Formation of New μ-Thioalkylidene and μ-Borohydride Dimolybdenum Complexes from the μ-Alkylidyne Precursor $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}CCH_2Ph)]$

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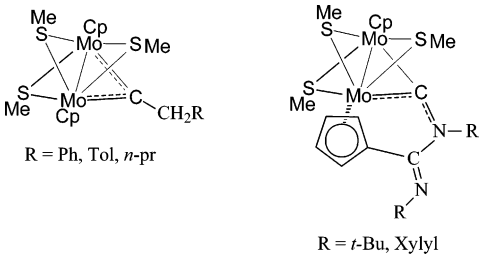
*Summary: The μ-alkylidyne complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}CCH_2Ph)]$ (**1**) reacts with HBF_4 in acetonitrile to give the unstable bis-nitrile species $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}CCH_2Ph)](NCCH_3)_2](BF_4)$ (**2**). Treatment with either borohydride or chloride converts **2** into $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}CCH_2Ph)(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-}BH_4)]$ (**3**) or $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}CCH_2Ph)(\mu\text{-}Cl)]$ (**4**), respectively. Clean evolution of **4** in non-degassed solvent affords the novel μ-thioalkylidene derivative $[Mo_2(O)(Cl)Cp_2(\mu\text{-}SMe)(\mu\text{-}MeSCCH_2Ph)]$(**5**).*

Introduction

Dinuclear (cyclopentadienyl) organometallic molecules incorporating a $\{Mo_2Cp'_2\}$ core ($Cp' = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5Me_5$, $\eta^5\text{-}C_5H_4Me$) exhibit a rich and original reactivity that continues to be explored in view of developing new tools for molecular activation.[1] We have recently reported the synthesis and the X-ray structure of novel tris-thiolato-bridged dimolybdenum derivatives featuring a μ-alkylidyne group (Chart 1).[2]

Their structural data and their reactivity suggest that the alkylidyne group weakens the bonding of the thiolate bridge in *trans* position, and even in some cases it could induce the loss of this bridging group.[2c] In the course of our systematic approach to the activity of sulfur-rich dimolybdenum complexes toward hydrocarbyl substrates we have studied the reactivity of the complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}CCH_2Ph)]$ (**1**) toward various electrophile and nucleophile reagents in order to compare the effect of a μ-alkylidyne group with that of a bridging thiolate on the reactivity of systems having a dimolybdenum core $\{Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}X)\}$ (X = CCH_2Ph or SMe). We wish to report here some aspects of the reactivity of the μ-alkylidyne, bis-acetonitrile species $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}CCH_2Ph)(MeCN)_2]^+$ (**2**) toward $NaBH_4$ and $(Et_4N)Cl$. The formation and the characterization of novel μ-borohydride and μ-thioalkylidene dimolybdenum complexes $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}CCH_2Ph)(\mu\text{-}\kappa\text{:}^1\kappa^1\text{-}BH_4)]$ (**3**) and $[Mo_2(O)(Cl)Cp_2(\mu\text{-}SMe)(\mu\text{-}MeSCCH_2Ph)]$ (**5**) are reported.

Chart 1



Treatment of **1** with 1 equiv of HBF_4-Et_2O in acetonitrile gave a purple solution of $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}CCH_2Ph)(MeCN)_2]^+$ (**2**) (Scheme 1). **2** could be isolated as a purple powder after its precipitation by the addition of diethyl ether, but fast decomposition occurred when the solvent was removed. This prevented any storage of **2** as a powder and any further spectroscopic characterization of the isolated powder. The ^1H NMR spectrum of a sample prepared by the addition of 1 equiv of tetrafluoroboric acid to a solution of **1** in CD_3CN, at 298 K, indicated without any ambiguity that **2** has lost a thiolate bridge and has retained a symmetrical bimetallic core, $\{Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}CCH_2Ph)\}^+$. Indeed, this spectrum exhibits a single resonance at 5.30 ppm for the two cyclopendadienyl ligands (intensity 10) and one peak at 1.82 ppm for two SMe bridges (intensity 6). Characteristic signals of the $CH_2-C_6H_5$ group are detected as a singlet at 4.52 ppm (intensity 2) and a multiplet at 7.17 ppm (intensity 5). In addition, the release of free HSMe is detected: a quadruplet at 1.61 ppm for one proton and a doublet at 1.97 ppm for three protons were unambiguously assigned to free HSMe.[3] The formation an S-protonated intermediate could not be evidenced by low-temperature NMR experiments. We concede that **2** could not be fully characterized; however its spectroscopic data are enough reliable to formulate with assurance this intermediate as a $\{Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}CCH_2Ph)\}^+$ core stabilized by two coordinated acetonitrile molecules. In similar reactional conditions, the loss of the chloro bridge in $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ has been reported to afford the tractable bis(acetonitrile) species $[Mo_2Cp_2(\mu\text{-}SMe)_3(MeCN)_2](BF_4)$.[4] We have also previously shown that a sulfur atom in tris-thiolato-bridged dimolybdenum(III) complexes could be methylated or protonated and that the

