SMe resonances was detected when R = Tol, whereas in the CO_2Me case, correlations were observed between the SCH_3 signal at 2.66 ppm and the CH resonance at 152.0 ppm ($^{3}J_{CH}$) and between the CH signal at 7.93 ppm and the carbon of the CS_2 group at 142.5 ppm ($^{3}J_{CH}$) and the carbon resonance of *C*O_2Me at 163.3 ppm ($^{3}J_{CH}$) (Figure 7). The vinyl−thioether dithiocarboxylate ligand may bind to the bimetallic site through the three sulfur atoms and the C=C double bond, giving the formally eight-electron-donor ligand (Scheme 5) required by the electron-counting rules.[33] The motion of such a ligand shown in Scheme 6 may explain the temperature dependence of the ^{1}H NMR spectra of complexes **9** and **10**.

4. Possible Mechanism of Oligomerization of Alkynes at the {$Mo_2Cp_2(\mu$-SMe}$_3$ Core. Reaction of monosubstituted acetylenes with the bis(nitrile) complex **1** gives first the alkyne complexes **2**. This reaction is reversible, since **2** can be converted back to **1** by dissolving it in acetonitrile solution (Scheme 7).The nature of the bonding of the alkyne to the dimolybdenum framework of **2** has not been established in detail. We suggest that the further addition to **2** of an unsaturated molecule L (L = RC≡CH, RN≡C, S=C=S) produces the intermediate vinyl−thioether complexes **11**. The incoming ligand L bonds to only one of the metal atoms and thereby labilizes a bridging Mo−S bond, into which is inserted the RCCH added in the previous step. Several examples of insertion of an alkyne into an M−SR bond in mononuclear[11] and dinuclear complexes[12] have been reported, and it has been shown that vinyl−thioether compounds are intermediates in the formation of thiometallacycles. It is worth noting that under very mild conditions only one isomer of most of the products was obtained in appreciable yield. This strongly suggests that these reactions are highly regioselective and that they depend on a delicate balance involving the electronic and steric properties of both the metallic framework and the alkyne substituents, as is

Scheme 7. Possible Pathways to the Formation of (a) Six-Membered Metallacycle Complexes 5 and thiophenium Complexes 6 and (b) Complexes 7, 8 and 9, 10



often observed in coupling or insertion processes. In the products the most electron-releasing alkyne substituent is adjacent to S: thus, if R = Ph, Tol, *n*Pr the MeSCR=CH ether is formed (**11a**) via a 1,2-insertion, but when R = CO_2Me, CF_3, i.e., is strongly electronegative, then the MeSCH=CR ether is formed (**11b**) via a 2,1-insertion (Scheme 2). When L = CNR, complexes **7** and **8** are the final products. When L = CS_2 is added to **2**, the initially formed **11a** or **11b** gives the expected final product **9** or **10** by insertion of CS_2 into the Mo−C σ bond. When L = RCCH, the second alkyne again inserts into the Mo−C σ-bond of **11a** or **11b** in such a way that the hydrogen-bearing alkyne carbon atom always ends up σ-bonded to molybdenum. For R = CO_2Me, CF_3, the outcome is therefore **12b** and reductive elimination gives the thiophenium complexes **6**. When R = Ph, Tol, the same insertion gives **12a** and a further 1,4-SMe migration through the metallacycle is needed to get the six-membered metallacycle **5** in which the SMe is borne by the less sterically hindered carbon atom (Scheme 2). This step is strongly reminiscent of the mechanism suggested by Davidson et al. for the formal insertion of an alkyne into the C−S bond of a thio−alkenyl species.[11d,34]

Conclusion

Transformations of terminal alkynes at the $\{Mo_2Cp_2(\mu\text{-SMe})_3^+\}$ core show that the bis(nitrile) complex $[Mo_2Cp_2(\mu\text{-SMe})_3(CH_3CN)_2](BF_4)$ (**1**) provides a protected but readily accessible bimetallic site for substrate transformations. Hydrocarbon ligands weaken one Mo−S bond to generate a coordination site together with C−S coupling. Our studies have demonstrated that alkyne dimerization or functionalization can be promoted by a C−S coupling at the bimetallic framework $\{Mo_2Cp_2(\mu\text{-SMe})_3\}$. It is noteworthy that fine modifications of such a bimetallic site, involving steric constraint by replacement of two thiolate bridges $(\mu\text{-SMe})_2$ with a $\mu\text{-}\eta^2\text{-}S_2CH_2$ ligand, seem to have a significant influence on its activity.[7] In conclusion, we have described well-defined syntheses of sulfur-rich dimolybdenum compounds containing alkyne, acetylide, and vinylidene ligands and established their structural relationships using spectroscopic and X-ray diffraction methods. Further transformations of these species are now under investigation.

