

C–C, C–S, and C–N Coupling versus Dealkylation Processes in the Cationic Tris(thiolato)dimolybdenum(III) Complexes $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3\text{L}_2]^+$ (L = xylNC, *t*-BuNC, CO, MeCN)

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Reductive coupling between isocyanide ligands attached to adjacent molybdenum atoms in the bis(aryl isocyanide) complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\text{xylNC})_2](\text{BF}_4)$ (**1**) was initiated by addition of the hydrosulfide anion (HS^-) to **1** under reflux in tetrahydrofuran, affording, in nearly quantitative yields, the dimetallaimido(ami-no)carbene derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3\{\mu\text{-}\eta^1(\text{C}):\eta^1(\text{C})\text{-C}(\text{NHxyl})\text{C}(\text{Nxyl})\}]$ (**7**), in which both isocyanide groups of **1** are now linked by a new C–C bond. When the previous reaction was conducted in the presence of a large excess of hydrosulfide (20 equiv), under similar experimental conditions, the dithiocarbonimidate compound $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_2(\mu\text{-S}_2\text{CNxyl})]$ (**8**) was obtained in quantitative yields. This product results from subsequent thiolate exchange and substitution reactions to afford a quadruply sulfur bridged intermediate, followed by free isonitrile addition to sulfido S atoms. Treatment of the coupled isocyanide derivative **7** with HBF_4 led exclusively to the formation of the starting complex **1** by reversible isocyanide ligand decoupling. The heating of a tetrahydrofuran solution of **1** with the base $\text{NaC}\equiv\text{CH}$ gave, in high yields, the μ -alkylidyne and μ -acetylide product $[\text{Mo}_2\text{Cp}(\mu\text{-SMe})_2\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_4)(\text{xylN})\text{CN}(\text{xyl})\text{C}\}(\mu\text{-CCH})]$ (**9**), in which a deprotonated Cp and both isocyanide ligands of **1** are now linked by new C–C and C–N bonds, and in addition an acetylide has replaced a thiolate ligand of **5**. Reaction of the μ -alkylidyne complex $[\text{Mo}_2\text{Cp}(\mu\text{-SMe})_2\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_4)(\text{xylN})\text{CN}(\text{xyl})\text{C}\}]$ (**5**) with $\text{NaC}\equiv\text{CH}$ under reflux in tetrahydrofuran produced, in high yields, the μ -alkylidyne and bis(μ -acetylide) cationic compound $[\text{Mo}_2\text{Cp}(\mu\text{-SMe})_2\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_4)(\text{xylN})\text{CN}(\text{xyl})\text{C}\}(\mu\text{-CCH})_2]\text{Br}$ (**10**), in which two xylNC ligands have replaced a thiolate group of **5**. Further reactions of the bis(μ -isocyanide) complex **10** with NaOH (suspension), on the one hand, and HBF_4 , on the other hand, under reflux in tetrahydrofuran or at room temperature in dichloromethane, respectively, led to the formation in high yields of the known mixed μ -alkylidyne and μ -amino-oxycarbene species $[\text{Mo}_2\text{Cp}(\mu\text{-SMe})_2\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_4)(\text{xylN})\text{CN}(\text{xyl})\text{C}\}\{\mu\text{-}\eta^1(\text{O}):\eta^1(\text{C})\text{-OCNHxyl}\}]$ (**12**) and the new tetrakis(isocyanide) dicationic derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_2(\text{xylNC})_4](\text{BF}_4)_2$ (**11**), respectively. The latter complex results from successive protonation at one carbon atom of the cyclopentadienyl ligand linked with isocyanides of **10** and decoupling between deprotonated Cp and isocyanide ligands. The heating of a tetrahydrofuran solution of a mixture of the bis(alkyl isocyanide) complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\textit{t}\text{-BuNC})_2](\text{BF}_4)$ (**2**) and NaSH proceeded exclusively through the dealkylation of one *tert*-butyl isocyanide ligand to afford the known product $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\textit{t}\text{-BuNC})](\text{CN})$ (**13**). Similar reaction of the dicarbonyl derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\text{CO})_2]\text{Cl}$ (**3**) with NaSH proceeded through dealkylation of one thiolate group to yield the new neutral sulfido species $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_2(\mu\text{-S})(\text{CO})_2]$ (**14**). Further heating of **14** in dichloromethane led to the formation of the chloromethanethiolate derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_2(\mu\text{-SCH}_2\text{Cl})(\text{CO})_2]\text{Cl}$ (**15**). Treatment of the bis(nitrile) species $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\text{MeCN})_2]\text{BF}_4$ (**4**) under reflux in tetrahydrofuran with NaSH afforded, in valuable yields, the thioamidato derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\mu\text{-MeCSNH})]$ (**18**). All new complexes have been characterized by elemental analyses and spectroscopic methods, supplemented for **7–10**, **11'**, **14**, and **15** by X-ray diffraction studies.

Introduction

Coupling reactions involving alkynes,¹ isocyanides,^{1,2} nitriles,³ and carbon monoxide,⁴ through the mediation of transition-metal complexes, lead to metallacyclic compounds via

consecutive insertions of these unsaturated molecules into M–C bonds. These insertion reactions are mostly initiated by oxidative addition of alkyl halides to $[\text{ML}_n]$ complexes (L = RNC, RCN, CO,...), by addition of an excess of two-electron-donor molecules to metal complexes, and also by thermolysis.⁵ Among the previously cited potential coupling molecules, isocyanides (RNC) are isoelectronic with CO and, accordingly, are expected to display similar chemical behavior. Indeed, many such similarities are apparent, but differences between the two are also observed, resulting from the fact that isocyanides are better σ -donors and weaker π -acceptors than carbon monoxide.⁶ In particular, almost all the carbonylation reactions are intramo-

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lecular, while most of the insertions of isocyanides into metal–carbon bonds are, in contrast, intermolecular,² in which the incoming ligand is the one inserted. Interestingly, almost all the examples of intramolecular coupling reactions between two isocyanides that have been investigated experimentally are induced in mononuclear transition-metal complexes by the carbon–carbon reductive coupling of adjacent ligands.⁷ Such reactions, which are reported in the literature, may be viewed formally as the addition of one electron and one proton to each of two isocyanide ligands, which then couple to one another. It has been demonstrated that the close nonbonded contact between ligands in mononuclear poly(isocyanide) complexes is a prerequisite for carbon–carbon bond formation.⁸ With this in mind, one can explain the lack, until now, of ligands resulting from C–C coupling between two isocyanides coordinated to adjacent metals in binuclear transition-metal complexes, in which the

nonbonded distance between isocyanides is obviously expected to be much longer than that observed in related mononuclear derivatives. Nevertheless, a few C–C coupling reactions on dinuclear transition-metal complexes have been reported; they involve either incoming isocyanides and unsaturated/saturated molecules already coordinated to the metals⁹ or both incoming isocyanides.¹⁰ In all these cases, the isolated products result from successive insertions of RNC into transition-metal–carbon bonds.

As part of our ongoing studies of metal-assisted coupling reactions involving RNC or/and R'CN, we have recently explored the reactivity toward bases having variable strengths of such systems coordinated to the bimetallic core {Mo₂Cp₂(μ-SMe)₃}. We have found, among other features, that on reacting the bis(*tert*-butyl isocyanide) complex [Mo₂Cp₂(μ-SMe)₃(*t*-BuNC)₂](BF₄) with *n*-BuLi the mixed isocyanide–cyanide derivative [Mo₂Cp₂(μ-SMe)₃(*t*-BuNC)(CN)] is exclusively formed by dealkylation of one isocyanide group. However, when *n*-butyllithium is replaced by milder bases, a mixture of two complexes is hence obtained in the reaction of [Mo₂Cp₂(μ-SMe)₃(*t*-BuNC)₂](BF₄) with NaOH or (Me₄N)OH: in addition to the previous dealkylated derivative, a μ-alkylidyne species, resulting from the coupling of a deprotonated Cp and two isocyanide ligands, is formed as a minor product. The yield of the latter compound is improved by conducting the reaction in the presence of an excess of *tert*-butyl isocyanide. It has been shown that the formation of the μ-alkylidyne ligand in these experiments involves first the deprotonation by the base of one Cp carbon atom, followed by its stepwise 1,1-migration to the carbon of an adjacent RNC ligand, and finally an isocyanide dimerization occurring via a C,N coupling reaction.¹¹ Interestingly, when the ligand L is xylNC, the formation in high yields of C,C and C,N coupling products is observed in the reaction of [Mo₂Cp₂(μ-SMe)₃L₂](BF₄) with bases (NaOH, (Me₄N)OH). When the latter reactions are conducted in the presence of RNC (R = xyl, *t*-Bu), μ-alkylidyne μ-aminocarbene complexes are produced by linking first a cyclopentadienyl and two isocyanide ligands and then a second isocyanide and hydroxide. All these reactions serve as a striking illustration of the importance of the nature of both isocyanide or nitrile ligands and bases for studies involving intramolecular coupling reactions. As an extension of the above studies, we have now investigated the reactivity of [Mo₂Cp₂(μ-SMe)₃L₂]A (**1–4**) and [Mo₂Cp₂(μ-SMe)₃{μ-(η⁵-C₅H₄)(xylCN)(xyl)C}] (**5**) (see Scheme 1) with several bases (NaSH, NaC≡CH, LiOCH₂CH₂Br, NaOH). We have found a remarkable variety of products with new functionalities. The results are also used to evaluate how both the strength of the bases and the nature of the terminal ligands L in [Mo₂Cp₂(μ-SMe)₃L₂]A influence whether or not coupling products are formed.

Results and Discussion

Reaction of 1 with Sodium Hydrosulfide. Previously, we have shown that the bis(xyl) isocyanide) complex **1** reacts with

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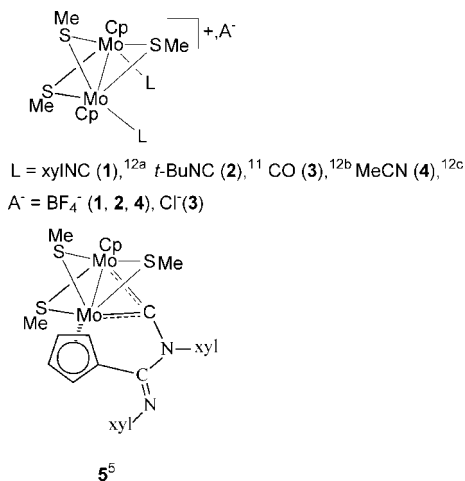
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Scheme 1. Tris(thiolato-bridged) Dimolybdenum Precursors Relevant to This Work


hydroxides to afford in nearly quantitative yields (84%) the μ -alkylidyne product [Mo₂Cp(μ-SMe)₃{μ-(η⁵-C₅H₄)(xylN)CN(xylC)}] (**5**) by cyclopentadienyl and isocyanide coupling.⁵ It is noteworthy that in this case reductive coupling of xylNC does not occur. We, therefore, decided to choose another added anionic reagent to perform the reaction. Accordingly, the hydrosulfide anion (HS[−]), which can act as a base or/and a reductant, would seem to be a suitable reagent for reaction with the bis(isocyanide) compound **1**. Indeed, reaction of **1** with 10 equiv of NaSH · xH₂O in tetrahydrofuran under reflux for 72 h proceeded with high selectivity, and the targeted reductive coupled-isocyanide derivative **7** was obtained (Scheme 2a).

The elemental analysis confirms the presence of two isocyanide units in **7**, while its NMR spectra clearly indicate a structure different from that of **5**. Particularly informative is the absence in the ¹H NMR pattern of the four resonances of relative intensity 1 expected for the four hydrogen atoms of a modified cyclopentadienyl ring. Instead, a single peak of relative intensity 10, detected at 5.09 ppm, is indicative of two unmodified cyclopentadienyl ligands in a symmetrical molecule. The spectroscopic features of **7** are consistent with protonation of a sole isocyanide at the nitrogen atom. Indeed, a single resonance assignable to an amino group is observed at 12.07 ppm in the ¹H NMR spectrum, in accordance with the presence of only one N–H stretching frequency at 3431 cm^{−1}. Moreover, a resonance characteristic of the Mo-bound ¹³C atom of a carbene-like species appears at low field (δ 248.2). In order to establish without any ambiguity the molecular structure of **7**, an X-ray analysis of a single crystal of that complex was undertaken. This structure is shown in Figure 1, in which the well-known {Mo₂Cp₂(μ-SMe)₃} unit is bridged by an imido(yl)amino)carbene group bonded to the Mo₂ unit through both carbon atoms (Mo–C = 2.093(5) and 2.144(5) Å). These two molybdenum–carbon lengths are consistent with multiple-bond character. The resulting C–N (1.317(7) and 1.286(6) Å) distances in the coupled ligand require multiple-bond character, while the mean C–N–C angle of 131.5° is consistent with the presence of N–H bonds. It should be noted that the C4–C5 distance (1.543(7) Å) is indicative of a single bond. That set of information is in accord with a coupled isocyanide ligand, showing substantial bond delocalization (see Chart 1). The complex achieves a closed-shell configuration if the ligand is viewed as a mono-carbene, as depicted by the two extreme forms in Chart 1. The

Mo1–Mo2 distance of 2.7254(7) Å is comparable to that of 2.705(7) Å in the cation [Mo₂Cp₂(μ-SMe)₃(μ-η¹:η¹-HCCCO₂-Me)]⁺,¹³ hence indicating a single bond. We consider that the X-ray study establishes **7** as a μ-η¹(C):η¹(C) complex and therefore formulate **7** as a dimetallaimido(yl)amino)carbene derivative, with a parallel orientation of the C–C axis of the coupled ligand relative to that of the Mo–Mo bond (C4–C5–Mo1–Mo2 torsion angle 1.2(3)°).