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(1) (a) Alvarez, M. A.; García, M. E.; Ramos, A.; Ruiz, M. A. *Organometallics* **2007**, *26*, 1461. (b) Amor, I.; García-Vivó, D.; García, M. E.; Ruiz, M. A.; Sáez, D.; Hamidov, H.; Jeffery, J. C. *Organometallics* **2007**, *26*, 466. (c) Alvarez, C. M.; Alvarez, M. A.; García, M. E.; Ramos, A.; Ruiz, M. A.; Graiff, C.; Tiripicchio, A. *Organometallics* **2007**, *26*, 321. (d) Newell, R.; Ohman, R.; Rakowski Dubois, M. *Organometallics* **2005**, *24*, 4406. (e) Appel, A. M.; DuBois, D. L.; Rakowski Dubois, M. *J. Am. Chem. Soc.* **2005**, *127*, 12717. (f) Le Goff, A.; Le Roy, C.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J. *New J. Chem.* **2007**, *31*, 265. (g) Ojo, W. S.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Organometallics* **2006**, *22*, 5503. (h) Stoffelbach, F.; Richard, P.; Poli, R.; Jenny, T.; Savary, C. *Inorg. Chim. Acta* **2006**, *14*, 4447. (i) Demirhan, F.; Cagatay, B.; Demir, D.; Baya, M.; Daran, J. C.; Poli, R. *Eur. J. Inorg. Chem.* **2006**, 757. (j) Demirhan, F.; Taban, G.; Baya, M.; Dinoi, C.; Daran, J. C.; Poli, R. *J Organomet. Chem.* **2006**, *691*, 648.

(2) (a) Cabon, N.; Schollhammer, P.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W. *Organometallics* **2002**, *21*, 448. (b) Cabon, N.; Paugam, E.; Schollhammer, P.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W. *Organometallics* **2003**, *22*, 4178. (c) Ojo, W.-S.; Paugam, E.; Schollhammer, P.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W. *Organometallics* **2006**, *25*, 4009.

(3) The chemical shifts were compared to those of an authentic sample of HSMe in CD_3CN.

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

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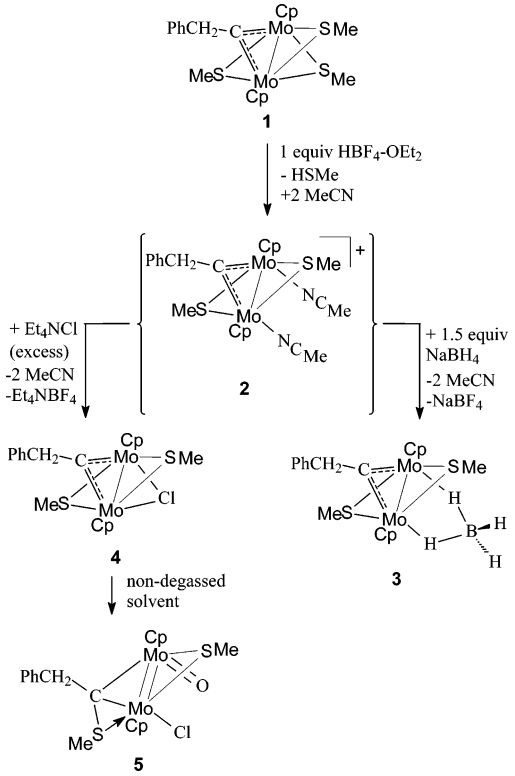
Scheme 1



release of MeSMe or HSMe could arise in acetonitrile solution, giving $[Mo_2Cp_2(\mu\text{-SMe})_{4-n}(MeCN)_{2n}]^{n+}$ cations.[5]

A 1.5 equiv amount of sodium borohydride was added to **2** in CH_3CN at room temperature to afford in high yield (90%) the purple borohydride compound $[Mo_2Cp_2(\mu\text{-SMe})_2(\mu\text{-}CCH_2Ph)(\mu\text{-}\kappa\text{:}^1\kappa^1\text{-}BH_4)]$ (**3**) (Scheme 1). No transfer of hydride to one of the acetonitrile ligands was detected. **3** was identified on the basis of its spectroscopic data and of its solid-state structure.