Experimental Section

General Procedures. The reactions were performed under nitrogen using standard Schlenk techniques. Solvents were deoxygenated and dried by standard methods. IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer from KBr pellets. Chemical analyses were performed by the Centre de Microanalyses du CNRS, Vernaison, France. NMR spectra (^1H, ^{13}C,^{19}F) were recorded on either a Bruker AC300 or AMX3 400 spectrometer and were referenced to $SiMe_4$ (^1H, ^{13}C) or $CFCl_3$ (^{19}F). The spectroscopic data for **2d** and **5a** have been revised[10] using new ^1H and ^{13}C spectra. Literature methods were used for the preparation of $[Cp_2Mo_2(\mu\text{-SMe})_3(CH_3CN)_2](BF_4)$ (**1**).[9]

Synthesis of $[Mo_2Cp_2(\mu\text{-SMe})_3(RCCH)](BF_4)$ (2). A solution of complex **1** (0.2 g, 0.32 mmol) in CH_2Cl_2 (15 mL) was stirred in the presence of 1 equiv of RCCH (R = Tol, v = 41 μL; R = Ph, v = 35 μL; R = $CH_3C{=}CH_2$, v = 30.5 μL; R = *n*Pr, v = 31.5 μL; R = CO_2Me, v = 28.5 μL) for 30 min at room temperature. The solution turned from red to green (R = CO_2Me) or brownish purple (R = Tol, Ph, $CH_3C{=}CH_2$, *n*Pr). The solvent was then concentrated, and Et_2O was added. Brown or green solids precipitated, were collected by filtration, and then were washed with pentane. In a similar procedure, the complex **2f** was obtained by reacting 3 equiv of CF_3CCH with complex **1** as a green powder. Yields: **2a** (R = Tol), 202 mg, 95%; **2b** (R = Ph), 198 mg, 95%; **2c** (R = $CH_3C{=}CH_2$), 178 mg, 95%; **2d** (R = *n*Pr), 184 mg, 90%; **2e** (R = CO_2Me), 195 mg, 85%; **2f** (R = CF_3), 165 mg, 80%.

2a. ^1H NMR (CD_3COCD_3, room temperature; δ): 12.90 (s, 1H, TolCC*H*), 7.15, 6.57 (2 × d, 4H, $CH_3C_6H_4$), 6.64 (s, 10H, C_5H_5), 2.44 (s, 3H, $CH_3C_6H_4$), 2.31 (s, 3H, SCH_3), 2.14 (s, 3H, SCH_3), 2.09 (s, 3H, SCH_3). ^1H NMR (CD_2Cl_2, 204 K; δ): 12.89 (s, 1H, TolCC*H*), 7.07, 6.35 (2d, J_{HH} = 8 Hz, 2 × 2H, $CH_3C_6H_4$), 6.46 (s, 5H, C_5H_5), 6.27 (s, 5H, C_5H_5), 2.28 (s, 3H, $CH_3C_6H_4$), 2.10 (s, 3H, SCH_3), 1.96 (s, 3H, SCH_3), 1.90 (s, 3H, SCH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): R*CC*H not observed, 150.0, 137.8, 128.5, 121.6 ($CH_3C_6H_4$), 101.6 (C_5H_5), 43.1, 21.1, 19.2, 18.9 ($CH_3C_6H_4$, 3 × SCH_3). Anal. Calcd for $C_{22}H_{27}BF_4Mo_2S_3$: C, 39.6; H, 4.0. Found: C, 38.4; H, 4.0.

2b. ^1H NMR (CD_2Cl_2, 25 °C; δ): 12.77 (s, 1H, PhCC*H*), 7.32, 7.19, 6.51 (m, 5H, C_6H_5), 6.38 (s, 10H, C_5H_5), 2.37 (s, 3H, SCH_3), 2.06 (s, 3H, SCH_3), 1.98 (s, 3H, SCH_3). ^1H NMR (CD_2Cl_2, 215 K; δ): 12.88 (s, 1H, PhCC*H*), 7.28−6.44 (m, 5H, C_6H_5), 6.47 (s, 5H, C_5H_5), 6.27(s, 5H, C_5H_5), 2.32 (s, 3H, SCH_3), 1.98 (s, 3H, SCH_3), 1.92 (s, 3H, SCH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): R*CC*H not observed, 153.1, 128.4, 127.4, 121.3 (C_6H_5), 101.7 (C_5H_5), 43.6 (S*C*H$_3$), 19.5 (S*C*H$_3$), 19.1 (S*C*H$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 208 K; δ): 290.1 and 279.0 (R*CC*H), 152.9, 127.6, 126.5, 120.2 (C_6H_5), 101.8, 100.1 (C_5H_5), 30.9 (S*C*H$_3$), 20.0 (S*C*H$_3$), 19.4 (S*C*H$_3$). Anal. Calcd for $C_{21}H_{25}BF_4Mo_2S_3$: C, 38.6; H, 3.8.Found: C, 37.4; H, 3.8.

Elemental analyses for **2a**,**b** were obtained under nitrogen on three independently prepared pure samples (NMR grade), but unreliable data were obtained, probably because the compounds slowly evolved with partial loss of alkyne, which could explain the slight lowering of the amount percent of carbon.