The present reaction (Scheme 2a) may be viewed as the addition of two electrons and one proton to the two isocyanide ligands in **1**, which then couple with one another through the carbon atom of each isocyanide to form a metallaimido(yl)amino)carbene complex. To the best of our knowledge, compound **1** is the first example of a dinuclear transition-metal derivative that promotes the reductive coupling of isocyanide ligands by use of an added anionic reagent, HS[−], acting as a reductant. The mechanism by which two isocyanide ligands are reductively coupled is presently uncertain, but it probably involves a pathway that facilitates a close nonbonded contact between the isocyanide ligands in **1**, which enhances the propensity for carbon–carbon bond formation. Accordingly, the first step of formation of **7** is postulated to be the one-electron reduction of [Mo₂Cp₂(μ-SMe)₃(xylNC)₂]⁺ by HS[−] (or S^{2−}). Hence, the electron back-donation from the metal into isocyanide π-acceptor orbitals favors the bending of the latter ligand, which in turn creates a basic nitrogen center that can be protonated to form the putative, transient aminocarbyne cation [Mo₂Cp₂(μ-SMe)₃(xylNC)(xylNHC)]⁺ (**A**). Thus, addition of a second electron to the cation **A** promotes the formation of a second carbenoid-type ligand, which activates the resulting molybdenum derivative for reductive coupling of two isocyanides attached to adjacent metals to afford the dimetallaimido(yl)amino)carbene complex **7**. It appears that the last step of formation of **7** is kinetically favored relative to that of the protonation of the second nitrogen atom of the carbenoid-type group resulting from the one-electron reduction. This prevents the formation of a bis(alkylamido)acetylene derivative, as found by Lippard et al. in several reductive coupling reactions involving mononuclear polycordinate transition-metal isocyanide complexes and a reductant (Zn). Requisite protons to react with the nitrogen of the isocyanide come from either wet tetrahydrofuran or, more probably, water present in the sodium sulfide reagent (NaSH · xH₂O). It should be noted that several attempts to react the bis(isocyanide) cationic compound **1** with zinc under reflux in wet tetrahydrofuran failed.

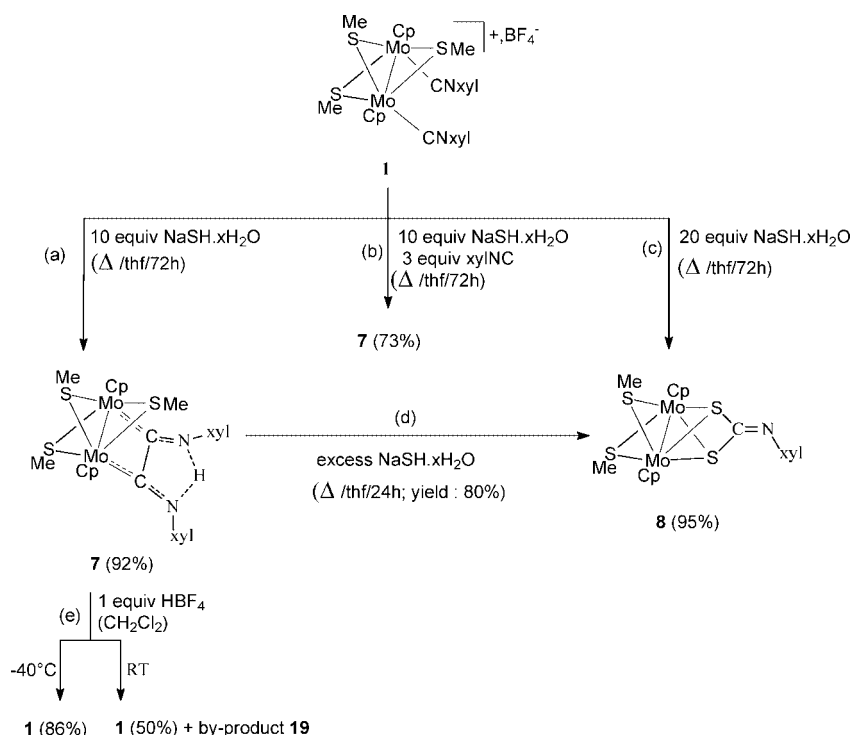
As suggested above, the closest parallel to the work reported in this part would appear to be the studies by Lippard et al. of reductive coupling of isocyanide ligands in mononuclear seven-coordinate metal complexes.⁷ In particular, these authors have also postulated a cationic aminocarbyne complex as an intermediate in related coupling reactions, in accordance with many examples in the literature where electron-rich isocyanide complexes have been converted to aminocarbynes by electrophilic attack (H⁺) at the nitrogen atom.¹⁴ However, notable differences are observed between the two chemistries. For example, though complex **1** has the majority of the requisite

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Scheme 2



electronic (high electron density at the metal center owing to both the reduced complex and the electron-releasing thiolate groups; presence of both Lewis acid (H⁺) and reductant in solution) and steric (high coordination number of the metal atom) properties to undergo reductive coupling, it does not, however, afford the bis(alkylamino)acetylene derivative⁷ but instead a dimetallaimido(yl)amino)carbene product, by reaction

with a reductant. Moreover, in our case the coupling reaction requires only one proton instead of two in Lippard's reactions, precluding the formation of bis(alkylamino) groups. Finally, it has been demonstrated that a prerequisite to carbon–carbon bond formation is a close contact of two isocyanide ligands in the parent complex,^{7e} which we concede is more easily reached in mononuclear than in dinuclear derivatives. Indeed, all the

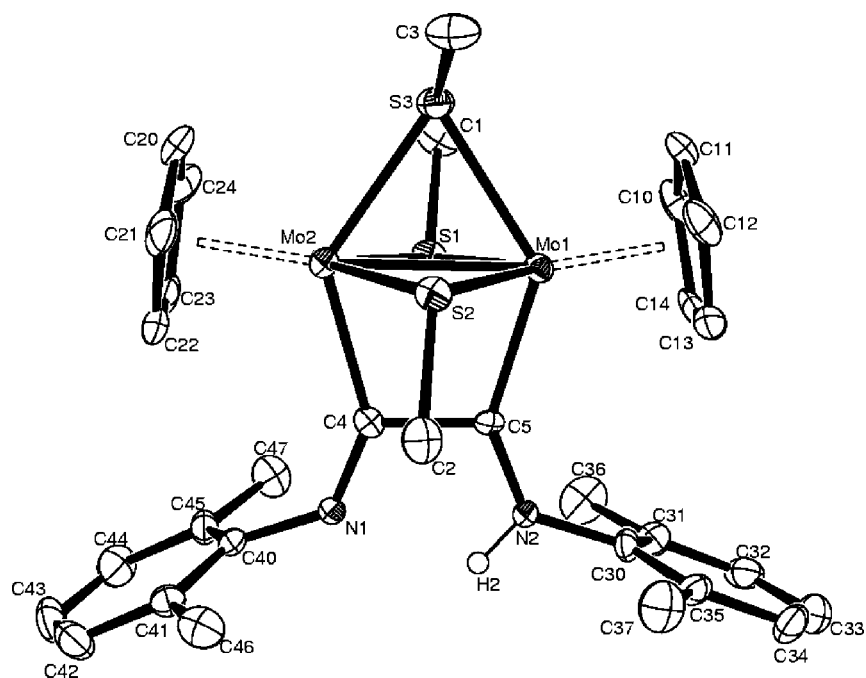
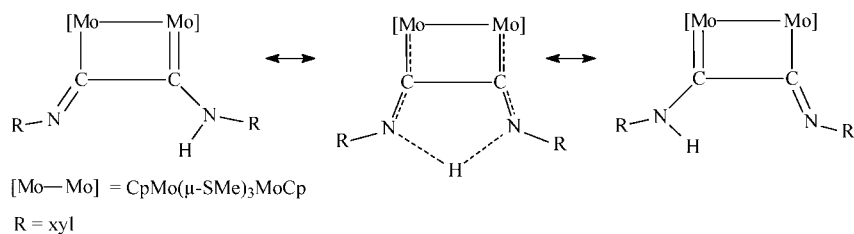


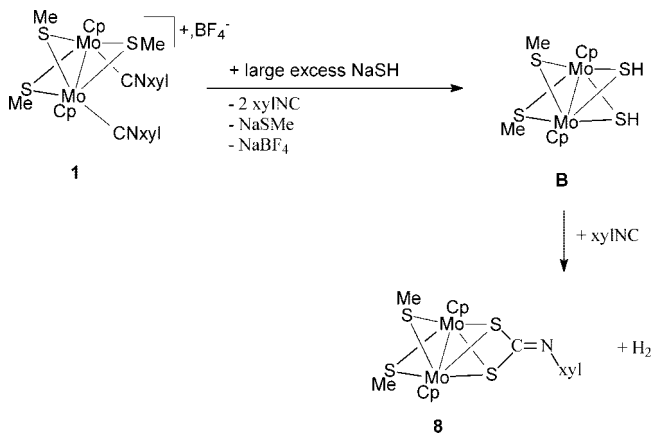
Figure 1. Molecular structure of **7**. Here and elsewhere non-hydrogen atoms are shown with ellipsoids at the 30% probability level. H atoms bonded to C atoms are omitted for clarity. Selected distances (Å), angles (deg), and torsion angles (deg): Mo1–Mo2 = 2.7254(7), Mo1–C5 = 2.093(5), Mo2–C4 = 2.144(5), C4–C5 = 1.543(7), C4–N1 = 1.286(6), C5–N2 = 1.317(7), N1–C40 = 1.414(7), N2–C30 = 1.430(7), Mo–S1 = 2.4533(15), Mo1–S2 = 2.4659(15), Mo1–S3 = 2.4623(15), Mo2–S1 = 2.4642(15), Mo2–S2 = 2.4488(15), Mo2–S3 = 2.4552(15); Mo1–C5–C4 = 107.1(3), Mo1–C5–N2 = 141.2(4), C4–C5–N2 = 111.5(4), C5–N2–C30 = 130.9(5), C5–Mo1–Mo2 = 74.31(15), Mo2–C4–C5 = 105.3(3), Mo2–C4–N1 = 142.3(4), C5–C4–N1 = 112.3(5), C4–N1–C40 = 132.2(5), C4–Mo2–Mo1 = 73.27(14); C4–C5–Mo1–Mo2 = 1.2(3), Mo1–S2–Mo2–S1 = 5.49(5), C4–C5–Mo1–S3 = –1.1(4).

Chart 1



mononuclear poly(isocyanide) complexes, having reductive carbon–carbon coupling behavior, contain nonbonded C–C contacts of 2.25–2.86 Å,^{7d,f,15} while such a distance in **1** could be evaluated, in the absence of X-ray structural data for **1**, at about 3.00 Å in comparison with that observed in the related bis(xyl)NC complex **10** (see below). Interestingly, in spite of this longer nonbonded C–C contact in **1**, its reaction with sodium hydrosulfide in protic solvents leads to the formation of coupled-isocyanide product. It could be suggested that both reduction and protonation of the starting complex bring the two isocyanide ligands closer and, hence, allow the coupling reaction.