Spectroscopic data of the borohydride bridge are very similar to those observed in other dimolybdenum complexes $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-}\kappa\text{:}^1\kappa^1\text{-}BH_4)]$[6a] and $[Mo_2Cp_2(\mu\text{-SMe})_2(\mu\text{-NCHMe})(\mu\text{-}\kappa\text{:}^1\kappa^1\text{-}BH_4)]$.[6b] The $^{11}B\{^1H\}$ NMR spectrum shows a single broad resonance at −20.1 ppm. A $^1H\{^{11}B\}$ NMR spectrum, recorded at 223 K, displays in addition to the expected resonances for the $\{Mo_2Cp_2(\mu\text{-SMe})_2(\mu\text{-}CCH_2Ph\}$ core a broad, high-field doublet at − 9.85 ppm assignable to two equivalent Mo−H−B bridges, and two other broad signals, at −1.09 and 1.04, attributed to the terminal hydrogens bound to the boron atom. A 2D $^1H-^1H\{^{11}B\}$ correlation experiment, performed at 188 K in CD_2Cl_2, confirms these assignments (Figure 1).

The broadening and the coalescence at 303 K of the two terminal (B−H) signals when a dichloromethane-d_2 solution of **3** is warmed from 188 to 313 K suggest that the molecule is fluxional in solution: an energy barrier of 55 (±1) kJ·mol^{-1} has been estimated.[7] It is worth noting that in the same range of temperatures no dynamic process was observed for the thiolate analogue $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-}\kappa\text{:}^1\kappa^1\text{-}BH_4)]$.[6a] One possible mechanism for the exchange of the two terminal hydrogens bound to the boron atom in **3** is shown in Chart 2. It may proceed via

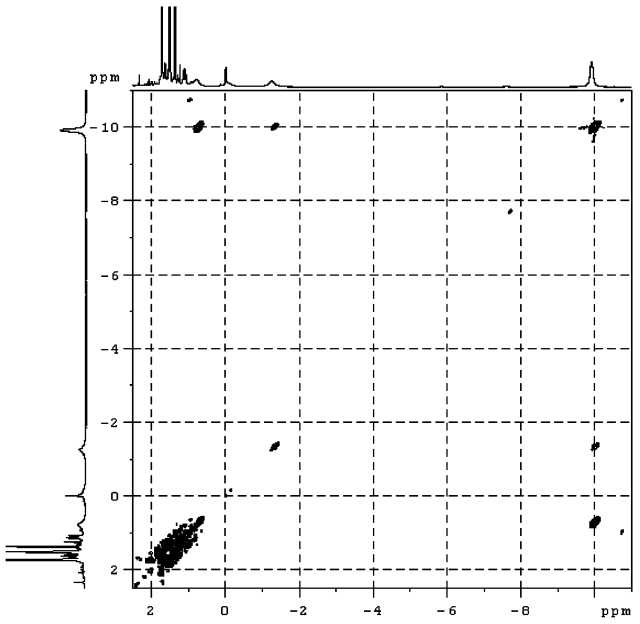
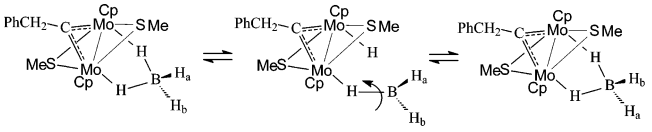


Figure 1. 2D $^1H-^1H\{^{11}B\}$ NMR spectrum of $[Mo_2Cp_2(\mu\text{-SMe})_2(\mu\text{-}CCH_2Ph)(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-}BH_4)]$ (**3**) recorded at 188 K in CD_2Cl_2 between 2 and −9.5 ppm

Chart 2. Possible Mechanism for the Exchange of the Two Terminal Hydrogens Bound to the Boron Atom in 3



the breaking of one B−H bond, as proposed for the compound $[ZrHCp_2(\kappa^2\text{-}H_2BC_5H_{10})]$ to explain the process of exchange between terminal and bridging hydride.[8] However, it should be noted that the low activation energy (55 kJ·mol^{-1}) calculated for this process would suggest another possible mechanism, which should involve lower energy decoordination instead of cleavage of B−H bonds, as proposed by Riera et al. in a related bridged borohydride dimanganese complex.[9] Nevertheless, such a mechanism cannot explain why the two bridging hydrogen atoms do not part in the observed coalescence phenomenon.