2c. ^1H NMR (CD_2Cl_2, 25 °C; δ): 12.92 (s, 1H, $CH_2{=}C(CH_3)$-CC*H*), 6.40 (s, 10H, C_5H_5), 4.64, 4.09 (2s, 2 × 1H, $CH_3C{=}CH_2$), 2.22 (s, 3H, $CH_3C{=}CH_2$), 2.10 (s, 3H, SCH_3), 2.01 (s, 3H, SCH_3), 1.91 (s, 3H, SCH_3).

2d. ^1H NMR (CD_3COCD_3, 25 °C; δ): 12.24 (s, 1H, *n*PrCC*H*), 6.54 (s, 10H, C_5H_5), 2.23 (s, 3H, SCH_3), 2.04 (s, 3H, SCH_3), 1.90 (s, 3H, SCH_3), 1.14 (m, 2H, $(CH_2)_2$), 0.80 (t, J_{HH} = 7.4 Hz, 3H, $(CH_2)_2CH_3$).

2e. ^1H NMR (CD_3COCD_3, 25 °C; δ): 13.17 (s, 1H $MeCO_2$-CC*H*), 6.82, 6.77 (2 × s, 2 × 5H, 2 × C_5H_5), 3.67 (s, 3H, CH_3-COOMe), 2.31 (s, 3H, SCH_3), 2.17 (s, 3H, SCH_3), 2.12 (s, 3H, SCH_3). ^{13}C NMR (CD_2Cl_2, 25 °C; δ): 272.3 (d, J_{CH} = 156.5 Hz, R*CC*H), 266.0 (s, R*CC*H), 185.7 (s, *C*O_2Me), 103.2 (d, J_{CH} = 181.0 Hz, C_5H_5), 101.7 (d, J_{CH} = 181.0 Hz, C_5H_5), 43.6 (q, J_{CH} = 142.0 Hz, CO_2CH_3), 21.3, 21.2 (q, J_{CH} = 142.0 Hz, SCH_3). IR (KBr pellets; cm^{-1}): 1690 (s) ν(CO), 1150−1050 (s) ν(BF).

2f. ^1H NMR (CD_2Cl_2, 25 °C; δ): 12.96 (s, 1H, CF_3CCH), 6.68 (s, 5H, C_5H_5), 6.61 (s, 5H, C_5H_5), 2.17 (s, 3H, SCH_3), 2.15 (s, 3H, SCH_3), 2.10 (s, 3H, SCH_3). ^{19}F NMR (CD_2Cl_2, 25 °C; δ): −61.1 (s, CF_3CCH), −149.7 (BF_4^-). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 25 °C; δ): 254.0 (q, J_{CF} = 30.3 Hz, CF_3CCH), 263.5 (m, CF_3CCH), 104.2 (C_5H_5), 103.5 (C_5H_5), 22.9 (SCH_3), 22.3 (SCH_3). Anal. Calcd for $C_{16}H_{20}BF_7Mo_2S_3$: C, 29.8; H, 3.1. Found: C, 29.9; H, 3.3.

Synthesis of $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-}\eta^1\text{:}\ \eta^2\text{-CCR})]$ (3). To a solution of $[Mo_2Cp_2(\mu\text{-SMe})_3(RCCH)](BF_4)$ (0.2 g: **2a**, 0.30 mmol; **2b**, 0.31 mmol; **2c**, 0.32 mmol; **2d**, 0.32 mmol; **2e**, 0.31

(33) (a) Adams, R. A.; Chen, L.; Wu, W. *Organometallics* **1994**, *13*, 1257. (b) Torres, M. R.; Perales, A.; Ros, J. *Organometallics* **1988**, *7*, 1223.

(34) Agh-Atabay, N. M.; Davidson, J. L. *J. Chem. Soc., Dalton Trans.* **1992**, 3531.

mmol) in CH_2Cl_2 was added a slight excess of Et_3N (1.5 equiv). The solution quickly turned green. After the mixture was stirred for a few minutes at ambient temperature, the solvent was evaporated and the compounds **3** were extracted with diethyl ether (3 × 10 mL). The diethyl ether was then removed in vacuo from the pooled extracts. Washing the residue with cold pentane gave **3** as brownish powders. Yields: **3a** (R = Tol), 121 mg, 70%; **3b** (R = Ph), 131 mg, 75%; **3c** (R = $CH_3C{=}CH_2$), 118 mg, 70%; **3d** (R = *n*Pr), 110 mg, 65%; **3e** (R = CO_2Me), 68 mg, 40%.

3a. ^{1}H NMR ($CDCl_3$, 25 °C; δ): 6.97 (2d, 4H, J_{HH} = 8.0 Hz, $CH_3C_6H_4$), 5.18 (s, 10H, C_5H_5), 2.29 (s, 3H, $CH_3C_6H_4$), 1.72 (s, 3H, SCH_3), 1.62 (s, 3H, SCH_3), 1.48 (s, 3H, SCH_3).

3b. ^{1}H NMR ($CDCl_3$, 25 °C; δ): 7.26 & 7.06 (2m, 5H, C_6H_5), 5.20 (s, 10H, C_5H_5), 1.69 (s, 3H, SCH_3), 1.63 (s, 3H, SCH_3), 1.48 (s, 3H, SCH_3). Anal. Calcd for $C_{21}H_{24}Mo_2S_3$: C, 44.7; H, 4.0. Found: C, 44.6; H, 4.4.

