Formation of C−C, C−N, and C−O Links between Isonitrile, Cyclopentadienyl, and Hydroxide Ligands Bound to Molybdenum(III): Syntheses and Crystal Structures of μ-Aminocarbyne and μ-Amino-oxycarbene Dimolybdenum Complexes

Wilfried-Solo Ojo, Eddy Paugam, François Y. Pétillon,* Philippe Schollhammer,* and Jean Talarmin

UMR CNRS 6521, Chimie, Electrochimie Moléculaires et Chimie Analytique, UFR Sciences et Techniques, Université de Bretagne Occidentale, CS 93837, 29238 Brest-Cedex 3, France

Kenneth W. Muir*

Chemistry Department, University of Glasgow, Glasgow G128QQ, U.K.

Received May 3, 2006

Reaction of the bis-isonitrile complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(xylNC)_2](BF_4)$ (**2b**) with NaOH (suspension) under reflux in tetrahydrofuran produced, in quantitative yields, the μ-alkylidyne species $[Mo_2Cp(\mu\text{-}SMe)_3\{\mu\text{-}(\eta^5\text{-}C_5H_4)(xylN)CN(xyl)C\}]$ (**4**), in which a deprotonated Cp and both isonitrile ligands of **2b** are now linked by new C−C and C−N bonds. Under prolonged reflux (72 h) in tetrahydrofuran **2b** with either NaOH (suspension) or $(Me_4N)OH$ (in MeOH) in the presence of excess isonitrile RNC (R = xyl, Bu^t) was converted in high yields into the mixed (μ-alkylidyne)(μ-amino-oxycarbene) derivatives $[Mo_2Cp(\mu\text{-}SMe)_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)(xylN)CN(xyl)C\}\{\mu\text{-}\eta^1(O),\eta^1(C)\text{-}OCNHR\}]$ (R = xyl (**5a1**), R = Bu^t (**5b2**)) and $[Mo_2Cp(\mu\text{-}SMe)_2\{\mu\text{-}(\eta^5C_5H_4)(xylN)CN(xyl)C\}\{\mu\text{-}\eta^1(O),\eta^1(C)\text{-}OCNMeR\}]$ (R = xyl (**6a**)). All these products result from hydroxide−isonitrile coupling reactions. When the mixture of **2b**, $(Me_4N)OH$ (excess), and Bu^tNC (excess) in tetrahydrofuran was heated under reflux for a short time (2 h), complex **5b1** was formed in good yields. Compounds **5b1** and **5b2** are linkage isomers, which differ only in the mode of coordination of the μ-amino-oxycarbene ligand to the Mo1−Mo2 unit; **5b1** converts into **5b2** on prolonged heating. Reaction of the secondary amino-oxycarbene derivative **5a1** with a base (NaOH) and an alkylating agent R''_4NBr (R″ = Et, Bu^n) afforded the corresponding tertiary(amino)-oxycarbene complexes $[Mo_2Cp(\mu\text{-}SMe)_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)(xylN)CN(xyl)C\}\{\mu\text{-}\eta^1(O),\eta^1(C)\text{-}OCNxylR''\}]$ [R″ = Et (**6b**), Bu^n (**6c**)]. On heating a tetrahydrofuran solution of the μ-alkylidyne compound **4** with NaOH (suspension) and an excess of either xylNC or Bu^tNC, the mixed μ-alkylidyne and μ-amino-oxycarbene species **5a1** and **5b2** were obtained, demonstrating that **4** is an intermediate in the formation of **5a1** and **5b2** from **2b**. Treatment of the mixed isonitrile−nitrile species $[Mo_2Cp_2(\mu\text{-}SMe)_3(MeCN)(xylNC)](BF_4)$ (**3**), containing a labile MeCN group, under reflux in tetrahydrofuran with NaOH (suspension) afforded quantitatively the μ-amino-oxycarbene compound $[Mo_2Cp_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1(O),\eta^1(C)\text{-}OCNHxyl\}]$ (**7**). All new complexes have been characterized by elemental analyses and spectroscopic methods, supplemented for **5a1**, **5b1**, **5b2**, **6a**, **6b**, and **7** by X-ray diffraction studies.

Introduction

The formation of new C−X bonds, where X = C, N, O, etc., through the mediation of transition metals is an important route to novel organic compounds and ligands.[1,2] For example, coupling reactions involving isocyanides have led to the successful synthesis of a wide variety of new nitrogen-containing organic ligands and compounds during the past decade.[3,4] These reactions can proceed either through metal-mediated reductive coupling of the isocyanides[5] or by consecutive insertion of isocyanides into M−C bonds to give N-chelated cyclic compounds. The insertion reaction can be initiated in various ways: by oxidative addition of alkyl halides to $[M(RNC)_n]$ complexes,[6] by addition of an excess of isocyanide to metal complexes,[4b,7] or by thermolysis.[8] Most coupling reactions between isocyanides involve formation of C−C bonds,[6−8] while only a few give rise to new C−N bonds.[9] It has been shown that many different alkyl or aryl groups can migrate onto an isocyanide carbon

* Corresponding authors. E-mail: francois.petillon@univ-brest.fr (F.Y.P); schollha@univ-brest.fr (P.S); ken@chem.gla.ac.uk (K.W.M).