When the bis(isocyanide) complex **1** was heated with a large excess of sodium hydrosulfide (20 equiv) under conditions similar to those used in Scheme 2a, the new complex **8** was obtained in nearly quantitative yield (95%) instead of the coupled-isocyanide product **7** (Scheme 2c). Elemental analysis and NMR spectroscopy (see the Experimental Section) indicate the presence of only one isocyanide and two thiolate ligands in **8**. Therefore, this compound was identified as a molybdenum dimer bridged by a dithiocarbonimidate ligand and two SMe groups on the basis of these analytical and spectroscopic data and the solid-state structure, as shown in Scheme 2c and Figure 2. The NMR data provided evidence for the presence of two isomers in solution, which differ only in the orientation (syn or anti) of the bridging SMe groups. The ¹H NMR spectra of isomers **8a** and **8b** (2:3 ratio), at room temperature, each exhibit a single resonance (relative intensity 10) at about 5.5 ppm for the two cyclopentadienyl ligands, suggesting a chemically symmetrical molecule. In other respects, the ¹³C{¹H} NMR spectra of **8** display a low-field resonance pointed at about 171.1 ppm, typical for a C=N group. Thus, the formulation of **8** as a μ-dithiocarbonimidate derivative was confirmed by X-ray analysis of a single crystal of **8a** obtained from a diethyl ether solution at room temperature (Figure 2). The structure contains two CpMo fragments bridged quasi-symmetrically by one dithiocarbonimidate and two SMe ligands, so that each Mo atom has a four-legged piano-stool coordination. The Mo–Mo distance (2.5897(6) Å) is typical for quadruply bridged {Mo₂^{III}Cp₂(μ-SR)_n} systems (n = 3, 4) with single metal–metal bonds.¹⁶ The dithiocarbonimidate N1–C5 bond distance (1.262(8) Å) is in accord with a bond order of 2; however, the angles at C5 (132.6(5) and 126.5(5)°) show some deviations from sp² hybridization but broadly agree with those found in a dithiocarbonimidato complex of palladium(II), [Pd(S₂CNCO₂Et)(PPh₃)₂] (128.2(4) and 123.3(4)°),¹⁷ and the anion [Ni(S₂CNCN)₂]²⁻ (132(2) and 120(2)°).¹⁸ Trends in bond angles at C5 reflect the constraint imposed by the attachment of the

Scheme 3. Proposed Route for the Formation of **8** from the Bis(isocyanide) Complex **1**

dithiocarbonimidate ligand to Mo1 and Mo2 through both S3 and S2, respectively. Otherwise, the Mo–S bond distances (average 2.448 Å) and Mo–S–Mo angles (average 63.8°) are in the ranges (2.42–2.49 Å and 62–66°) generally observed for quadruply bridged dimolybdenum derivatives with a variable number of μ-thiolato ligands.¹⁹ Several examples of related dimolybdenum cyclopentadienyl complexes featuring bridging dithiocarbonimidate ligands have been reported,²⁰ but to the best of our knowledge **8** is the first compound of this series to be structurally characterized by X-ray analysis.

The presence of a large excess of NaSH prevents the coupling of the isocyanide ligands in **1**, when this complex reacts with this basic nucleophile. Although no transient species has been detected, the pathway of formation of **8** can be accounted for as summarized in Scheme 3. Indeed, there is precedent for the first step of the mechanism that involves subsequent thiolate exchange^{20b} and substitution reactions to afford the quadruply

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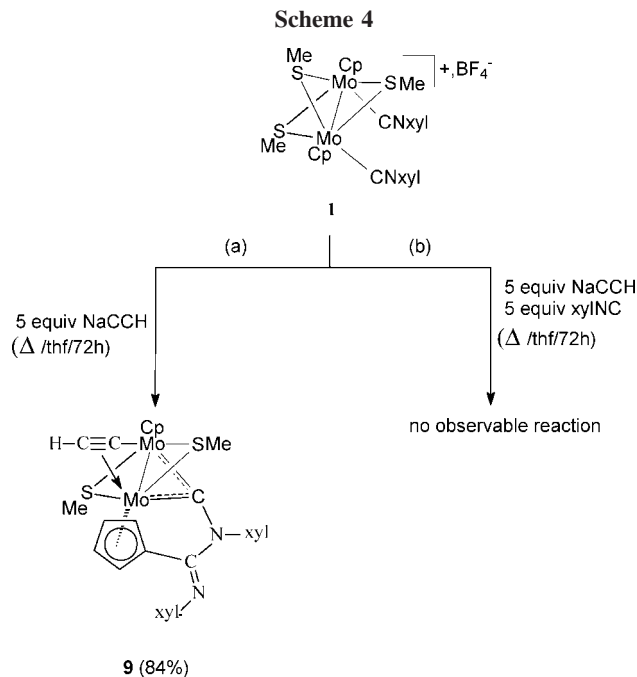
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bridged intermediate $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_2(\mu\text{-SH})_2]$ (**B**). Concerted dissociation from hydrosulfido ligands and free isonitrile addition to sulfido S atoms finally leads to the formation of the bridging dithiocarbonimidate ligand in complex **8**. It is known that the elimination of hydrogen from bis(hydrosulfido) complexes is facilitated by the presence of unsaturated molecules.²¹ The proposed pathway is consistent with the observation that a large excess of basic nucleophile must be present in order to account for the first step, leading finally to **8** via elimination of dihydrogen. It is worth noting that under similar reaction conditions complex **8** was also obtained in good yields (80%) from **7** (Scheme 2d). We assume that this transformation proceeds logically via a mechanism involving the same bis(hydrosulfido) intermediate **B** (Scheme 3) as that postulated in Scheme 2c. Another possible pathway involving attack of SH^- on the coordinated isocyanide ligand to give thioaminocarbene intermediates has also been considered, but the absence of such complexes in reactions of **1** with a very large excess of hydrosulfide makes such a mechanism unlikely.

We have shown previously that reaction of **1** with hydroxides leads to the formation of μ -aminocarbyne products, (e.g., **5**), which involves the coupling of one cyclopentadienyl and two isocyanide ligands at the $\{\text{Mo}_2(\mu\text{-SMe})_3\}$ nucleus. Hence, when this reaction is undertaken in the presence of a large excess of isocyanide, complexes are formed containing at one and the same time bridging aminocarbyne and amino-oxycarbene ligands.⁵ These products result from coupling reactions involving cyclopentadienyl and isocyanide ligands, on the one hand, and hydroxide and isocyanide groups, on the other hand. In the hope of getting amino-thiocarbene adducts, we reacted complex **1** in tetrahydrofuran with sodium hydrosulfide in the presence of 3 equiv of xylNC under reflux for 72 h. The desired product was not formed; instead, the coupled-isocyanide derivative **7** was obtained in good yields (73%) (Scheme 2b). These data indicate clearly that the imido(yl)amino)carbene ligand in **7** is unable to activate the $\{\text{Mo}_2(\mu\text{-SMe})_3\}$ nucleus to undergo the sulfide–isocyanide coupling; this is in contrast with the aminocarbyne group in **5** that clearly performs the related hydroxide–isocyanide coupling.

Interestingly, complex **7** reacted with 1 equiv of HBF_4 at low temperature (-40°C) to give the starting compound **1** in high yields (86%) (Scheme 2e). When the reaction was conducted at room temperature, severe decomposition was observed: complex **1** (50% yield) was obtained together with the side product **19**, which was characterized only by its NMR data (see the Experimental Section). Thus, the treatment of the coupled-isocyanide derivative **7** with H^+ leads to the decoupling of the isocyanide ligands via carbon–carbon bond cleavage and dihydrogen elimination. These results contrast strongly with those reported by Lippard et al.,⁷ which indicate that the double protonation of the isocyanide ligands in mononuclear polycordinate transition-metal isocyanide complexes affords coupled-isocyanide products.

Reaction of **1 with Sodium Acetylide.** As stated in the Introduction, the reactivity of bis(isocyanide) derivatives toward basic nucleophiles depends markedly on the nature of these reagents. In particular, we have shown above that the hydrosulfide anion (HS^-) is unable to deprotonate one cyclopentadienyl ligand in **1** and, therefore, to promote a cyclopentadienyl–isocyanide coupling, instead it acts as a reductive coupling agent. We thus decided to check whether the reaction of complex **1** with distinct types of basic nucleophiles, e.g. $\text{NaC}\equiv\text{CH}$, induce C–C or C–N coupling among cyclopentadienyl, isocyanide,



and acetylide ligands. Accordingly, compound **1** reacted with an excess of sodium acetylide (5 equiv) in tetrahydrofuran under reflux for 2 h, to give the coupled-isocyanide product $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_2\{\mu-(\eta^5\text{-C}_5\text{H}_4)(\text{xylNC})(\text{xylC})(\mu\text{-CCH})\}]$ (**9**) in high yields (84%) (Scheme 4a). The formation of this compound was initiated by the deprotonation of one cyclopentadienyl ligand by reaction of **1** with acetylide, which acted as a base. This was followed by C–C and C–N coupling between the deprotonated Cp and the two isocyanide groups, generating a bridging aminocarbyne ligand. An additional, relevant feature of the reaction of formation of **9** was the substitution of acetylide for one thiolate group. However, the desired isocyanide–acetylide coupling reaction was not observed. Nevertheless, this result clearly shows that the bridging alkylidyne ligand in the μ -aminocarbyne transient complex has the expected labilizing, trans effect toward one SMe group. Surprisingly, no reaction was observed when complex **1** was heated with an excess of sodium acetylide (5 equiv) in the presence of xylNC (5 equiv) (Scheme 4b). In particular, no trace of a complex showing isocyanide–acetylide coupling was detected in the ^1H and ^{13}C NMR spectra of solutions of the crude product. This behavior contrasts unaccountably with that noted for previous reactions of **1** with hydroxides in the presence of excess isocyanide, which give μ -aminocarbyne (amino-oxycarbene) compounds in high yields.⁵

The structure of compound **9** was confirmed through a single-crystal X-ray diffraction study (Figure 3). The molecule of **9** contains an $\text{Mo}_2(\mu\text{-SMe})_2\text{Cp}$ moiety, stabilized by bridging $(\eta^5\text{-C}_5\text{H}_4)(\text{xylNC})(\text{xylC})$ alkylidyne and acetylide ligands. The $(\text{C}_5\text{H}_4)(\text{xylNC})(\text{xylC})$ alkylidyne ligand arises from condensation of a Cp and two xylNC ligands. Thus, the structure of **9** strongly resembles those of the related bridging aminocarbyne compound $[\text{Mo}_2\text{Cp}(\mu\text{-SMe})_3\{\mu-(\eta^5\text{-C}_5\text{H}_4)(\text{xylNC})(\text{xylC})\}]$ (**5**) and μ -aminocarbyne (μ -amino-oxycarbene) derivatives $[\text{Mo}_2\text{Cp}(\mu\text{-SMe})_2\{\mu-(\eta^5\text{-C}_5\text{H}_4)(\text{xylNC})(\text{xylC})\}(\mu\text{-CCNRR}')]]$ that we have described previously.⁵ The three-electron-donor acetylide in **9** σ -bonds terminally to Mo2 and π -bonds unsymmetrically via its C3–C4 triple bond to Mo1. Valuable back-donation from Mo2 is responsible for the shortening of the Mo2–C3 to 2.096(7) Å and the lengthening of the C3–C4 bond to 1.176(9) Å. In **9**, the coordination of the sp-hybridized C4 carbon atom

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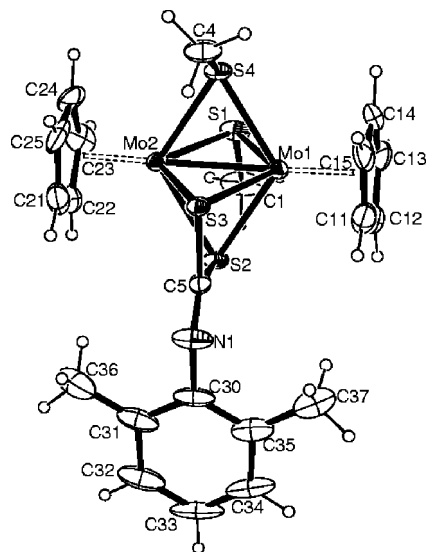


Figure 2. Molecular structure of **8a**. H atoms are omitted for clarity. Selected distances (Å) and angles (deg): Mo1–Mo2 = 2.5897(6), Mo1–S1 = 2.4400(17), Mo1–S2 = 2.465(3), Mo1–S3 = 2.4524(15), Mo1–S4 = 2.433(3), Mo2–S1 = 2.4422(17), Mo2–S2 = 2.466(2), Mo2–S3 = 2.4662(15), Mo2–S4 = 2.433(3), C5–S2 = 1.786(7), C5–S3 = 1.770(7), C5–N1 = 1.262(8), N1–C30 = 1.440(9); Mo1–S2–C5 = 88.3(2), Mo2–S2–C5 = 88.5(2), Mo1–S3–C5 = 89.1(2), Mo2–S3–C5 = 89.2(2), S2–C5–S3 = 100.9(3), S2–C5–N1 = 132.6(5), S3–C5–N1 = 126.5(5), C5–N1–C30 = 122.3(6), Mo1–S1–Mo2 = 64.07(4), Mo1–S2–Mo2 = 63.36(6), Mo1–S3–Mo2 = 63.69(4), Mo1–S4–Mo2 = 64.31(7).

deviates notably from linearity and the Mo2–C3–C4 angle (151.2(5)°) is somewhat outside of the range (158–162°)²² expected for the $M_2(\mu-\eta^1:\eta^2\text{-CCR})$ moiety.¹⁶ Lastly, the *S*-methyl groups are syn to the Mo₂S₂ plane and enfold the CCH ligand.