3c. ^{1}H NMR ($CDCl_3$, 25 °C; δ): 5.26 (s, 10H, C_5H_5), 5.15, 4.80 (2s, 2 × 1H, $CH_3C{=}CH_2$), 1.72. (s, 3H, SCH_3), 1.60 (s, 6H, 2 × SCH_3), 1.42 (s, 3H, $CH_3C{=}CH_2$).

3d. ^{1}H NMR (Tol-d_8, 25 °C; δ): 5.07 (s, 10H, C_5H_5), 1.81 (t, J_{HH} = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 1.62 (s, 3H, SCH_3), 1.59 (s, 3H, SCH_3), 1.54 (s, 3H, SCH_3), 1.32 (sext, J_{HH} = 7.2 Hz, 2H, $CH_2CH_2CH_3$), 0.84 (t, J = 7.4 Hz, 3H, $CH_2CH_2CH_3$).

3e. ^{1}H NMR ($CDCl_3$, 25 °C; δ): 5.52 (s, 10H, C_5H_5), 3.63 (s, 3H, CO_2CH_3), 1.61 (s, 3H, SCH_3), 1.48 (s, 3H, CH_3), 1.37 (s, 3H, CH_3).

Synthesis of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}C{=}CHR](BF_4)$ (4a–d). To a solution of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}CCR)]$ (0.2 g: **3a**, 0.35 mmol; **3b**, 0.35 mmol; **3c**, 0.38 mmol; **3d**, 0.38 mmol) in Et_2O was added 1 equiv of $H[BF_4]{\cdot}Et_2O$. Blue solids of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}C{=}CHR](BF_4)$ precipitated from the solution and were collected by filtration and then washed with pentane Yields: **4a** (R = Tol), 228 mg, 98%; **4b** (R = Ph), 217 mg, 95%; **4c** (R = $CH_3C{=}CH_2$), 222 mg, 95%; **4d** (R = *n*Pr), 225 mg, 96%.

4a. ^{1}H NMR (CD_2Cl_2, 25 °C; δ): 7.65 (s, 1H, =C=C(Tol)*H*), 7.09 (d, 2H, $CH_3C_6H_4$), 6.90 (d, 2H, $CH_3C_6H_4$), 6.02 (s, 10H, C_5H_5), 2.29 (s, 3H, $CH_3C_6H_4$), 1.85 (s, 3H, SCH_3), 1.68 (s, 3H, SCH_3), 1.50 (s, 3H, SCH_3). Anal. Calcd for $C_{22}H_{27}BF_4Mo_2S_3$: C, 39.6; H, 4.0. Found: C, 37.4; H, 4.7.

4b. ^{1}H NMR (CD_3COCD_3, 25 °C; δ): 7.99 (1H, s, =C=C(Ph)-*H*), 4.78–7.15 (5H, m, C_6H_5), 6.28 (10H, s, C_5H_5), 1.93 (3H, s, SCH_3), 1.76 (3H, s, SCH_3), 1.55 (3H, s, SCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C; δ): 368.4 (=*C*=CHPh), {(131.6, s), (130.3, dt, J_{CH} = 162.0 Hz, J_{CH} = 7.3 Hz), (129.1, dm, J_{CH} = 164.0 Hz), (128.9, dm, J_{CH} = 165.0 Hz) C_6H_5}, 115.4 (d, J_{CH} = 163.0 Hz, =C=*C*HPh), 98.2 (d, J_{CH} = 181.0 Hz, C_5H_5), 19.4 (q, J_{CH} = 141.0 Hz, SCH_3), 10.6 (q, J_{CH} = 141.0 Hz, SCH_3), 6.7 (q, J_{CH} = 141.0 Hz, SCH_3). Anal. Calcd for $C_{21}H_{25}BF_4Mo_2S_3$: C, 38.6; H, 3.8. Found: C, 37.8; H, 4.0.

Repeated poor analytical results were obtained for spectrospically (NMR) pure samples of **4a**,**b** for reasons similar to those for **2a**,**b** (see above).

4c. ^{1}H NMR (CD_3COCD_3, 25 °C; δ): 7.46 (s, 1H, =C=CR*H*), 6.27 (s, 10H, C_5H_5), 5.31, 4.97 (2 × m, 2 × 1H, $CH_3C{=}CH_2$), 1.92. (s, 3H, SCH_3), 1.68 (s, 3H, SCH_3), 1.58 (s, 3H, SCH_3), 1.52 (q, J_{HH} = 0.7 Hz, 3H, $CH_3C{=}CH_2$).