(1) For recent reviews see: (a) Negishi, E.-i.; Anastasia, L. *Chem. Rev.* **2003**, *103*, 1979. (b) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359. (c) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009. (d) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

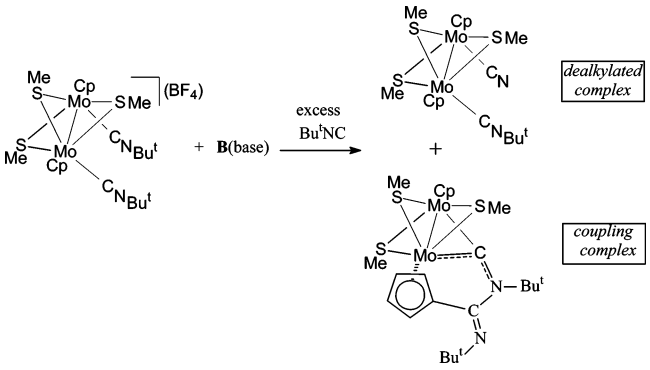
(2) For recent examples see: (a) Ruiz, J.; Mosquera, M. E. G.; García, G.; Marquínez, F.; Riera, V. *Angew. Chem., Int. Ed.* **2005**, *44*, 102. (b) Pittard, K. A.; Cundari, T. R.; Gunnoe, T. B.; Day, C. S.; Petersen, J. L. *Organometallics* **2005**, *24*, 5015. (c) Bokach, N. A.; Kukushkin, V. Y.; Haukka, M.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *Inorg. Chem.* **2003**, *42*, 3602. (d) Makarycheva-Mikhailova, A. V.; Kukushkin, V. Y.; Nazarov, A. A.; Garnovskii, D. A.; Pombeiro, A. J. L.; Haukka, M.; Keppler, B. K.; Galanski, M. *Inorg. Chem.* **2003**, *42*, 2805.

(3) (a) Pombeiro, A. J. L.; Guedes da Silva, M. F. C.; Michelin, R. A. *Coord. Chem. Rev.* **2001**, *218*, 43. (b) Michelin, R. A.; Pombeiro, A. J. L.; Guedes da Silva, M. F. C. *Coord. Chem. Rev.* **2001**, *218*, 75. (c) Tamm, M.; Hahn, F. E. *Coord. Chem. Rev.* **1999**, *182*, 175.

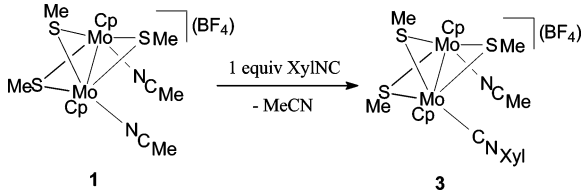
10.1021/om060383v CCC: $33.50 © 2006 American Chemical Society
Publication on Web 06/24/2006

atom.[10] In contrast, there are only very few examples involving a comparable migratory insertion of cyclopentadienyl, despite its ubiquity as a ligand.[11] Accordingly, we have tried to exploit the close proximity of the two isonitrile and two cyclopentadienyl groups in the readily accessible bis-isonitrile derivative $[Mo_2Cp_2(\mu\text{-}SMe)_3(RNC)_2](BF_4)$ (**2**) in attempts to induce coupling between these ligands. We have already shown[12] that **2a** (R = Bu^t) reacts with various bases (OH^-, Bu^-) to give both the dealkylated product $[Mo_2Cp_2(\mu\text{-}SMe)_3(CN)(Bu^tNC)]$ and the μ-alkylidyne derivative $[Mo_2Cp(\mu\text{-}SMe)_3\{\mu\text{-}(\eta^5\text{-}C_5H_4)(Bu^tN)\text{-}CN(Bu^t)C\}]$. In the μ-alkylidyne derivative new C−C and C−N bonds link a deprotonated Cp and both isonitrile ligands of the starting complex **2a**. These reactions occur in both the presence and absence of excess isonitrile, but the ratio of dealkylated to μ-alkylidyne product strongly depends on the reaction conditions, dealkylation being favored in the absence of excess isonitrile. The unusual character of these transformations, which are summarized in Scheme 1, has prompted us to follow up our preliminary study[12] with a wider investigation of the activity of $[Mo_2Cp_2(\mu\text{-}SMe)_3(RNC)_2](BF_4)$ (**2**) toward hydroxides. We now describe the reaction with hydroxide of complex **2b**, which contains aromatic isocyanide ligands (namely, XylNC) in place of the aliphatic isocyanides present in **2a**, and of the mixed isonitrile−nitrile compound $[Mo_2Cp_2(\mu\text{-}SMe)_3(MeCN)(xylNC)](BF_4)$ (**3**). The reactions have been performed under thermolytic conditions in both the presence and absence of excess isocyanide. The products contain novel μ-alkylidyne and μ-aminooxycarbene ligands. The results are used to evaluate how the terminal ancillary ligands in tris(μ-thiolato)dimolybdenum complexes $[Mo_2Cp_2(\mu\text{-}SMe)_3L_2](BF_4)$ influence reactivity toward bases.