Purple crystals of **3** were obtained at room temperature from diethyl ether solution. The X-ray analysis of **3** is of poor quality, mainly because of unresolved twinning, but the results are consistent with a structure based on a $\{Mo_2Cp_2(\mu\text{-SMe})_2(\mu\text{-}CCH_2Ph)^+\}$ core bridged through Mo−H−B bonds by a distorted tetrahedral BH_4^- anion (Figure 2). The geometry of the $\{Mo_2(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-}BH_4)\}$ group, in particular the Mo−Mo distance [2.6238(9) Å], is comparable to those in the related complexes $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-}BH_4)]$[6a] and $[Mo_2Cp_2(\mu\text{-SMe})_2(\mu\text{-N=C(H)Me})(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-}BH_4)]$.[6b] The Mo···B distances [2.753 and 2.740 Å] in **3** are too long for direct Mo−B bonding.[6a] Other distances and angles [in particular, Mo−C3, 1.978(7), 1.993(7) Å; Mo1−C3−Mo2, 82.7(3)°] are close to those observed in the μ-alkylidyne derivative $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-}CCH_2\text{-}n\text{Pr})]$.[2a] The Cp ligands bend away from the borohydride bridge, adopting a *cis* disposition relative to the Mo−Mo axis with Cp−Mo−Mo angles of 167.6° (Cp = ring centroid), the thiolate Me groups have an *anti* orientation, and the BH_4^- group is *trans* to the alkylidyne bridge.

(5) (a) Schollhammer, P.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W. *Inorg Chim. Acta* **1999**, *284*, 107. (b) Cabon, N.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *J. Organomet. Chem.* **2006**, *691*, 566.

(6) (a) Schollhammer, P.; Cabon, N.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W. *Chem. Commun.* **2000**, 2708. (b) Cabon, N.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Dalton Trans.* **2004**, 2708.

(7) (a) Shanan-Atidi, H.; Bar-Eli, K. H. *J. Phys. Chem.* **1970**, *74*, 961. (b) Gutowsky, H. S.; Holm, C. H. *J. Phys. Chem.* **1956**, *25*, 1228.

(8) Liu, F.-C.; Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 3293.

(9) Carreño, R.; Riera, V.; Ruiz, M. A.; Bois, C.; Jeannin, Y. *Organometallics* **1993**, *12*, 1946.