4d. ^{1}H NMR (CD_2Cl_2, 25 °C; δ): 6.60 (s, broad, 1H, =C=C(nPr)*H*), 6.07 (s, 10H, C_5H_5), 1.89 (s, 3H, SCH_3), 1.68 (m, 2H, $(CH_2)_2$), 1.57 (s, 3H, SCH_3), 1.48 (m, 2H, $(CH_2)_2$), 1.45 (s, 3H, SCH_3), 0.93 (t, J_{HH} = 7.2 Hz, 3H, $(CH_2)_2CH_3$). ^{13}C NMR (CD_2Cl_2, 25 °C; δ): 365.3 (=*C*=CH(*n*Pr)), 114.2 (d, J_{CH} = 163.2 Hz, =C=*C*H(*n*Pr)), 97.4 (d, J_{CH} = 168.0 Hz, C_5H_5), 25.0 (t, J_{CH} = 128.5 Hz, CH_2), 13.4 (q, J_{CH} = 125.5 Hz, CH_3), 9.9 (q, J_{CH} = 142.0 Hz, SCH_3), 6.3 (q, J_{CH} = 141.1 Hz, SCH_3). One SCH_3 has not been assigned.

Synthesis of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\ \eta^2\text{-}C{=}CH_2](BF_4)$ (4e). A solution of complex **1** (0.2 g, 0.32 mmol) in CH_2Cl_2 (15 mL) was stirred with an excess of Me_3SiCCH (v = 250 μL) for 1 h at 25 °C. The solution turned from red to blue-green. The solvent was then concentrated, and Et_2O was added. A blue solid precipitated. It was collected by filtration and then washed with pentane. Yield: **4e** (R = H), 175 mg, 95%,

4e. ^{1}H NMR (CD_2Cl_2, 25 °C; δ): 6.44 (s, broad, 5H, C_5H_5), 6.00 (s, broad, 5H, C_5H_5), 5.64 and 5.20 (AB, J_{HH} = 18.7 Hz, 2H, =C=CH_2), 1.95 (s, 3H, SCH_3), 1.60 (s, 3H, SCH_3), 1.42 (s, 3H, SCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C; δ): 371.5 (=*C*=CH_2), 99.9 (C_5H_5), 94.3 (C_5H_5), 87.1 (=C=*C*H_2), 21.8 (SCH_3), 9.4 (SCH_3), 6.8 (SCH_3).

Reaction of $[Mo_2Cp_2(\mu\text{-}SMe)_3(RCCH)](BF_4)$ (2a,b,d–f) with Additional RCCH. A solution of the alkyne complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(RCCH)](BF_4)$ (0.2 g: **2a**, 0.30 mmol; **2b**, 0.31 mmol; **2d**, 0.32 mmol; **2e**, 0.31 mmol; **2f**, 0.31 mmol) in CH_2Cl_2 (15 mL) was stirred in the presence of an excess (4 equiv) of the same RCCH alkyne (R = Tol, v = 154 μL; R = Ph, v = 136 μL; R = *n*Pr, v = 126 μL; R = CO_2Me, v = 110 μL; CF_3[10]) for 24 h at room temperature. The solution turned brownish green. The solvent was then concentrated, and Et_2O was added. Brownish green solids precipitated. They were collected by filtration and then washed with pentane. Yields: **5a** (R = Tol), 164 mg, 70%; **5b** (R = Ph), 175 mg, 75%; **5c** (R = *n*Pr), 143 mg, 65%; **6a** (R = CF_3), 96 mg, 42% yield; **6b** (R = CO_2Me), 100 mg, 45%.

5a.[10] ^{1}H NMR (CD_3COCD_3, 25 °C; δ): [7.80 (d, J_{HH} = 8.5 Hz, 2H), 7.36 (d, J_{HH} = 8.5 Hz, 2H), 7.02 (d, J_{HH} = 8.5 Hz, 2H), 6.58 (J_{HH} = 8.5 Hz, 2H, d)] 2 × $C_6H_4CH_3$, 7.12 and 5.03 (2 × d, J_{HH} = 1.4 Hz, 2 × 1H, −C*H*=CRC*H*=CR−), 5.56 (s, 5H, C_5H_5), 5.39 (s, 5H, C_5H_5), 2.45, 2.42, 2.28, 2.24, 1.86 (5 s, 5 × 3H, 2 × $C_6H_4CH_3$ and 3 × SCH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): 141.7, 136.6, 136.5, 136.0, 132.2, 130.1, 129.4, 128.4, 127.2, 126.7 (*TolC*=*C*H=*CTol*=*C*HSMe), 98.5 (C_5H_5), 94.3 (C_5H_5), 21.2, 20.9, 26.1, 22.9, 19.7 (2 × $C_6H_4CH_3$ + 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.

5b. ^{1}H NMR (CD_3COCD_3, 25 °C; δ): δ 7.91 and 7.53 (m, 5H, *Ph*C=CH=C*Ph*=CHSMe), 7.19 & 6.70 (m, 5H, *Ph*C=CH=C*Ph*=CHSMe), 7.14 (d, J_{HH} = 1.3 Hz, 1H, PhC=C*H*=C(Ph)=C*H*SMe), 5.60 (s, 5H, C_5H_5), 5.40 (s, 5H, C_5H_5), 5.05 (d, J_{HH} = 1.3 Hz, 1H, PhC=C*H*=C(Ph)=C*H*SMe), 2.45 (s, 3H, SCH_3), 2.27 (s, 3H, SCH_3), 1.87 (s, 3H, SCH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): 152.8, 138.9, 132.4, 130.9, 130.0, 129.2, 127.9, 127.1, 126.9, 126.8 (*PhC*=*C*H=*CPh*=*C*HSMe), 98.6 (C_5H_5), 94.4 (C_5H_5), 23.8 (SCH_3), 15.7 (SCH_3), 11.1 (SCH_3). Anal. Calcd for $C_{29}H_{31}BF_4Mo_2S_3$: C, 46.2; H, 4.1. Found: C, 46.4; H, 4.2.