The spectroscopic data in solution for compound **9** are essentially consistent with its solid-state structure (see the Experimental Section). The results are in agreement with the coupling of one cyclopentadienyl ring via one of its carbon atoms with an adjacent coordinated isocyanide. The ¹H NMR pattern shows a singlet of relative intensity 1 at 4.78 ppm, consistent with an acetylide hydrogen atom in **9**. Moreover, a resonance characteristic of the Mo-bound ¹³C atom of an μ -alkylidyne moiety appears at low field (δ 362.9), and a signal that could be assigned to an imine-like carbon (C=Nxyl) is detected at 156.0 ppm. Salient characterization features of **9** include ¹H–¹³C HMBC and HMQC experiments, which allow the assignment of resonances detected at 142.5 and 101.8 ppm to C_α and C_β atoms of the Mo–C_α≡C_β–H moiety, respectively.

Reaction of 5 with Basic Nucleophiles. Upon heating the bis(isocyanide) μ -trithiolato complex **1** with sodium acetylide, we have shown in the previous section that any attempt to couple isocyanide and acetylide via this way failed. Instead, compound **1** had been found to readily undergo consecutive couplings of cyclopentadienyl and isocyanides in addition to the substitution of an acetylide for a thiolate group. Thus, we were interested in whether coupled isocyanide–acetylide, isocyanide–sulfide, and isocyanide–halogenoalkyl ligands could be prepared by reaction of compound **5** with various basic nucleophiles, given

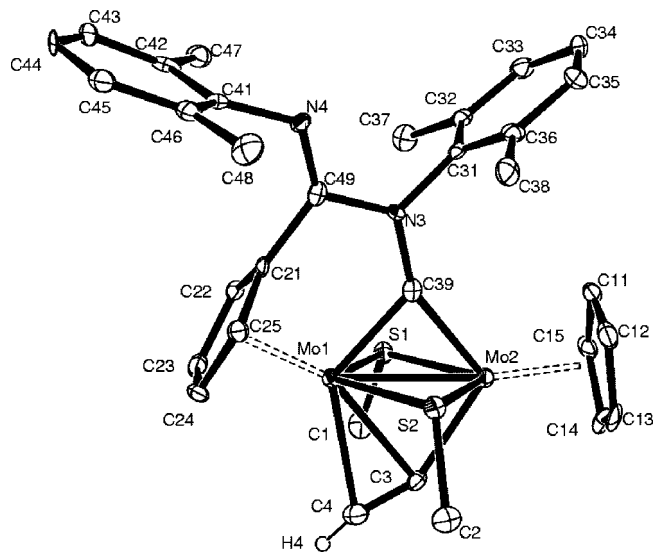
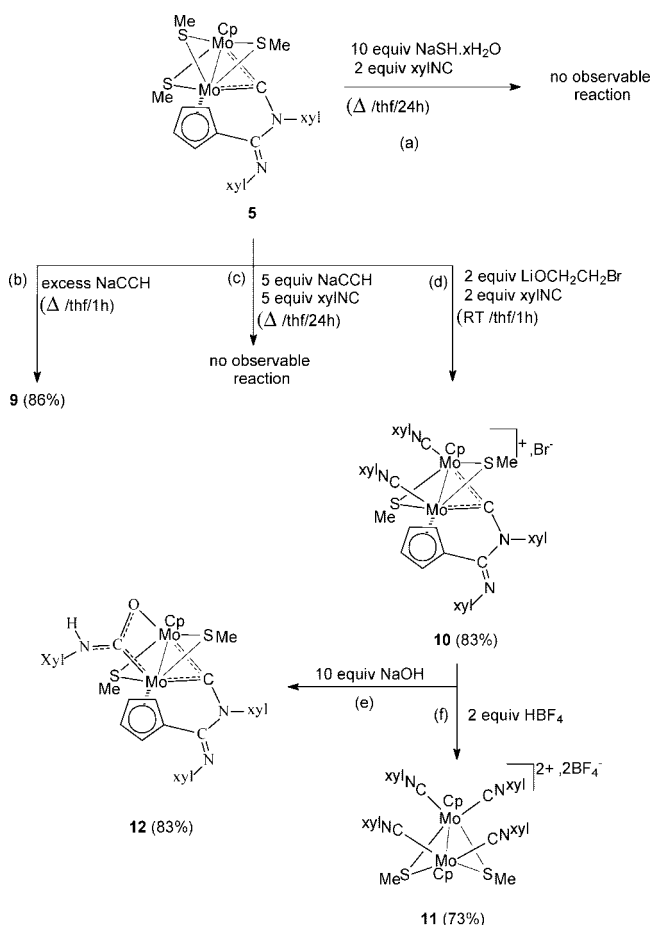


Figure 3. Molecular structure of **9**. Selected distances (Å) and angles (deg): Mo1–Mo2 = 2.6352(8), Mo1–C39 = 1.999(6), Mo2–C39 = 1.997(6), C39–N3 = 1.369(7), N3–C31 = 1.454(7), N3–C49 = 1.410(7), C49–N4 = 1.263(7), N4–C41 = 1.420(7), C49–C21 = 1.513(8), Mo1–C3 = 2.353(6), Mo2–C3 = 2.096(7), C3–C4 = 1.176(9); Mo1–C39–Mo2 = 82.5(2), Mo1–C39–N3 = 124.0(4), Mo2–C39–N3 = 153.2(4), C39–N3–C49 = 118.3(5), C39–N3–C31 = 119.7(5), C31–N3–C49 = 122.0(5), N3–C49–N4 = 120.7(5), N4–C49–C21 = 129.4(5), Mo1–C3–Mo2 = 72.38(18), Mo1–C3–C4 = 78.8(5), Mo1–C4–C3 = 72.7(4), Mo2–C3–C4 = 151.2(5).

that **5** already contains a μ -aminocarbyne group that could favor the desired metal-assisted couplings. Unfortunately, perhaps due to its neutral nature, complex **5** did not react with a large excess of sodium sulfide, in the presence of 2 equiv of xylNC in tetrahydrofuran under reflux for 24 h (Scheme 5a). However, when **5** was heated with a stronger base, e.g. an excess of sodium acetylide, in tetrahydrofuran for 1 h, complex **9** was obtained in high yields (86%) via the substitution of acetylide for one thiolate ligand (Scheme 5b). This last result shows clearly that complex **5** serves as an intermediate in the reaction of formation of **9** when **1** is heated with NaC≡CH (see Scheme 4a). Like the bis(isocyanide) derivative **1**, complex **5** unexpectedly did not react with an excess of sodium acetylide upon heating a tetrahydrofuran solution of the related mixture for 24 h in the presence of 5 equiv of xylNC, the starting compound being totally recovered (Scheme 5c). In contrast with the data for the two precedents (Scheme 5a,c), the neutral compound **5** readily reacted with 2 equiv of lithium bromoethylate, probably due to a higher strength of this basic nucleophile, in the presence of 2 equiv of xylNC to give the new cationic bis(isocyanide) complex $[\text{Mo}_2\text{Cp}(\mu\text{-SMe})_2\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_4)(\text{xylNC})\text{CN}(\text{xyl})\text{C}\}(\text{xylNC})_2]\text{Br}$ (**10**) in high yields (83%) (Scheme 5d). Interestingly, subsequent addition of a large excess of sodium hydrox

Scheme 5



to the formation of the tetrakis(isocyanide) dicationic derivative [Mo₂Cp₂(μ-SMe)₂(xylNC)₄](BF₄)₂ (**11**) in good yields (73%) (Scheme 5f). This rearrangement is unexpected, although it offers some similarities with that observed in the reaction of the dimetallaimido(yl)(amino)carbene complex **7** with HBF₄ (see Scheme 2e); it could involve concomitant proton addition at the Cp-substituted carbon and decoupling between isocyanide and cyclopentadienyl ligands. Therefore, it appears from the data summarized in Scheme 5 that coupling reactions involving isocyanide ligands are only observed when the reagents utilized in this study have appreciable or even high basicities (NaC≡CH, NaOH). Moreover, it should be noted that metal-assisted coupling reactions involving isocyanide do not occur when **5** reacts with a moderate base such as the bromoethylate ion; however, substitution of isocyanides for one thiolate ligand is observed in this case. Finally, the basicity of the hydrosulfide ion is apparently too low to undergo any reaction with **5**.

The characterization of compounds **9** and **12** was made by comparison of their spectroscopic data with those of authentic samples (see above for **9** and ref 5 for **12**). The formulation of the cation of **10** as a bis(isocyanide) μ-aminocarbyne complex was confirmed through a single-crystal X-ray diffraction study of 10·2CH₂Cl₂ (Figure 4). The results are unambiguous, the composition and connectivity being consistent with the structure presented, in which the original Cp-aminocarbyne group is retained and the bridging thiolate located trans to that ligand and has been displaced by two xylNC ligands pendant from the molybdenum atoms. The coordination geometry around each Mo atom is that of a distorted square pyramid, with two sulfur atoms, one isocyanide carbon atom, and one carbyne carbon atom in the basal plane and the centroid of an η⁵-cyclopenta-

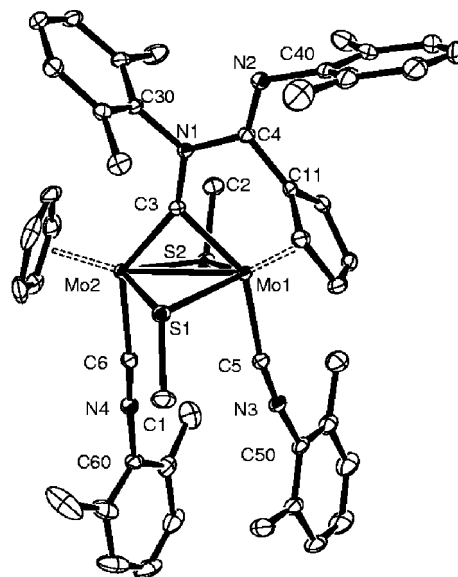


Figure 4. View of the [Mo₂Cp₂(μ-SMe)₂{μ-(η⁵-C₅H₄)-(Nxy)CN(xyl)C}(xylNC)₂]²⁺ cation in the crystal of 10·2CH₂Cl₂, showing 30% probability ellipsoids and a partial atom-labeling scheme. Selected distances (Å) and angles (deg): Mo1–Mo2 = 2.7720(4), Mo2–C3 = 2.032(3), Mo1–C3 = 2.049(3), C3–N1 = 1.363(3), N1–C4 = 1.409(4), N1–C30 = 1.454(3), C4–C11 = 1.499(4), C4–N2 = 1.259(4), N2–C40 = 1.430(4), Mo1–C5 = 2.113(3), C5–N3 = 1.153(4), N3–C50 = 1.397(4), C5–C6 = 2.9872(1), Mo2–C6 = 2.131(3), C6–N4 = 1.151(4), N4–C60 = 1.397(4); Mo1–C3–Mo2 = 85.58(10), Mo2–C3–N1 = 149.7(2), Mo1–C3–N1 = 124.62(19), C3–N1–C30 = 125.2(2), C3–N1–C4 = 116.6(2), C4–N1–C30 = 117.6(2), N1–C4–C11 = 111.3(2), C11–C4–N2 = 126.8(3), N1–C4–N2 = 121.9(3), C4–N2–C40 = 116.1(3), Mo1–C5–N3 = 169.6(3), C5–N3–C50 = 167.1(3), Mo2–C6–N4 = 174.9(3), C6–N4–C60 = 175.4(3).