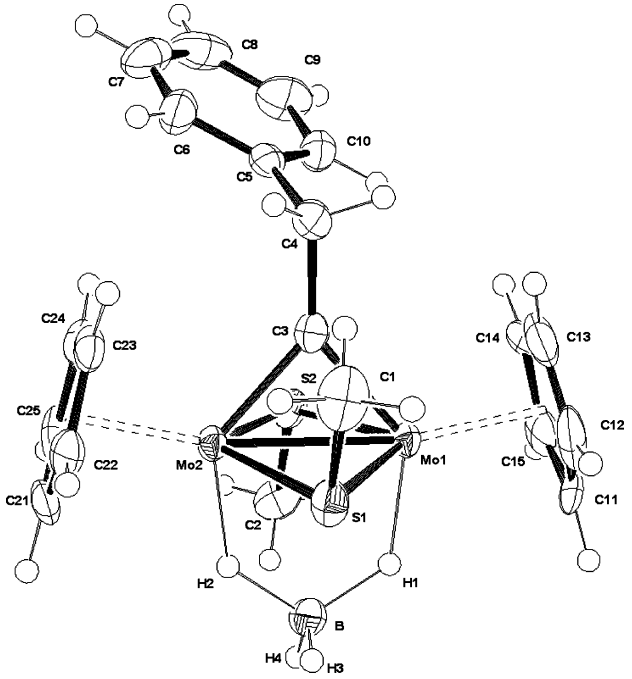


Figure 2. View of a molecule of $[Mo_2Cp_2(\mu\text{-SMe})_2(\mu\text{-CCH}_2\text{Ph})(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-BH}_4)]$ (**3**) showing 50% probability ellipsoids. Hydrogen atoms are drawn as spheres of arbitrary radius. Selected bond lenghts (Å) and angles (deg): Mo1−Mo2, 2.6238(9); Mo1−H1, 1.74(8); Mo2−H2, 1.77(8); B−H1, 1.31(8); B−H2, 1.27(9); B−H3, 1.01(9); B−H4, 1.14(8); Mo1−C3, 1.978(7); Mo2−C3, 1.993(7); Mo1−B, 2.753(9); Mo2−B, 2.740(10); H3−B−H4, 116(6); H3−B−H2, 108(6); H3−B−H1, 109(6); H4−B−H2, 101(6); H4−B−H1, 109(6); H2−B−H1, 114(5); Mo1−C3−Mo2, 82.7(3), Mo1−C3−C4, 139.4(5); Mo2−C3−C4, 137.9(5); B−H1−Mo1, 127.2; B−H2−Mo2, 127.41

Treatment of a solution of **2** in CH_2Cl_2 with an excess of Et_4NCl at room temperature afforded in valuable yield (60%) the purple, air-sensitive, chloro-bridged compound $[Mo_2Cp_2(\mu\text{-SMe})_2(\mu\text{-CCH}_2\text{Ph})(\mu\text{-Cl})]$ (**4**) (Scheme 1). The ^{1}H NMR ($CDCl_3$) spectrum of **4** is typical of a complex with a $\{Mo_2Cp_2(\mu\text{-SMe})_2(\mu\text{-CCH}_2\text{Ph})\}$ framework. It exhibits a single resonance at 5.40 ppm for the two cyclopentadienyl ligands, two peaks, between 1.5 and 2.0 ppm, for the two SMe bridges, and the expected set of resonances of a benzyl group, $PhCH_2-$ [4.97 (s, 2H) and 7.00−7.26 (m, 5H)]. Attempts to obtain elemental analyses and single crystals of **4** were unsuccessful due to its high instability. A striking feature of our work was the reproducible evolution of **4** in non-degassed solvent to give cleanly the oxo species $[Mo_2(O)(Cl)Cp_2(\mu\text{-SMe})(\mu\text{-MeSCCH}_2\text{Ph})]$ (**5**) (Scheme 1). **5** has been characterized by NMR and IR spectroscopy, microanalysis, and single-crystal X-ray diffraction analysis. The ^{1}H NMR pattern of complex **5** indicates the presence in the molecule of two cyclopentadienyl rings, two SMe, and a $CH_2C_6H_5$ group. The IR spectrum in KBr pellets shows a band at 818 cm^{-1}, which is characteristic of ν(M═O), and elemental analyses are consistent with the formula $C_{20}H_{23}ClOMo_2S_2$. These data are fully compatible with the results of a single-crystal X-ray diffraction study of **5**. The recrystallization of **5** from diethyl ether at room temperature afforded brown crystals. The molecule contains {CpMoCl} and {CpMo═O} units bridged by a SMe group and a η^1(C):η^2(C,S)-thioalkylidene ligand {MeSCCH$_2$Ph}, which results from an intramolecular C−S coupling between one SCH_3 thiolate group and the bridging carbon atom of the alkylidyne (C3−S1, 1.775(10) Å). The bridging coordination mode of the thioalkylidene group is not