5c. ^{1}H NMR ($CDCl_3$, 25 °C; δ): 6.35 (s, broad, 1H, (*n*Pr)C=C*H*=C(*n*Pr)=C*H*SMe), 5.50 (s, 5H, C_5H_5), 5.13 (s, 5H, C_5H_5), 4.29 (s, broad, 1H, (*n*Pr)C=C*H*=C(*n*Pr)=C*H*SMe), 2.40 (m, 2H, $(CH_2)_2$), 2.26 (s, 3H, SCH_3), 1.90 (m, 4H, $(CH_2)_2$), 1.88 (s, 3H, SCH_3), 1.79 (s, 3H, SCH_3), 1.40 (m, 2H, $(CH_2)_2$), 1.17 (t, J_{HH} = 7.2 Hz, 3H, CH_3), 0.96 (t, J_{HH} = 7.2 Hz, 3H, CH_3).

6a.[10] ^{1}H NMR (CD_3COCD_3, 25 °C; δ): 5.97 (s, 10H, C_5H_5), 3.38 (s, 2H, $C_4(CF_3)_2H_2SCH_3^+$), 2.73 (s, 3H, $C_4(CF_3)_2H_2SCH_3^+$), 2.33 (s, 3H, SCH_3), 2.10 (s, 3H, SCH_3). ^{19}F NMR (CD_3COCD_3, 25 °C; 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.

6b. ^{1}H NMR (CD_3COCD_3, 25 °C, δ): 5.84 (s, 10H, C_5H_5), 3.67 (s, 2H, $C_4(CO_2CH_3)_2H_2SCH_3^+$), 3.33 (s, 2H, $C_4(CO_2CH_3)_2H_2SCH_3^+$), 2.70 (s, 3H, $C_4(CO_2CH_3)_2H_2SCH_3^+$), 2.13 (s, 3H, SCH_3), 1.95 (s, 3H, SCH_3).

Reaction of $[Mo_2Cp_2(\mu\text{-}SMe)_3(RCCH)](BF_4)$ (2b,e) with RNC (R = *t*Bu, Xylyl). A solution of $[Mo_2Cp_2(\mu\text{-}SMe)_3(PhCCH)](BF_4)$ (**2b**; 0.2 g, 0.30 mmol) in CH_2Cl_2 (15 mL) was stirred with 1 equiv of RNC (R = *t*Bu, v = 34 μL; R = xylyl, m = 39.3 mg) for 1 h at room temperature. The solution readily turned orange. The solvent was then concentrated, and Et_2O was added. Orange solids precipitated. They were collected by filtration and then washed with pentane. Yields: **7a** (R = Ph, L = *t*BuNC), 198 mg, 90%; **7b** (R = Ph, L = xylylNC), 200 mg, 85%. The same procedure was applied to **2e** (0.2 g, 0.31 mmol)

Table 3. Crystal Data and Structure Refinement Details[a]

	3a	4b	7a
empirical formula	$C_{22}H_{26}Mo_2S_3 \cdot 0.5C_5H_{12}$	$C_{21}H_{25}BF_4Mo_2S_3$	$C_{27}H_{36}BCl_2F_4Mo_2NS_3$
fw	614.56	652.28	820.34
cryst syst	monoclinic	monoclinic	monoclinic
space group	*Cc*	$P2_1/c$	$P2_1/c$
a, Å	14.1852(8)	15.7730(15)	10.2490(6)
b, Å	22.5726(10)	8.5305(6)	12.2493(12)
c, Å	7.9974(3)	17.7108(7)	25.9798(17)
β, deg	90.695(4)	90.285(6)	91.212(5)
V, Å^3	2560.6(2)	2383.0(3)	3260.9(4)
Z	4	4	4
D_{calcd}, Mg/m^3	1.594	1.818	1.671
μ, mm^{-1}	1.234	1.354	1.167
F(000)	1244	1296	1648
cryst size, mm	0.47 × 0.16 × 0.11	0.30 × 0.28 × 0.13	0.30 × 0.13 × 0.05
θ range, deg	2.9−30.4	2.3−27.0	2.3−26.9
index ranges	$-20 \le h \le 20$	$-20 \le h \le 2$	$-13 \le h \le 13$
	$-19 \le k \le 32$	$-10 \le k \le 1$	$-2 \le k \le 15$
	$-11 \le l \le 6$	$-22 \le l \le 22$	$-3 \le l \le 33$
no. of rflns collected	8598	6768	8766
no. of indep rflns	5221 (R_{int} = 0.015)	5206 (R_{int} = 0.035)	7037 (R_{int} = 0.020)
no. of obsd rflns with $I > 2\sigma(I)$	4835	3502	5077
abs cor	analytical	ι-scans	analytical
T_{max}, T_{min}	0.896−0.669	0.769−0.709	0.950−0.906
no. of data/params	5221/255	5206/284	7037/365
goodness of fit on F^2	1.033	0.918	1.010
R1, wR2 ($I > 2\sigma(I)$)	0.022, 0.056	0.042, 0.073	0.039, 0.093
R1, wR2 (all data)	0.028, 0.058	0.101, 0.083	0.071, 0.106
Flack param	0.07(3)		
$\Delta\rho$ range, e Å^{-3}	+0.43 to −0.30	+0.66 to −0.50	+0.85 to −0.88