dienyl ring at the apical position. The S1 and S2 methyl groups adopt an anti orientation relative to the Mo₂S1S3 plane, in contrast with the syn orientation of the related S-methyl groups in **9**. The intermetallic length (2.7720(4) Å) in **10** is consistent with the formulation of a single Mo–Mo bond for a triply bridging thiolato–dimolybdenum(III) complex^{12b} under the EAN formalism. This distance is somewhat longer than those observed in related quadruply bridged thiolato–dimolybdenum(III) derivatives (range 2.584(1)–2.660(1) Å for eight compounds^{5,11}), this reflects the lowering of the number (three) of bridging ligands in **10** with regard to that in the latter complexes. The two Mo–C3 bond distances (2.032(3) and 2.049(3) Å) are close, and although they are somewhat long, they lie between the value of 1.894(5) Å for the formal double bond Mo=C in the vinylidene compound [Mo₂Cp₂(μ-SMe)₃(μ-η¹:η²-C=CHTol)]-(BF₄) and that of 2.068(3) Å for the single Mo–C bond in the acetylide derivative [Mo₂Cp₂(μ-SMe)₃(μ-η¹:η²-C≡CPh)]^{19c}; they thus indicate a nearly symmetrical coordination of the alkylidyne group through Mo–C bonds of order 1.5–2. The presence in the ¹³C{¹H} NMR spectrum of **10** of a low-field resonance at 386.8 ppm, characteristic of a Mo-bound ¹³C atom of an μ-alkylidyne moiety, confirms the above crystallographic observation. The angles at C3 show severe deviations (see the caption for Figure 4) from sp² hybridization but closely agree with those found in **9** (see above) and related μ-alkylidyne derivatives [Mo₂Cp₂(μ-SMe)₂{μ-(η⁵-C₅H₄)(xylNC)CN(xyl)C}X] (X = SMe,¹¹ μ-η¹(O):η²(C,O)-CNRR⁵). The aromatic rings of the xylNC ligands are nearly parallel (dihedral angle 8.11(17)°). Departures from linear coordination at C5 and C6 and more especially at N3 and N4 (C–N–C = 167.1(3) and 175.4(3)°)

(see the caption to Figure 4) ensure that there are no short intramolecular contacts between these rings. As for compound **9**, the spectroscopic data in solution for **10** (see the Experimental Section) are consistent with its solid-state structure. In particular, the presence of a μ -alkylidyne ligand, $(\eta^5\text{-C}_5\text{H}_4(\text{xylN})\text{CN}(\text{xyl})\text{C})$, in the complex can be deduced from the NMR spectra, which closely resemble those of **9**, except in the xylNC region. Thus, typical Mo-bound ^{13}C isocyanide resonances are detected at 180.95 and 176.95 ppm, which obviously are absent in the related spectrum of compound **9**. Other distinctive features of the ^1H NMR spectra of **10** and **9** are the *S*-methyl resonances: these appear in the 2.31–1.44 ppm range as two singlets for **10** and a singlet for **9**. This difference may be ascribed to the orientations of the bridging SMe groups: anti in the bis(isocyanide) derivative **10** and syn in the acetylidyne compound **9**.

Complex **11** has been characterized by spectroscopy (^1H NMR and IR) and elemental analysis (see the Experimental Section). ^1H NMR spectroscopy shows the equivalence of the Cp rings, but not that of the two SMe groups, consistent with a *cis* disposition of the cyclopentadienyl rings relative to the Mo–Mo axis and with a mutually anti orientation of the methyl groups, respectively. The latter observation contrasts with that made for the related tetrakis(nitrile) complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_2(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (**6**), in which the SMe groups adopt a mutually syn orientation.²³ The formulation of **11** as a tetrakis(isocyanide) dicationic derivative was confirmed by a X-ray analysis of crystals of the tetraphenylborate salt $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_2(\text{xylNC})_4](\text{BPh}_4)_2$ (**11'**·0.5OEt₂), obtained as described in the Experimental Section. The cation of **11'** (Figure 5) contains two nearly similar CpMo(xylNC)₂ units linked through SMe bridging groups supported by a rather long Mo–Mo bond of 3.0642(5) Å. This intermetallic length in **11'** is, however, consistent with the formulation of a single Mo–Mo bond for the doubly bridged thiolato–dimolybdenum compounds $[\text{Mo}_2\text{Cp}_2(\mu\text{-SR})_2\text{L}_2](\text{BF}_4)_2$, for which values in the range of 3.008(3)–3.0000(6) Å were found.^{23,24} The dication of **11'** is structurally close to that of $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_2(\text{MeCN})_4](\text{BF}_4)_2$ (**6**),²³ with a similar butterfly Mo₂($\mu\text{-S}$)₂ core. The geometry around each molybdenum atom is based on a four-legged piano stool with a *cis*-C2S2 base. The Mo–N–C–C isocyanide groups are slightly bent: substantial deviations from 180° are noted for Mo–C–N angles (average 171.5°) and C–N–C angles (average 170.9°).

Reaction of 2–4 with Bases. In a previous paper,¹¹ we have shown that the reaction of strong bases (*n*-BuLi, NaOH) with the bis(alkyl isocyanide) complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(t\text{-BuNC})_2](\text{BF}_4)$ (**2**) mainly resulted in dealkylation at one of its isocyanide ligands, together with formation of a small quantity of coupled Cp–isocyanide product in the case of sodium hydroxide. Thus, we were interested in whether coupled ligands could be formed on reacting the bis(*tert*-butyl isocyanide) derivative **2** with bases weaker than *n*-BuLi or NaOH, given that small amounts of coupled Cp–isocyanide compounds were obtained in the reaction of **2** with sodium hydroxide. Unfortunately, treatment of solutions of complex **2** in tetrahydrofuran under reflux with 10 equiv of NaSH·xH₂O gave only the dealkylated complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(t\text{-BuNC})(\text{CN})]$ (**13**) in good yields (69%) (Scheme 6): i.e., the same product that was

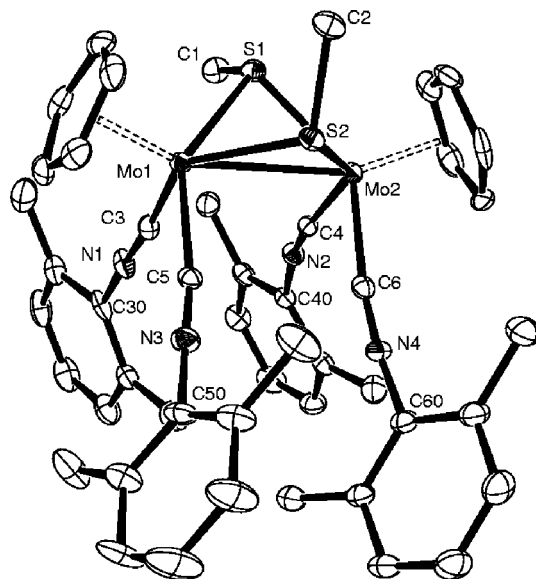
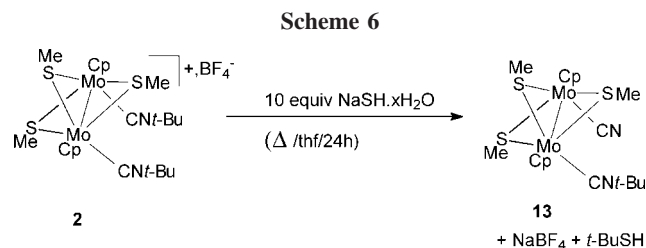


Figure 5. View of the $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_2(\text{xylNC})_4]^+$ cation in crystals of **11'**·0.5OEt₂, showing 30% probability ellipsoids and partial atom-labeling scheme. Selected distances (Å) and angles (deg): Mo1–Mo2 = 3.0642(5), Mo1–C3 = 2.062(5), C3–N1 = 1.158(5), N1–C30 = 1.407(6), Mo1–C5 = 2.079(5), C5–N3 = 1.149(5), N3–C50 = 1.417(6), Mo2–C4 = 2.085(5), C4–N2 = 1.172(5), N2–C40 = 1.403(6), Mo2–C6 = 2.081(5), C6–N4 = 1.158(5), N4–C60 = 1.406(6), Mo1–S1 = 2.4393(12), Mo1–S2 = 2.4573(12), Mo2–S1 = 2.4241(12), Mo2–S2 = 2.4645(12); Mo1–C3–N1 = 172.0(4), C3–N1–C30 = 175.6(4), Mo1–C5–N3 = 169.6(4), C5–N3–C50 = 172.6(5), Mo2–C4–N2 = 172.1(4), C4–N2–C40 = 168.3(5), Mo2–C6–N4 = 172.5(4), C6–N4–C60 = 167.2(5).



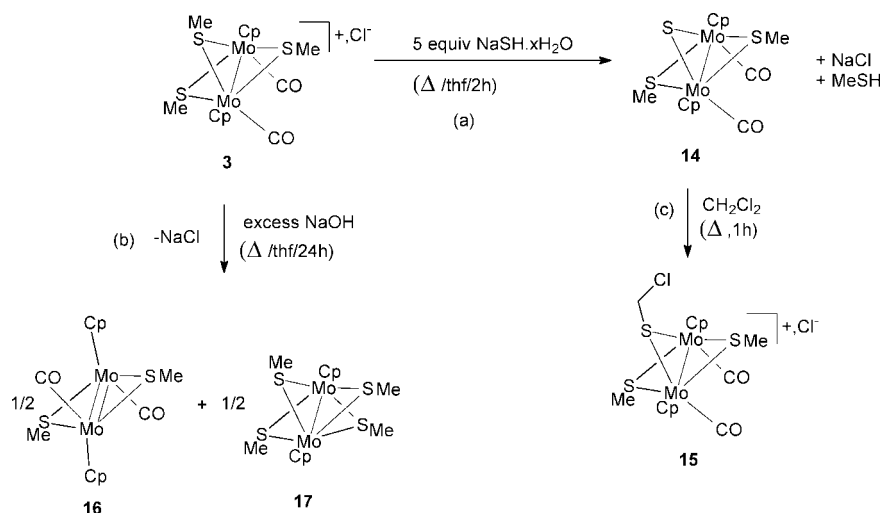
formed previously with strong bases.¹¹ Therefore, whatever the base may be, reaction of a bis(alkyl isocyanide) dinuclear transition-metal complex with bases results mainly in dealkylation of the isocyanide ligand.

As shown in the first part of this work, reductive couplings of isocyanide ligands are mediated by transition metals in reactions of the related complexes with anionic reagents. As carbon monoxide and isocyanide are isolobal, similar types of reactivity are expected for each. Thus, good π -back-donation from thiolato–molybdenum centers, $\{\text{CpMo}(\mu\text{-SMe})_3\text{MoCp}\}$, could have sufficient strength to render the carbonyl carbon atoms electrophilic in the related complexes to be susceptible to nucleophilic attack and then to undergo reductive C–C coupling reactions.^{4c} Accordingly, the cationic bis(carbonyl) complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\text{CO})_2]\text{Cl}$ (**3**) was allowed to react with a large excess of a good reducing agent such as NaSH·xH₂O. Unhappily, no reductive coupling of carbonyl ligands was observed; instead, dealkylation at one sulfur atom occurred with loss of MeSH to give the new neutral bridging sulfido derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_2(\mu\text{-S})(\text{CO})_2]$ (**14**) in high yields (95%) (Scheme 7a). Cleavage of S–CH₃ bonds has been reported previously; it was electrochemically induced in dimo-

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Scheme 7



lybdenum thiolate/thioether- and bis(thioether)- bridged complexes, $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})(\mu\text{-SMe}_2)(\text{CO})(\text{CN})]$ and $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe}_2)_2(\text{CO})(\text{CN})]$, by increasing the electron density on the Mo_2S_2 core to give the anionic derivatives $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe}_2)_2(\text{CO})(\text{CN})]^-$.²⁵ Similar S–C(alkyl) bond cleavage was also observed in the bis(μ -thiolate) μ -sulfido cationic complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-S}_2\text{CH}_2)(\mu\text{-SCMe}_3)(\mu\text{-S})]^+$ by reaction with bromide salts, to afford the bis(μ -sulfido) μ -sulfido compound $[\text{Mo}_2\text{Cp}_2(\mu\text{-S}_2\text{CH}_2)(\mu\text{-S})_2]$ and Me_3CBr .²⁶ The reaction was proposed to proceed via either the dissociation of the carbenium ion, whose stability is well-known,²⁷ or a dissociative mechanism involving the reversible elimination of isobutene and formation of a μ -hydrogenosulfide transient complex, which in turn was deprotonated by Br^- , and finally addition of the resulting HBr to the olefin would give the final products.²⁶ In light of these observations, we suggest that the driving force of the demethylation reaction of a thiolate group in **3** could be the nature of the reactant, associated with the stability of the thiol product (MeSH). Further reaction of the bis(carbonyl) complex **3** with a good basic nucleophile such as hydroxide anion gave neither reductive coupling of the carbonyl ligand nor dealkylated products; instead, a mixture of the two already known complexes $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_2(\text{CO})_2]$ ²⁸ (**16**) and $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_4]$ ²⁹ (**17**) was obtained (Scheme 7b). These two compounds were characterized by comparing their spectroscopic data with those of authentic samples.