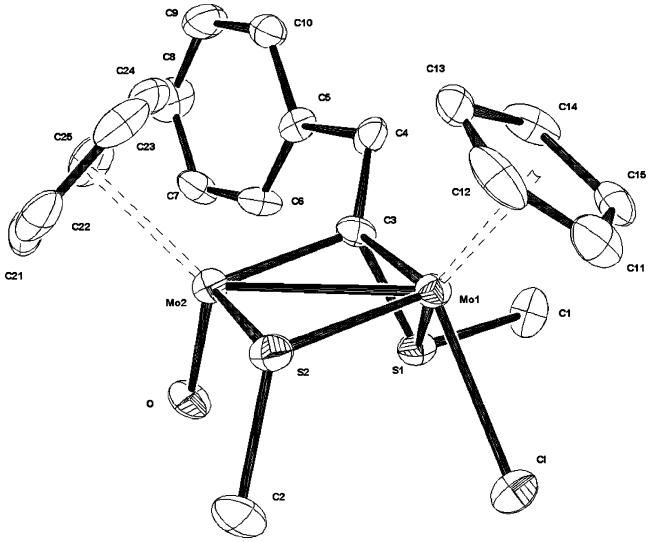


Figure 3. View of a molecule of $[Mo_2(O)(Cl)Cp_2(\mu\text{-SMe})(\mu\text{-MeSCCH}_2\text{Ph})]$ (**5**) showing 50% probability ellipsoids. Selected bond lenghts (Å) and angles (deg): Mo1−Mo2, 2.7680(14); Mo2−O, 1.698(6); Mo2−S2, 2.365(3); Mo2−C3, 2.133(10); Mo1−Cl, 2.507(3); Mo1−S2, 2.372(3); Mo1−S1, 2.442(3); Mo1−C3, 2.094-(10); C3−C4, 1.529(13); C3−S1, 1.775(10); Mo2−Mo1−Cl, 114.43(7); Mo1−Mo2−O, 107.8(2); Mo1−C3−Mo2, 81.8(4); Mo1−C3−C4, 134.4(7); Mo2−C3−C4, 128.3(7); S1−C3−C4, 117.0(7); S1−Mo1−S2, 114.17(10); S2−Mo1−C3, 103.7(3); S2−Mo2−C3, 102.7(3).

unusual,[10] it is σ-bonded to Mo1 and Mo2 atoms through the C3 atom (Mo2−C3, 2.133(10) Å; Mo1−C3, 2.094(10) Å) and σ-bonded to Mo1 through the S1 atom (Mo1−S1, 2.442(3) Å). The Mo−Mo bond length (2.7680(14) Å) is consistent with a bond order of 2 required by the usual electron-counting rule, with the presence of two bridging groups.[11] The Mo−O and Mo−Cl distances (1.698(6) and 2.507(3) Å, respectively) are typical of terminal Mo═O and Mo−Cl bonds.[11]Several examples of dimolybdenum cyclopentadienyl complexes featuring oxo ligands have been reported,[11,12] but it is worth noting that in the clean transformation of **4** into **5** the incoming oxygen induces the formation of a C−S bond, giving rise to the thioalkylidene ligand and the opening of the chloro bridge. The formation of thioalkylidene species is generally based either on the addition of a nucleophile to a bridging alkylidyne carbon or on

(10) (a) Busetto, L.; Zanotti, V. *J. Organomet. Chem.* **2005**, *690*, 5430. (b) Xiao, N.; Xu, Q.; Sun, J.; Chen, J. *Dalton Trans.* **2005**, 3250. (c) Qiu, Z.; Sun, J.; Chen, J. *Organometallics* **1998**, *17*, 600. (d) Bordini, S.; Busetto, L.; Camiletti, C.; Zanotti, V.; Albano, V. G.; Monari, M.; Prestopino, F. *Organometallics* **1997**, *16*, 1224. (e) Albano, V. G.; Bordini, S.; Busetto, L.; Camiletti, C.; Monari, M.; Prestopino, F.; Zanotti, V. *J. Chem. Soc., Dalton Trans.* **1996**, 3693. (f) Matachek, J. R.; Angelici, R. J.; Schugart, K. A.; Haller, K. J.; Fenske, R. F. *Organometallics* **1984**, *3*, 1038.

(11) Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Coord. Chem. Rev.* **1998**, *178*−*180*, 203.

(12) (a) Adatia, T.; McPartlin, M.; Mays, M. J.; Morris, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1989**, 1555. (b) Davies, J. E.; Feeder, N.; Gray, C. A.; Mays, M. J.; Woods, A. D. *J. Chem. Soc., Dalton Trans.* **2000**, 1695. (c) Stichbury, J. C.; Mays, M. J.; Davies, J. E.; Raithby, P. R.; Shields, G. P.; Finch, A. G. *Inorg. Chim. Acta* **1997**, *262*, 9. (d) Stichbury, J. C.; Mays, M. J.; Raithby, P. R.; Rennie, M.-A; Fullalove, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1269. (e) Adams, H.;Gill, L. J.; Morris, M. J. *J. Chem. Soc., Dalton Trans.* **1998**, 2451. (f) García, G.; García, M. E.; Melon, S.; Riera, V.; Ruiz, M. A.; Villafãne, F. *Organometallics* **1997**, *16*, 624. (g) Saurenz, D.; Demirhan, F.; Richard, P.; Poli, R.; Sitzmann, H. *Eur. J. Inorg. Chem.* **2002**, 1415. (h) Gun, J.; Modestov, A.; Lev, O.; Saurenz, D.; Vorotyntsev, M. A.; Poli, R. *Eur. J. Inorg. Chem.* **2003**, 482. (i) Bottomley, F.; Ferris, E. C.; White, P. S. *Organometallics* **1990**, *9*, 1166. (j) Bottomley, F.; Boyle, P. D.; Chen, J. *Organometallics* **1994**, *13*, 370. (k) Benson, I. B.; Killops, S. D.; Knox, S. A. R.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1137.