[a] All measurements were made at 20 °C with Mo Kα radiation, λ = 0.710 73 Å, on a Nonius CAD4 diffractometer.

and afforded in the presence of an equimolar amount of *t*BuNC (v = 35 μL) the complex **8** as an orange powder Yield: 204 mg, 92%.

7a. ^{1}H NMR (CD_2Cl_2, 25 °C; δ): 7.37 & 7.0 (m, 5H, C_6H_5), 6.76 (s, 1H, MeSCR=C*H*), 5.21 (s, 5H, C_5H_5), 5.11 (s, 5H, C_5H_5), 2.16 (s, 3H, SCH_3), 1.96 (s, 3H, SCH_3), 1.59 (s, 3H, SCH_3), 1.36 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C; δ): 166.3 (*C*NC(CH$_3$)$_3$), 151.8 (MeSC*R*=*C*H), 139.0, 129.2, 128.9, 127.9 (C_6H_5), 111.7 (MeS*C*R=CH), 93.8 (C_5H_5), 91.4 (C_5H_5), 59.1 (*C*(CH$_3$)$_3$), 29.9 (C(*C*H$_3$)$_3$), 23.9 (S*C*H$_3$), 22.4 (S*C*H$_3$), 14.1 (S*C*H$_3$). IR (KBr pellets; cm^{-1}): 2120 (s) ν(CN), 1150−1050 (s) ν(BF). Anal. Calcd for $C_{26}H_{34}NBF_4Mo_2S_3 \cdot CH_2Cl_2$: C, 39.5; H, 4.4; N, 1.7. Found: C, 39.4; H, 4.4, N, 2.2.

7b. ^{1}H NMR (CD_2Cl_2, 25 °C; δ): 7.4−6.9 (m, 8H, $C_6H_3(CH_3)_2$ and C_6H_5), 6.86 (s, 1H, MeSCR=C*H*), 5.27 (s, 5H, C_5H_5), 5.26 (s, 5H, C_5H_5), 2.37 (s, 6H, $C_6H_3(CH_3)_2$), 2.28 (s, 3H, SCH_3), 1.88 (s, 3H, SCH_3), 1.67 (s, 3H, SCH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C; δ): 187.1 (*C*NC$_6$H$_3$(CH$_3$)$_2$), 150.8 (MeS*C*R=CH), 139.0−127.0 ($C_6H_3(CH_3)_2$ and C_6H_5), 111.7 (MeSCR=*C*H), 94.2 (C_5H_5), 92.1 (C_5H_5), 24.9 (S*C*H$_3$), 23.1 (S*C*H$_3$), 19.5 (CNC$_6$H$_3$(*C*H$_3$)$_2$), 14.5 (S*C*H$_3$). IR (KBr pellets; cm^{-1}): 2060 (s) ν(CN), 1150−1050(s) ν(BF). Anal. Calcd for $C_{30}H_{34}NBF_4Mo_2S_3 \cdot CH_2Cl_2$: C, 42.8; H, 4.1; N, 1.6. Found: C, 42.6; H, 4.1, N, 1.7.

8. ^{1}H NMR ($CDCl_3$, 25 °C; δ): 6.83 (s, 1H, CR=C*H*SCH$_3$), 5.45 (s, 5H, C_5H_5), 5.11 (s, 5H, C_5H_5), 3.58 (s, 3H, CO$_2$CH_3), 2.37 (s, 3H, CR=CHSCH_3), 2.26 (s, 3H, SCH_3), 1.71 (s, 3H, SCH_3), 1.41 (s, 9H, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 25 °C; δ): 175.6 (*C*O$_2$CH$_3$), 164.2 (*C*NC(CH$_3$)$_3$), 129.6 (*C*R=CHSCH$_3$), 100.2 (CR=*C*HSCH$_3$), 93.7 (C_5H_5), 91.5 (C_5H_5), 58.5 (*C*(CH$_3$)$_3$), 51.8 (CO$_2$*C*H$_3$), 29.6 (C(*C*H$_3$)$_3$), 23.6 (S*C*H$_3$), 21.7 (CR=CHS*C*H$_3$), 13.4 (S*C*H$_3$).