The first attempts to crystallize the bridging sulfido complex **14**, carried out at room temperature from dichloromethane solutions of **14**, failed. Instead, crystals of the complex **15** were isolated, in which ¹H NMR spectroscopy indicated the presence of a SCH_2X ligand. This was confirmed after an X-ray analysis, whose results are consistent with a structure based on a $\{\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_2(\mu\text{-SCH}_2\text{Cl})^+\}$ core bridged by a chloromethane thiolate ligand (see below). In order to find a convenient method for introducing such a functionalized organic

chain into the dimolybdenum framework, we decided to heat the μ -sulfido derivative **14** in dichloromethane at reflux. Within 1 h, the resonances (¹H NMR) associated with this compound disappeared, and the single product that resulted from the reaction was the monocationic dimer **15** with the SCH_2Cl resonance at ca. 4.6 ppm (see Scheme 7b). The alkylation of sulfido ligands by organic halides has been observed previously for related permethylcyclopentadienyl dimolybdenum complexes.³⁰ A priori, a higher electron density in the $\{\text{Mo}_2\text{S}_n\}$ ($n = 1, 2$) core would enhance the nucleophilicity of sulfido ligands, as a result of the electron-releasing C_5Me_5 group. The reactions involving the molybdenum(III) carbonyl complexes $[\text{Mo}_2\text{Cp}'_2(\mu\text{-SMe})_2(\mu\text{-S})(\text{CO})_2]$ ($\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$,^{30c,d} $\eta^5\text{-C}_5\text{H}_5$ (this work)) illustrate this trend. Thus, alkylation of the sulfido bridge in the pentamethylcyclopentadienyl complex is achieved at room temperature,^{30c,d} while in the related cyclopentadienyl derivative it requires heating. It is known that the presence of carbonyl ligands in bimetallic compounds tends to remove the electronic density from the metal, which by transmission reduces the nucleophilic character of the sulfido ligand in carbonyl derivatives compared to that in non-carbonyl complexes. In spite of all this, the displacement of a chloride from dichloromethane is similarly observed in both reactions with sulfido ligands in the dicarbonyl derivative **14** and the non-carbonyl complex $[\text{Mo}_2\text{Cp}_2^*(\mu\text{-S}_2\text{CH}_2)(\mu\text{-S})_2]$ ^{30b} ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), by heating dichloromethane solutions of these complexes. These results indicate that the lower electron density in the $\{\text{Mo}_2\text{S}_n\}$ core, induced by CO ligands in **14**, with respect to that present in the non-carbonyl derivative $[\text{Mo}_2\text{Cp}_2^*(\mu\text{-S}_2\text{CH}_2)(\mu\text{-S})_2]$ is balanced by the lower formal oxidation state of the metal in **14** relative to that in the related noncarbonyl complex: i.e., III and IV, respectively.

The new compound **14** has been characterized by spectroscopy (¹H and ¹³C NMR and IR) and elemental analysis (see the Experimental Section). ¹H and ¹³C NMR spectra of **14** show the equivalence of the Cp rings and SMe groups, which implies that this complex is a *cis,syn* isomer. Crystals of $\mathbf{14} \cdot 0.5(\text{tolu-}$

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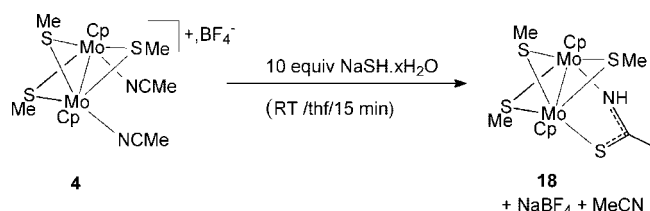
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Scheme 8



temperature with a large excess of $\text{NaSH} \cdot x\text{H}_2\text{O}$ (10 equiv) readily led to the formation of the thio-amidato derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\text{MeCSNH})]$ (**18**) as the major product (Scheme 8). As all attempts to obtain crystals of **18** suitable for X-ray analysis failed, the formulation of this complex was deduced from the IR and NMR data. The ^1H NMR spectrum displays two resonances for the cyclopentadienyl groups and four peaks in the SMe and MeCN regions, indicating that the $\{\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3\}$ core is retained in **18**, that one MeCN is lost relative to **4**, and that the fourth bridge is unsymmetric (see the Experimental Section). In addition, a resonance of relative intensity 1 is detected at δ 4.80, which can be assigned to the NH group of a thio-amidato ligand. This assignment is confirmed by a typical broad band in the IR spectrum of **18** at 3094 cm^{-1} attributable to $\nu(\text{NH})$ of the amine group. The absence in this IR spectrum of a broad band between 1200 and 900 cm^{-1} , expected for a $\nu(\text{BF})$ of the tetrafluoroborate ion, indicates clearly that **18** does not contain this counterion and is therefore neutral. Formation of **18** could involve, in the initial step, the replacement of the two nitrile ligands by one hydrosulfido group to give the neutral intermediate $[\text{Mo}_2\text{Cp}_2(\mu\text{-SH})(\mu\text{-SMe})_3]$. This further reacts with free nitrile to undergo 1,2-addition of the SH group in the tetrakis(μ -thiolate) species to the $\text{C}\equiv\text{N}$ bond in nitrile; subsequent internal rearrangement finally gives **18**. This pathway is supported by the well-established tendency for nitriles to undergo 1,2-addition reactions.^{20c} However, a mechanism similar to that proposed for the formation of the related amidato-molybdenum complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\mu\text{-MeCONH})]$ ³⁴ cannot be ruled out. It would involve a direct attack of the nucleophile SH^- at the carbon atom of a nitrile group, followed by a tautomerization reaction affording the thio-amidato complex **18**.

Concluding Remarks

Because of its reductant and basic nucleophile characters, the hydrosulfide anion (HS^-) reacts with the bis(xylyl isocyanide) complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\text{xyINC})_2](\text{BF}_4)$ (**1**) to give quantitatively the reductive coupled isocyanide derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3\{\mu\text{-}\eta^1(\text{C})\text{:}\eta^1(\text{C})\text{-C}(\text{NHxy})\text{C}(\text{Nxy})\}]]$ (**7**). The presence of electron-releasing ligands in **1**, such as thiolates, could have promoted this reductive coupling of isocyanide ligands attached to adjacent molybdenum atoms. However, when the same reaction is conducted in the presence of a large excess of hydrosulfide, no coupled isocyanide product could be isolated; instead, the dithiocarbonimidate derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\mu\text{-S}_2\text{CNxy})]$ (**8**) is obtained. Thus, the use of a distinct type of basic nucleophile as reagent with **1**, e.g. $\text{NaC}\equiv\text{CH}$, promotes the deprotonation of one cyclopentadienyl ligand, and hence successive couplings between deprotonated cyclopentadienyl and two isocyanide ligands afford compound **9**. Additional reactions of either hydrosulfide or acetylide anions to the coupled ligand adduct **5**, in the absence or presence of isocyanide, give rise to

replacement of a thiolate in **5** by an acetylide group, affording **9**, or to no reaction, respectively. The attempted isocyanide coupling in bis(alkyl isocyanide) derivative **2** by its reaction with hydrosulfide anion proceeds through dealkylation of one *tert*-butyl isocyanide to yield compound **13**. In contrast, when electron-attracting carbonyl groups are bounded to the molybdenum atoms in the tris(μ -thiolate) complex, the dealkylation at the sulfur atoms is favored on reacting **3** with NaSH. This is not obtained when the carbonyl groups are replaced by nitrile as ligands in the tris(μ -thiolate) dimolybdenum derivatives. Indeed, the reaction of the base NaSH (in excess) with the bis(nitrile) complex **4** affords instead the thio-amido complex **18**. Finally, it should be noted that couplings of ligands are observed in the reactions of the tris(μ -thiolate) cationic complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3\text{L}]^+$ with bases, only when L is an aryl isocyanide.

Experimental Section

General Procedures. All reactions were routinely carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Some of the starting materials, $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3\text{L}_2](\text{BF}_4)$ (L = xyINC (**1**),^{12a} *t*-BuNC (**2**),¹¹ CO (**3**),^{12b} MeCN (**4**)^{12c}), $[\text{Mo}_2\text{Cp}(\mu\text{-SMe})_3\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_4)(\text{xyIN})\text{CN}(\text{xy})\text{C}\}]]$ (**5**),⁵ $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_2(\text{MeCN})_4](\text{BF}_4)_2$ (**6**),²³ and $\text{LiOCH}_2\text{CH}_2\text{Br}$,³⁵ were prepared as described previously. $\text{NaSH} \cdot x\text{H}_2\text{O}$ (Aldrich) and other reagents were purchased commercially and used as received. Infrared spectra were recorded on a Nicolet-Nexus FT IR spectrophotometer from KBr pellets. Chemical analyses were performed by the Service de Microanalyse ICSN-CNRS, Gif sur Yvette, France. Yields of all products are relative to the starting dimolybdenum complexes. The NMR spectra (^1H , ^{13}C) were recorded at room temperature in CDCl_3 , CD_2Cl_2 , C_6D_6 , or CD_3CN solutions with a Bruker AMX 400 spectrometer and were referenced to SiMe_4 . ^1H – ^{13}C experiments were carried out on a Bruker DRX 500 spectrometer.

Reaction of $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\text{xyINC})_2](\text{BF}_4)$ (1**) with an Excess of NaSH: Synthesis of $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3\{\mu\text{-}\eta^1\text{:}\eta^1\text{-C}(\text{N-Hxy})\text{C}(\text{Nxy})\}]]$ (**7**) and $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_2\{\mu\text{-S}_2\text{C}(\text{Nxy})\}]]$ (**8**).** Complex **1** (400 mg, 0.492 mmol) and 10 equiv of NaSH (276 mg) were heated in tetrahydrofuran (30 mL) at reflux for 72 h. After filtration the solvent was removed under vacuum and the residue was washed with diethyl ether ($3 \times 15\text{ mL}$), giving complex **7** as a maroon powder (329 mg, 92% yield). Crystals of **7** suitable for X-ray analysis were obtained by crystallization from a cold $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ (1:1) solution.

Similarly, compound **1** (200 mg, 0.246 mmol) was treated with a large excess of NaSH (20 equiv, 276 mg) in refluxing tetrahydrofuran (20 mL) for 72 h. After filtration the solvent was removed under reduced pressure and the residue washed three times with cold pentane ($3 \times 15\text{ mL}$), affording a violet powder of **8** (143 mg, 95% yield). Complex **8** was formed as a mixture of two isomers, **8a** and **8b**, in a 2:3 ratio inseparable by chromatography. Crystals of **8**, suitable for X-ray analysis, were obtained by crystallization at room temperature from a diethyl ether solution.

Data for **7** are as follows. Anal. Calcd for $\text{C}_{31}\text{H}_{38}\text{Mo}_2\text{N}_2\text{S}_3$: C, 51.23; H, 5.27; N, 3.85. Found: C, 52.00; H, 4.90; N, 4.00. IR (KBr, cm^{-1}): $\nu(\text{NH})$ 3431 (m), $\nu(\text{CN})$ 1590 (s). ^1H NMR (CDCl_3): δ 12.07 (s, 1H, NH), 7.07–6.98 (m, 6H, $\text{C}_6\text{H}_3\text{Me}_2$), 5.09 (s, 10H, C_5H_5), 2.19 and 2.09 (s, 6H, CH_3 (xyl)), 2.02, 1.73, and 1.72 (SCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 248.2 (MoC), 147.7 (C_i (xyl)), 131.0 and 130.6 (C_o (xyl)), 127.7, 127.6, and 124.3 ($\text{C}_6\text{H}_3\text{Me}_2$), 89.9 (C_5H_5), 24.5 (SCH₃), 19.7 and 19.2 ($\text{C}_6\text{H}_3\text{Me}_2$), 10.4 and 8.9 (SCH₃).

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Data for **8** are as follows. Anal. Calcd for $C_{21}H_{25}Mo_2NS_4$: C, 41.24; H, 4.12; N, 2.29. Found: C, 42.18; H, 4.23; N, 2.03. IR (KBr, cm^{-1}): $\nu(CN)$ 1624 (m). 1H NMR ($CDCl_3$): **8a**, δ 7.05–6.95 (m, 3H, $C_6H_3Me_2$), 5.51 (s, 10H, C_5H_5), 2.07 (s, 6H, $CH_3(xyl)$), 1.62 (s, 6H, SCH_3); **8b**, δ 6.90–6.81 (m, 3H, $C_6H_3Me_2$), 5.50 (s, 10H, C_5H_5), 2.06 (s, 6H, $CH_3(xyl)$), 1.70 and 1.66 (s, 3H, SCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): **8a**, δ 171.05 (S_2CN), 143.8 ($C_i(xyl)$), 135.2 ($C_p(xyl)$), 127.9 and 123.45 ($C_6H_3Me_2$), 91.45 (C_5H_5), 25.4 (SCH_3), 18.65 ($C_6H_3Me_2$); **8b**, δ 171.2 (S_2CN), 143.7 ($C_i(xyl)$), 135.0 ($C_p(xyl)$), 127.8 and 127.4 ($C_6H_3Me_2$), 91.5 (C_5H_5), 25.2 (SCH_3), 18.25 ($CH_3(xyl)$), 10.95 (SCH_3).