intramolecular rearrangements of μ-alkylidyne complexes.[10a] This reaction is similar to previous results that we have reported concerning C−C and C−S couplings, induced by reaction of electron-donating substrates such as RNC, CS_2, and RCCH with alkyne complexes $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}RCCH)](BF_4)$.[13] In addition, this reaction points out the reactional versatily of such μ-alkylidyne complexes. They react with a proton in CH_2Cl_2 to give cationic alkylidene compounds $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}CHCH_2R)](BF_4)$,[2a] but on the other hand the formation of **5** in this work reveals the possibility of nucleophilic addition to the bridging carbon.

The reactions of complexes $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}X)]$ (X = SMe, PPh_2, CCH_2Ph) toward sodium borohydride also demonstrate the influence of the bridging ligands on the activity of these dimolybdenum systems and particularly the *trans*-influence of some bridges. Indeed, the complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-}BH_4)]$ has been isolated from the reaction of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ with $NaBH_4$.[6a] If the thiolate bridge in *trans* position to the μ-chloride is replaced by a phosphido group, the formation of the μ-borohydride analogue is not observed and the reaction of $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)]$ with $NaBH_4$ leads to the hydride compound $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(\mu\text{-}H)]$.[6b] This result suggests strongly that the PPh_2 bridge is able to induce the cleavage of a B−H bond in the borohydride anion. On the other hand, the fluxional behavior of **3** reveals that the alkylidyne bridge is able either to weaken a B−H bond but not to break it or to labilize the Mo−H bonds. Such a labilization is not observed if the hydrocarbyl bridge is replaced by a thiolate group. Indeed, the complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-}BH_4)]$ does not present in similar conditions such a dynamic behavior. In addition, the instability of complexes $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}CCH_2Ph)(CH_3CN)_2]^+$ and $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}CCH_2Ph)(\mu\text{-}Cl)]$ compared to their analogues of the tris-thiolato-bridged series suggests also a *trans* influence of the alkylidyne bridge. Finally, the results reported here may suggest new strategies to synthesize original dimolybdenum thio-alkylidene molecules.

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. Literature methods were used for the synthesis of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}CCH_2Ph)]$ (**1**).[2a] Other reagents were purchased from the usual commercial suppliers 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). The NMR spectra (^1H, ^{11}B) were recorded in CD_2Cl_2, $CDCl_3$, or CD_3CN solutions with a Bruker AMX 400 spectrometer and were referenced to $SiMe_4$ (^1H) and $BF_3{-}Et_2O$ (^{11}B). 2D experiments were carried out on a Bruker DRX 500 spectrometer.

Preparation of 2. To a blue solution of **1** (130 mg, 0.23 mmol) in MeCN (20 mL) was added 32 μL (1 equiv) of $H[BF_4]\cdot Et_2O$. The solution readily turned purple. After the mixture was stirred for 15 min at ambient temperature, the volume was reduced under vacuum and diethyl ether was added to precipitate a purple powder. This powder was collected by filtration and immediately used.

Reaction of 2 with $NaBH_4$: Synthesis of 3. A purple powder of **2** was prepared from **1** (130 mg, 0.23 mmol) as described above, and it was immediately added to a solution of $NaBH_4$ (14 mg, 0.37 mmol) in CH_3CN (10 mL). This mixture was stirred for 20 min, then the solvent was removed in vacuo. **3** was extracted with diethyl ether (3 × 20 mL). The solvent was removed in vacuo from the pooled extracts. The residue was washed with cold pentane, and **3** was obtained as a purple powder (110 mg, 90%). Crystals of **3** were obtained at room temperature from $CH_2Cl_2{-}Et_2O$ solution. IR (KBr, cm^{-1}): ν(B−H) 2458 (m), 2367 (m), 2340 (m), 2060 (f), 1923 (f). $^1H\{^{11}B\}$ NMR ($CDCl_3$, 223 K) : δ 6.92−7.29 (m, 5H, C_6H_5), 5.37 (s, 10H, C_5H_5), 4.99 (s, 2H, CCH_2Ph), 1.81 (s, 3H, SCH_3), 1.47(s, 3H, SCH_3), −1.09 and 1.04 (2s, 1H + 1H, $Mo_2(\mu\text{-}H)_2BH_2$), −9.85 (d, 2H, $^2J_{HH}$ = 12.5 Hz, $Mo_2(\mu\text{-}H)_2BH_2$). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 223 K): δ −20,1 (s, br, BH_4). Anal. Calcd for $C_{20}H_{27}BMo_2S_2\cdot CH_2Cl_2$: C, 40.74; H, 4.72; B, 1.75. Found: C, 40.40; H, 4.98; B, 2.49.