Reaction of $[Mo_2Cp_2(\mu\text{-SMe})_3(RCCH)](BF_4)$ (2a,b,e) with CS_2. A solution of the complex $[Mo_2Cp_2(\mu\text{-SMe})_3(RCCH)](BF_4)$ (0.2 g: **2a**, 0.30 mmol; **2b**, 0.31 mmol; **2e**, 0.31 mmol) in CH_2Cl_2 (15 mL) was stirred with excess CS_2 (2 mL) for 2 h at room temperature. The solution turned brownish red. The solvent was then concentrated, and Et_2O was added. Brown solids precipitated. They were collected by filtration and then washed with pentane. Yields: **9a** (R = Tol), 184 mg, 80%; **9b** (R = Ph), 186 mg, 85%; **10** (R = CO_2Me), 189 mg, 86%.

9a. ^{1}H NMR (CD_3COCD_3, 25 °C; δ): 7.31−7.26 (m, 4H, C_6H_4), 6.44 (s, broad, 5H, C_5H_5), 6.08 (s, 1H, −C*H*=CRSCH$_3$), 5.76 (s, broad, 5H, C_5H_5), 2.36 (s, 3H, $C_6H_4CH_3$), 2.19 (s, 3H, SCH_3), 2.14 (s, 3H, SCH_3), 2.06 (s, 3H, −CH=CRSCH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C; δ): 146.6 (−CH=*C*R−SCH$_3$), 142.6 (*C*S$_2$), 140.0, 135.2, 130.1, 129.3 (C_6H_4), 133.3 (−*C*H=CRSCH$_3$), 103.1 (C_5H_5), 94.6 (C_5H_5), 26.2 (S*C*H$_3$), 21.1 ($C_6H_4CH_3$), 16.8 (−CH=CRS*C*H$_3$), 10.3 (S*C*H$_3$). Anal. Calcd for $C_{23}H_{27}BF_4Mo_2S_5 \cdot CH_2Cl_2$: C, 34.7; H, 3.7. Found: C, 34.8; H, 3.5.

9b. ^{1}H NMR (CD_3COCD_3, 25 °C; δ): 7.42 (m, 5H, C_6H_5), 6.28 (s, broad, 5H, C_5H_5), 6.09 (s, 1H, −C*H*=CR−), 5.76 (s, broad, 5H, C_5H_5), 2.14 (s, 3H, SCH_3), 2.10 (s, 3H, SCH_3), 2.05 (s, 3H, SCH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C; δ): 147.6, 142.3, 137.3, 132.3, 129.7, 129.2, 129.0 (C_6H_5 + −*C*H=*C*R− + *C*S$_2$), 102.2 (C_5H_5), 93.9 (C_5H_5), 26.5 (S*C*H$_3$), 19.7 (S*C*H$_3$), 10.9 (S*C*H$_3$). IR (KBr pellets; cm^{-1}): 1150−1050 (s) ν(BF). Anal. Calcd for $C_{22}H_{25}BF_4Mo_2S_5 \cdot CH_2Cl_2$: C, 33.9; H, 3.3. Found: C, 34.2; H, 3.5.

10. ^{1}H NMR (CD_3COCD_3, 25 °C; δ): 7.93 (s, 1H, CH$_3$SC*H*=CR−), 6.34 (s, broad, 5H, C_5H_5), 5.74 (s, broad, 5H, C_5H_5), 3.72 (s, 3H, CO$_2$CH_3), 2.66 (s, 3H, CH_3SCH=CR), 2.17 (s, 3H, SCH_3), 2.15 (s, 3H, SCH_3). ^{13}C{^{1}H} NMR (CD_3COCD_3, 25 °C; δ): 152.0 (CH$_3$S*C*H=CR−), 163.3 (*C*O$_2$CH$_3$), 142.5 (*C*S$_2$), 127.1 (CH$_3$SCH=*C*R−), 102.9 (C_5H_5), 94.4 (C_5H_5), 52.6 (CO$_2$*C*H$_3$), 25.7 (*C*H$_3$SCH=CR), 20.5 (S*C*H$_3$), 10.2 (S*C*H$_3$). Anal. Calcd for $C_{18}H_{23}BF_4Mo_2O_2S_5$: C, 30.4; H, 3.2. Found: C, 30.2; H, 3.3.

Crystal Structure Determinations of 3a, 4b, and 7a. Pertinent data are summarized in Table 3. In general, the structures were refined with anisotropic displacement parameters for non-hydrogen atoms and hydrogen atoms were subject to riding constraints during refinement.[35] However, the hydrogen atoms attached to C5 in **4b** and to C9 in **7a** were located in difference syntheses and their parameters were then

(35) Programs used: Sheldrick, G. M. SHELX97−Programs for Crystal Structure Analysis (Release 97-2); Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998. Farrugia, L. J. WinGX−A Windows Program for Crystal Structure Analysis. *J. Appl. Crystallogr.* **1999**, *32*, 837.

successfully refined. The crystal of **3a** contained highly disordered solvent, believed to be *n*-pentane, which was modeled approximately by including the seven most highly populated atomic sites in the structure factor calculations as C atoms with 50% occupancy. The position of each site was taken from a difference synthesis, and subsequently, only its U_{iso} parameter was refined. Crystals of **7a** contain ordered dichloromethane.

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Supporting Information Available: For **3a**, **4b**, and **7a**, tables giving details of structure determinations, non-hydrogen atomic positional parameters, all bond distances and angles, anisotropic displacement parameters, and hydrogen atomic coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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