Reaction of $[Mo_2Cp_2(\mu-SMe)_3(xylNC)_2](BF_4)$ (1**) with NaSH in the Presence of Excess $xylNC$: Formation of **7**.** Complex **1** (200 mg, 0.246 mmol) was treated with an excess of NaSH (138 mg, 10 equiv) in the presence of 3 equiv of $xylNC$ (97 mg) in refluxing tetrahydrofuran (30 mL) for 72 h. After filtration, the solvent was removed and the residue analyzed in $CDCl_3$ by 1H NMR spectroscopy, which indicated the presence of only one NMR-detectable organometallic product, **7**. Then, the crude product was washed three times with diethyl ether (3×15 mL), affording **7** as a maroon powder (130 mg, 73% yield).

Reaction of $[Mo_2Cp_2(\mu-SMe)_3\{\mu-\eta^1-C(NHxyl)C(Nxyl)\}]$ (7**) with an Excess of NaSH: Formation of **8**.** To a tetrahydrofuran solution (20 mL) of **7** (100 mg, 0.163 mmol) was added 10 equiv of NaSH (77 mg), and the mixture was heated under reflux for 24 h. The solution was then filtered. Removal of the solvent from the filtrate under vacuum yielded a dark residue, which was washed with pentane (3×15 mL) to give compound **8** as a dark violet powder (67.3 mg, 80% yield).

Reaction of $[Mo_2Cp_2(\mu-SMe)_3\{\mu-\eta^1-C(NHxyl)C(Nxyl)\}]$ (7**) with an Excess of $HBf_4 \cdot OEt_2$: Formation of **1**.** To a cold solution of **7** (100 mg, 0.137 mmol) in dichloromethane (5 mL) was added a drop of $HBf_4 \cdot OEt_2$. The mixture was stirred for 20 min at $-40^\circ C$, and the solution turned from maroon to gray. A powder was then precipitated from the solution by addition of diethyl ether (20 mL), collected by filtration, and washed with diethyl ether (2×15 mL), affording compound **1** as a light brown powder (95.7 mg, 86% yield). Complex **1** was identified as the bis(isonitrile) $[Mo_2Cp_2(\mu-SMe)_3(xylNC)_2](BF_4)$ by comparison of its 1H NMR spectra with that of an authentic sample.^{12a}

When the reaction was conducted at room temperature, the bis(isonitrile) derivative **1** was formed in lower yields, together with the byproduct **19** in the molar ratio 1.6:1 according to the 1H NMR analysis of an acetonitrile-*d* solution of the mixture. Attempts to separate cleanly the two complexes by chromatography failed. However, on the basis of 1H NMR spectra of the mixture the yields of **1** were estimated at 50%. The other compound, **19**, was characterized by its 1H NMR pattern (δ 6.53 (s, 10H), 2.40 (s br, 6H), and 2.31 (s, 6H)), but no more effort to identify that complex has been made.

Reaction of $[Mo_2Cp_2(\mu-SMe)_3(xylNC)_2](BF_4)$ (1**) with an Excess of $NaC\equiv CH$: Synthesis of $[Mo_2Cp(\mu-SMe)_2\{\mu-(\eta^5-C_5H_4)(xylN)CN(xyl)C\}(\mu-CCH)]$ (**9**).** To a tetrahydrofuran solution (30 mL) of $[Mo_2Cp_2(\mu-SMe)_3(xylNC)_2](BF_4)$ (**1**; 150 mg, 0.185 mmol) was added a large excess of sodium acetylide (300 μL), and the mixture was heated under reflux for ca. 3 h. The solution was then filtered to remove $Na(BF_4)$, and the residue was washed with diethyl ether (3×15 mL), affording an orange powder of **9** (109 mg, 84% yield). Orange crystals of **9**, suitable for X-ray analysis, were obtained at room temperature by slow evaporation from a $CH_2Cl_2-Et_2O$ (1:1) solution. Anal. Calcd for $C_{32}H_{34}Mo_2N_2S_2$: C, 54.70; H, 4.88; N, 3.98. Found: C, 55.25; H, 5.05; N, 3.14. IR (KBr, cm^{-1}): $\nu(CN)$ 1650 (s). 1H NMR ($CDCl_3$): δ 7.26–6.82 (m, 6H, $C_6H_3Me_2$), 5.86 and 5.10 (m, 2H, C_5H_4), 5.11 (s, 5H, C_5H_5), 4.78 (s, 1H, $C\equiv CH$), 2.23 and 2.17 (s, 6H, $CH_3(xyl)$), 1.44 (s, 6H, SCH_3). $^{13}C\{^1H\}$ ($CDCl_3$): δ 362.9 (Mo_2C), 156.0 ($C\equiv N$), 142.5 ($C\equiv CMO$), 146.85, 142.8, 135.5, 128.55, 128.4,

127.9, 127.5, and 123.0 ($C_6H_3Me_2$), 109.6 and 99.8 (C_5H_4), 101.8 ($HC\equiv CMO$), 91.75 (C_5H_5), 90.0 and 84.1 (C_5H_4), 19.1 and 18.4 ($C_6H_5Me_2$), 10.3 (SCH_3).

Reaction of $[Mo_2Cp_2(\mu-SMe)_3(xylNC)_2](BF_4)$ (1**) with an Excess of $NaC\equiv CH$ in the Presence of Excess $xylNC$.** Complex **1** (100 mg, 0.123 mmol) was treated with 5 equiv of sodium acetylide (29.6 mg) in the presence of excess $xylNC$ (81 mg, 5 equiv) in refluxing tetrahydrofuran (20 mL) for 72 h. The solution was then filtered, and the solvent was removed from the filtrate. The resulting residue was analyzed by 1H NMR spectroscopy, which indicated the presence of only one NMR detectable organometallic starting compound, **1**.

Reaction of $[Mo_2Cp(\mu-SMe)_3\{\mu-(\eta^5-C_5H_4)(xylN)CN(xyl)C\}]$ (5**) with an Excess of $NaC\equiv CH$: Formation of **9**.** Complex **5** (120 mg, 0.165 mmol) was treated with a large excess of sodium acetylide (40 mg, 0.833 mmol) in refluxing tetrahydrofuran (20 mL) for 1 h. After filtration, the solvent was removed and the residue washed three times with diethyl ether (3×15 mL), affording an orange powder of **9** (100 mg, 86% yield).

Reaction of $[Mo_2Cp(\mu-SMe)_3\{\mu-(\eta^5-C_5H_4)(xylN)CN(xyl)C\}]$ (5**) with an Excess of $NaC\equiv CH$ in the Presence of Excess $xylNC$.** Complex **5** (100 mg, 0.138 mmol) was treated with 5 equiv of sodium acetylide (33 mg) in the presence of 5 equiv of $xylNC$ (90.5 mg) in refluxing tetrahydrofuran (20 mL) for 24 h. After filtration, the solvent was removed under pressure and the resulting solid analyzed by 1H NMR spectroscopy, which showed the presence of only the starting material **5** in acetone-*d* solution.

Reaction of $[Mo_2Cp(\mu-SMe)_3\{\mu-(\eta^5-C_5H_4)(xylN)CN(xyl)C\}]$ (5**) with Lithium Bromoethanolate in the Presence of $xylNC$: Synthesis of $[Mo_2Cp(\mu-SMe)_2\{\mu-(\eta^5-C_5H_4)C(Nxyl)N(xyl)C\}-(xylNC)_2]Br$ (**10**).** To a tetrahydrofuran solution (20 mL) of **5** (200 mg, 0.276 mmol) were added 2 equiv of $LiOCH_2CH_2Br$ (40 μL) and 2 equiv of $xylNC$ (72 mg), and the mixture was stirred at room temperature for 1 h. After evaporation of the solvent, the product was extracted from the residue with dichloromethane (10 mL). Then, diethyl ether (30 mL) was added to precipitate **10** as a powder (233.5 mg, 83% yield).

In order to facilitate the formation of crystals of **10**⁺, we first synthesized the tetraphenylborate complex $[Mo_2Cp_2(\mu-SMe)_2\{\mu-(\eta^5-C_5H_4)C(Nxyl)N(xyl)C\}(xylNC)_2](BPh_4)$ (**10'**) via a metathetical reaction involving compound **10** as starting material. The formulation of **10'** was proved by 1H NMR spectroscopy. The first attempt to crystallize **10'** from a CH_2Cl_2 solution layered with diethyl ether failed; instead, crystals of the tetrakis(isonitrile) derivative $[Mo_2Cp_2(\mu-SMe)_2(xylNC)_4](BPh_4)_2$ (**11'**) were formed. Finally, in a second attempt we got crystals of **10**·2 CH_2Cl_2 , suitable for X-ray analysis, by crystallization at room temperature from a CH_2Cl_2 solution of **10** layered with diethyl ether. Data for **10** are as follows. Anal. Calcd for $C_{48}H_{51}BrMo_2N_4S_2$: C, 56.53; H, 5.04; N, 5.49. Found: C, 56.75; H, 5.14; N, 4.65. IR (KBr, cm^{-1}): $\nu(C\equiv N)$ 2113 (s) and 2095 (s), $\nu(C=N)$ 1666 (s). 1H NMR (CD_2Cl_2): δ 7.35–6.81 (m, 12H, $C_6H_3Me_2$), 5.64, 5.59, 5.47, and 5.25 (m, 1H, C_5H_4), 5.12 (s, 5H, C_5H_5), 2.56 and 2.23 (s, 3H, $C_6H_5Me_2$), 2.31 (s, 3H, SCH_3), 2.21 (s, 6H, $C_6H_3Me_2$), 2.15 (s, 3H, SCH_3), 2.13 (s, 6H, $C_6H_3Me_2$), 2.10 (s, 6H, $C_6H_3Me_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 386.8 ($Mo_2(\mu-C)$), 180.95 and 176.95 ($MoCNxyl$), 155.45 ($xylN=C$), 145.2, 142.4, 136.35, 135.65, 135.5, 135.1, 130.55, 130.35, 129.75, 129.5, 129.35, 128.65, 128.45, 128.4, 126.7, and 124.2 ($C_6H_3Me_2$), 109.75, 99.0, and 97.0 (C_5H_4), 92.2 (C_5H_5), 87.2 and 83.8 (C_5H_4), 30.3, 29.25, 19.80, and 19.10 ($CH_3(xyl)$), 19.25 (SCH_3).

Reaction of $[Mo_2Cp(\mu-SMe)_3\{\mu-(\eta^5-C_5H_4)(xylN)CN(xyl)C\}]$ (5**) with NaSH in the Presence of Excess $xylNC$.** A mixture of **5** (120 mg, 0.165 mmol) and NaSH (93 mg, 10 equiv) was heated in the presence of 2 equiv of $xylNC$ (43.4 mg) in tetrahydrofuran (20 mL) at reflux for 24 h. After filtration the solvent was removed under reduced pressure and the residue analyzed by 1H NMR

Table 1. Crystallographic Data for Complexes 7, 8a, 9, 10·2CH₂Cl₂, 11'·0.5OEt₂, 14·0.5(toluene), and 15·H₂O