Reaction of 2 with Et_4NCl: Synthesis of 4. Similarly, a purple powder of **2** was prepared from **1** (120 mg, 0.21 mmol) and was added to a solution of Et_4NCl (33 mg, 0.42 mmol) in CH_2Cl_2 (10 mL). This mixture was stirred for 30 min, then the solvent was removed in vacuo. **4** was extracted with diethyl ether (4 × 15 mL). The solvent was removed in vacuo from the pooled extracts. The residue was washed with cold pentane, and **4** was obtained as a purple powder (70 mg, 60%). ^1H NMR ($CDCl_3$, 298 K): δ 7.26−7.00 (m, 5H, C_6H_5), 5.40 (s, 10H, C_5H_5), 4.97 (s, 2H, CCH_2Ph), 1.79 (s, 3H, SCH_3), 1.58 (s, 3H, SCH_3). The high instability of **4** prevented any elemental analysis.

Evolution of 4 in Non-degassed Solvent: Synthesis of 5. A solution of **4** (50 mg,0.09 mmol) in non-degassed diethyl ether (10 mL) was stirred overnight (15 h). The solvent was then removed, and the residue was washed with cold pentane (2 × 10 mL). **5** was obtained as a yellow powder (30 mg, 60%). IR (KBr, cm^{-1}): ν(Mo═O) 818 (s). ^1H NMR ($CDCl_3$, 298 K): δ 8.00−7.50 (m, 5H, C_6H_5), 5.47 (s, 5H, C_5H_5), 5.09 (s, 5H, C_5H_5), 4.60 (d, 1H, $^2J_{HH}$ = 17 Hz, CCH_2Ph), 3.76 (d, 1H, $^2J_{HH}$ = 17 Hz, CCH_2Ph), 2.41 (s, 3H, SCH_3), 2.26 (s, 3H, SCH_3). Anal. Calcd for $C_{20}H_{23}ClOMo_2S_2$: C, 42.08; H, 4.06; Cl, 6.21. Found: C, 41.41; H, 4.08; Cl, 5.53.

Crystallographic Data. X-ray crystal data for **3**: $C_{20}H_{27}BMo_2S_2$, fw = 534.23, monoclinic, space group $P2_1/c$, a = 8.5218(7) Å, b = 30.503(2) Å, c = 7.8636(6) Å, β = 94.602(7)°, V = 2035.3(3) Å^3, T = 170 K, Z = 4, d_{calcd} = 1.743 g/cm^3; 4926 unique, absorption-corrected intensities with θ(Mo Kα) < 25.0°. $R(F)$ = 0.0807 for 4926 reflections with $I > 2\sigma(I)$ and $wR(F^2)$(all data) = 0.1290 after refinement of 240 parameters. $|\Delta\rho|$ < 1.318 e Å^{-3}. X-ray crystal data for **5**: $C_{20}H_{23}ClMo_2OS_2$, fw = 570.83, monoclinic, space group $C2/c$, a = 30.947(4) Å, b = 8.3832(8) Å, c = 17.010(3) Å, β = 112.995(15)°, V = 4062.4(9) Å^3, T = 170 K, Z = 8, d_{calcd} = 1.867 g/cm^3; 2092 unique, absorption-corrected intensities with θ(Mo Kα) < 25.0°. $R(F)$ = 0.0611 for 2092 reflections with $I > 2\sigma(I)$ and $wR(F^2)$(all data) = 0.0986 after refinement of 235 parameters. $|\Delta\rho|$ < 0.607 e Å^{-3}.

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Supporting Information Available: For **3** and **5** tables giving details of structure determination, non-hydrogen atomic positional parameters, all bond distances and angles, anisotropic parameters, and hydrogen atomic coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Schollhammer, P.; Cabon, N.; Capon, J-F.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W. *Organometallics* **2001**, *20*, 1230.