	7	8a	9	10·2CH ₂ Cl ₂	11'·0.5OEt ₂	14·0.5(toluene)	15·H ₂ O
formula	C ₃₁ H ₃₈ Mo ₂ N ₂ S ₃	C ₂₁ H ₂₅ Mo ₂ NS ₄	C ₃₂ H ₃₄ Mo ₂ N ₂ S ₂	C ₃₀ H ₃₅ BrCl ₄ Mo ₂ N ₄ S ₂	C ₃₈ H ₃₇ Br ₂ Mo ₂ N ₄ O _{0.5} S ₂	C ₃₅ H ₄₀ Mo ₄ O ₄ S ₆	C ₁₅ H ₂₀ Cl ₂ Mo ₂ O ₃ S ₃
<i>M_r</i>	726.69	611.54	702.61	1189.69	1616.42	550.39	607.27
cryst size/mm	0.20 × 0.06 × 0.05	0.17 × 0.10 × 0.06	0.17 × 0.05 × 0.03	0.40 × 0.40 × 0.12	0.20 × 0.11 × 0.08	0.27 × 0.08 × 0.07	0.25 × 0.10 × 0.10
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	8.3452(5)	9.8972(8)	8.4425(6)	15.2743(6)	15.6411(6)	16.0830(9)	10.8247(7)
<i>b</i> /Å	22.6264(13)	12.5566(7)	11.7806(14)	18.2217(6)	15.8771(4)	10.1516(5)	12.9834(5)
<i>c</i> /Å	16.2627(10)	9.3093(7)	14.4002(16)	19.7904(8)	17.5708(5)	13.2453(8)	16.0843(10)
α /deg	90	90	100.234(10)	90	93.078(2)	90	90
β /deg	98.299(6)	90.261(7)	95.882(7)	107.814(4)	95.249(3)	110.900(7)	113.652(7)
γ /deg	90	90	90.150(7)	90	93.064(3)	90	90
<i>V</i> /Å ³	3038.6(3)	1156.90(14)	1401.7(2)	5244.0(3)	4331.4(2)	2020.25(19)	2070.6(2)
<i>Z</i>	4	2	2	4	2	2	4
<i>D_c</i> /Mg m ⁻³	1.589	1.756	1.665	1.507	1.239	1.810	1.948
<i>T</i> /K	170(2)	170(2)	170(2)	170(2)	170(2)	170(2)	170(2)
μ /mm ⁻¹	1.055	1.453	1.069	1.561	0.386	1.559	1.784
range of θ (deg)	3.39–24.11	3.00–25.35	3.33–22.98	2.64–30.51	2.62–23.82	2.60–25.02	3.13–26.37
<i>N_{meas}</i> ^a	14471	7108	6813	100 367	24 348	12 117	17 477
<i>N_{unique}</i> ^a / <i>N_{params}</i>	4368/354	3616/257	3136/352	15 988/590	11 345/984	3270/229	4226/231
<i>R_{int}</i>	0.0676	0.0362	0.0413	0.0397	0.0339	0.0269	0.0416
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>), <i>N_{obs}</i> ^a)	0.0431, 3257	0.0317, 2467	0.0352, 2346	0.0365, 10 873	0.0379, 7516	0.0451, 2701	0.0353, 3264
<i>R</i> 1 (all data)	0.0654	0.0589	0.0566	0.0757	0.0670	0.0564	0.0497
w <i>R</i> 2 (all data)	0.1037	0.0616	0.0752	0.1091	0.1091	0.1214	0.0842
goodness of fit on <i>F</i> ²	0.997	0.862	0.991	1.151	0.929	1.191	0.993
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ /e Å ⁻³	0.698, –0.454	0.469, –0.531	0.563, –0.444	1.856, –0.963	0.884, –0.261	1.974, –0.783	1.123, –0.606

^a Legend: *N_{meas}* = total number of intensity measurements; *N_{unique}* = number of intensity measurements after averaging according to point symmetry; *N_{obs}* = number of these with intensities *I* > 2 σ (*I*).

spectroscopy, which indicated the presence of only the starting complex **5** in acetone-*d* solution.

Reaction of [Mo₂Cp(μ-SMe)₂(μ-(η⁵-C₅H₅)C(Nxyl)N(xyl)C)-(xylNC)₂]Br (10**) with NaOH: Formation of [Mo₂Cp(μ-SMe)₂(μ-(η⁵-C₅H₅)C(Nxyl)N(xyl)C)-(μ-OCNHxyl)] (**12**).** Complex **10** (200 mg, 0.196 mmol) was treated with a large excess of NaOH (201 mg) in refluxing tetrahydrofuran (20 mL) for 24 h. After filtration the solvent was removed under reduced pressure and the residue washed three times with diethyl ether (3 × 15 mL), affording an orange powder of the already known compound **12**⁵ (132 mg, 83% yield).

Reaction of [Mo₂Cp(μ-SMe)₂(μ-(η⁵-C₅H₅)C(Nxyl)N(xyl)C)-(xylNC)₂]Br (10**) with HBF₄·OEt₂. Synthesis of the Tetrakis(isonitrile) Complex [Mo₂Cp₂(μ-SMe)₂(xylNC)₄](BF₄)₂ (**11**).** A solution of **10** (233 mg, 0.228 mmol) in dichloromethane (20 mL) was stirred in the presence of 2 equiv of HBF₄·OEt₂ (100 μL) for 15 min at room temperature. The solvent was then removed under vacuum, and the crude products were analyzed in CD₃CN by ¹H NMR spectroscopy. Compound **11** and an uncharacterized byproduct were respectively formed in about a 2.75:1 ratio. On the basis of ¹H NMR spectra of the mixture the yields of **11** were estimated at 73%. Compound **11** was characterized by comparison of its ¹H NMR data with those of an authentic sample, which was synthesized via a more improved way, as described below.

The complex [Mo₂Cp₂(μ-SMe)₂(MeCN)₄](BF₄)₂ (**6**)²³ (100 mg, 0.132 mmol) was treated with 4 equiv of xylNC (148 μL) in refluxing dichloromethane (50 mL) for 6 h. The volume of the solution was then reduced under vacuum, and diethyl ether (20 mL) was added to precipitate a red-brown powder that was washed with diethyl ether (4 × 15 mL). After drying, **11** was obtained in good yields (119.2 mg, 81%) as an analytically pure solid.

Crystals of the tetraphenylborate salt [Mo₂Cp₂(μ-SMe)₂(xylNC)₄](BPh₄)₂ (**11'**·OEt₂), suitable for X-ray analysis, were obtained as described above. Data for **11** are as follows. Anal. Calcd for C₄₈H₅₂B₂F₈Mo₂N₄S₂: C, 51.72; H, 4.70; N, 5.02. Found: C, 51.15; H, 4.98; N, 4.51. IR (CH₂Cl₂, cm⁻¹): ν(CN) 2097(s). ¹H NMR (CD₃CN): δ 7.17–6.76 (m, 12H, C₆H₃Me₂), 5.75 (s, 10H, C₅H₅), 2.85 (s, 3H, SCH₃), 2.25 and 2.20 (s, 12H, C₆H₃Me₂), 1.99 (s, 3H, SCH₃).

Reaction of [Mo₂Cp₂(μ-SMe)₃(*t*-BuNC)₂](BF₄) (2**) with an Excess of NaSH: Formation of [Mo₂Cp₂(μ-SMe)₃(*t*-BuNC)(NC)] (**13**).** A tetrahydrofuran solution (20 mL) of **2** (185 mg, 0.258 mmol) and 10 equiv of NaSH (144.7 mg) were heated under reflux for ca. 72 h. After filtration and evaporation of the solvent, the products were extracted with diethyl ether (3 × 15 mL). The diethyl ether was then removed in vacuo from the pooled extracts. Spectroscopic (¹H NMR) analysis of the residue showed the presence in CDCl₃ of only one NMR detectable organometallic compound, **13**, previously characterized by us.¹¹ After the usual workup, **13** was obtained as a maroon powder (102 mg, 69% yield).

Reaction of [Mo₂Cp₂(μ-SMe)₃(CO)₂]Cl (3**) with an Excess of NaSH: Synthesis of [Mo₂Cp₂(μ-SMe)₂(μ-S)(CO)₂] (**14**).** **Reaction of **14** with CH₂Cl₂: Synthesis of [Mo₂Cp₂(μ-SMe)₂(μ-SCH₂Cl)]Cl (**15**).** A solution of **3** (400 mg, 0.72 mmol) in tetrahydrofuran (20 mL) was stirred in the presence of 5 equiv of NaSH (202 mg) for 2 h at room temperature. After filtration and evaporation of the solvent, the residue was washed three times with diethyl ether (3 × 15 mL), affording compound **14** as a green powder (346.5 mg, 95% yield). Crystals of **14**·0.5(toluene) suitable for X-ray analysis were formed in a cold toluene solution of **14**.

Complex **14** (150 mg, 0.297 mmol) was heated in dichloromethane (20 mL) at reflux for 1 h. The solution turned from light green to green-yellow. Then, the solution was concentrated and 20 mL of diethyl ether was added to give a green-yellow solid. After filtration the residue was washed with OEt₂ (3 × 15 mL), affording a dark yellow powder of **15** (136 mg, 78% yield). **15** was obtained as a mixture of the two inseparable isomers **15a** and

15b (in about an 8:1 ratio) by chromatography. Crystals of **15**·H₂O, suitable for X-ray analysis, were obtained at room temperature by slow evaporation of a CH₂Cl₂–OEt₂ solution of **14**.

Data for **14** are as follows. Anal. Calcd for C₁₄H₁₆Mo₂O₂S₃: C, 33.34; H, 3.20. Found: C, 33.03; H, 3.31. IR (KBr, cm⁻¹): ν(CO) 1946 (s). ¹H NMR (CDCl₃): δ 5.43 (s, 10H, C₅H₅), 2.43 (s, 6H, SCH₃). ¹³C{¹H} NMR (CDCl₃): δ 240.95 (CO), 90.95 (C₅H₅), 28.45 (SCH₃).

Data for **15** are as follows. Anal. Calcd for C₁₅H₁₈Cl₂Mo₂O₂S₃: C, 30.57; H, 3.08. Found: C, 30.76; H, 3.51. ¹H NMR (CD₂Cl₂): **15a** (major isomer), δ 5.99 (s, 10H, C₅H₅), 4.60 (s, 2H, SCH₂Cl), 2.68 and 2.65 (s, 3H, SCH₃); **15b** (minor isomer), δ 6.00 (s, 10H, C₅H₅), 4.69 (s, 2H, SCH₂Cl), 2.67 and 2.63 (s, 3H, SCH₃).

Reaction of [Mo₂Cp₂(μ-SMe)₃(CO)₂]Cl (3**) with an Excess of NaOH: Formation of [Mo₂Cp₂(μ-SMe)₂(CO)₂] (**16**) and [Mo₂Cp₂(μ-SMe)₄] (**17**).** Complex **3** (200 mg, 0.360 mmol) was treated with a large excess of NaOH (201 mg) in refluxing tetrahydrofuran (20 mL) for 24 h. Then NaOH in excess and NaCl were eliminated by filtration, and the solvent was removed under reduced pressure. The resulting residue was washed three times with cold pentane (3 × 15 mL), affording a brown greenish solid. The ¹H NMR spectrum of the resultant powder (176 mg) in CDCl₃ indicated the presence of the two organometallic compounds **16**²⁵ and **17**,²⁶ together with small amounts of the *trans*,*syn*/*anti*-[Mo₂Cp₂(μ-SMe)₂(O)(CO)]³⁶ byproduct, in the molar ratio 1:1:0.12. These three complexes have been identified by comparison of their NMR data with those of pure samples. On the basis of the ¹H NMR spectra of the mixture the yields of *trans*,*syn*/*anti* **16** and **17** were both estimated at about 47%.

Reaction of [Mo₂Cp₂(μ-SMe)₃(MeCN)₂](BF₄) (4**) with an Excess of NaSH: Synthesis of [Mo₂Cp₂(μ-SMe)₃(μ-CH₃CSNH)] (**18**).** A solution of **4** (100 mg, 0.153 mmol) in tetrahydrofuran (20 mL) was stirred in the presence of 5 equiv of NaSH (44 mg) for 15 min at room temperature. After filtration the solvent was removed under vacuum, and the organometallic products were extracted with diethyl ether (3 × 15 mL). The diethyl ether was removed, and the greenish crude product (61 mg) was analyzed in C₆D₆ by ¹H NMR spectroscopy. Compound **18** and one uncharacterized side product were respectively formed in a 4:1 ratio. On the basis of ¹H NMR spectra of the mixture the yield of **18** was estimated at 58%. Attempts to cleanly separate the complexes by chromatography failed, owing to severe decomposition on the column. For this reason, no elemental analysis is available for **18** and, therefore, that compound was only characterized by spectroscopy. Data for **18** are as follows. IR (KBr, cm⁻¹): ν(N–H) 3094 (m, br). ¹H NMR (C₆D₆): 5.27 and 5.21 (s, 5H, C₅H₅), 4.80 (s, 1H, NH), 1.81, 1.72, 1.65, and 1.61 (s, 3H, CCH₃ and SCH₃).

X-ray Structural Determinations. Measurements for compounds **7**–**9**, **10**·2CH₂Cl₂, **11'**·0.5OEt₂, **14**·0.5(toluene), and **15**·H₂O were carried out on a Oxford Diffraction X-Calibur-2 CCD diffractometer equipped with a jet cooler device. Graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) was used in all experiments. The structures were solved and refined by standard procedures.³⁷ H atoms were positioned using stereochemical considerations. For **14**·0.5(toluene), the CH₃ group attached to the toluene ring is distributed over two alternative sites, suggesting 0.50:0.50 disorder. Selected bond lengths and angles are collected in the caption to Figures 1–7. Crystal data and data collection and processing parameters are given in Table 1.

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Supporting Information Available: CIF files giving X-ray crystallographic data for **7**, **8a**, **9**, **10**·2CH₂Cl₂, **11'**·0.5OEt₂, **14**·0.5(toluene), and **15**·H₂O. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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