Scheme 1



Scheme 2



Results and Discussion

Synthesis and Characterization of the Precursors 2b and 3. The dimolybdenum complexes $[Mo_2Cp_2(\mu\text{-}SMe)_3(xylNC)_2](BF_4)$ (**2b**) and $[Mo_2Cp_2(\mu\text{-}SMe)_3(MeCN)(xylNC)](BF_4)$ (**3**), suitable precursors for **4**−**6** and **7**, respectively, were prepared from $[Mo_2Cp_2(\mu\text{-}SMe)_3(MeCN)_2](BF_4)$ (**1**) by a double or single substitution process,[13] using either 2 or 1 equiv of isonitrile as reagent. The synthesis and the characterization of **2b** have already been reported,[14] but those of **3** are novel. The formulation of **3** (Scheme 2) was deduced from the IR and NMR data (see Experimental Section).

Reaction of 2 with Bases. We have shown previously that **2a** reacts with hydroxides to afford mainly the dealkylation product $[Mo_2Cp_2(\mu\text{-}SMe)_3(Bu^tNC)(NC)]$ via α-cleavage of one isonitrile; **4′** is also formed in low yield by isonitrile coupling [see Scheme 3 (a)].[12] The stability of the Me_3C^+ ion favors dealkylation in the case of **2a**.[15] This effect does not operate in the case of **2b**. It is, therefore, not surprising that the only product of the reaction of **2b** with NaOH under reflux in THF is the μ-alkylidyne derivative **4**. **4** is obtained in nearly quantitative yield (84%) [Scheme 3 (b)] without the presence of excess xylNC. When **2a** reacts with OH^- in the presence of excess Bu^{t}NC, the yield of the μ-alkylidyne complex **4′** improves (e.g., from 30 to 69%, when NaOH is used as a base).[12]

The elemental analysis confirms the coupling of two isonitrile units in **4**, while its NMR spectra clearly indicate a structure analogous to **4′**, which has been reliably characterized.[12] Particularly informative are the four resonances of relative intensity 1 at 6.00, 5.66, 5.29, and 5.00 ppm in the ^{1}H NMR spectrum assigned to the four hydrogen atoms of a modified cyclopentadienyl ring, whereas a single peak of relative intensity 5, detected at 5.10 ppm, is indicative of an unmodified

(4) (a) Ruiz, J.; García, G.; Mosquera, M. E. G.; Perandones, B. F.; Gonzalo, M. P.; Vivanco, M. *J. Am. Chem. Soc.* **2005**, *127*, 8584. (b) Deng, L.; Chan, H.-S.; Xie, Z. *J. Am. Chem. Soc.* **2005**, *127*, 13774. (c) Hahn, F. E.; Langenhahn, V.; Meier, N.; Lügger, T.; Fehlhammer, W. P. *Chem. Eur. J.* **2003**, *9*, 704. (d) Homrighausen, C. L.; Alexander, J. J.; Krause-Bauer, J. A. *Inorg. Chim. Acta* **2002**, *334*, 419. (e) Becker, T. M.; Alexander, J. J.; Krause-Bauer, J. A.; Nauss, J. L.; Wireko, F. C. *Organometallics* **1999**, *18*, 5594. (f) Tanase, T.; Ohizumi, T.; Kobayashi, K.; Yamamoto, Y. *Organometallics* **1996**, *15*, 3404.

(5) (a) Acho, J. A.; Lippard, S. J. *Organometallics* **1994**, *13*, 1294. (b) Carnahan, E. M.; Protasiewicz, J. D.; Lippard, S. J. *Acc. Chem. Res.* **1993**, *26*, 90, and references therein.

(6) See for example: (a) Basset, J. M.; Green, M.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1779. (b) Otsuka, S.; Nakamura, A.; Yoshida, T. *J. Am. Chem. Soc.* **1969**, *91*, 7196.

(7) Recent references: (a) Ramakrishna, T. V. V.; Lushnikova, S.; Sharp, P. R. *Organometallics* **2002**, *21*, 5685. (b) Owen, G. R.; Vilar, R.; White, A. J. P.; Williams, D. J. *Organometallics* **2002**, *21*, 4799. (c) Stroot, J.; Saak, W.; Haase, D.; Beckhaus, R. *Z. Anorg. Allg. Chem.* **2002**, *628*, 755. (d) Vicente, J.; Abad, J.-A.; Martinez-Viviente, E.; Jones, P. G. *Organometallics* **2002**, *21*, 4454. (e) Yamamoto, M.; Onitsuka, K.; Takahashi, S. *Organometallics* **2000**, *19*, 4669. (f) Bashall, A.; Collier, P. E.; Gade, L. H.; McPartlin, M.; Mountford, P.; Pugh, S. M.; Radojevic, S.; Schubart, M.; Scowen, I. J.; Trösch, D. J. M. *Organometallics* **2000**, *19*, 4784. (g) Tomaszewski, R.; Lam, K.-C.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1999**, *18*, 4174.

(8) (a) Ang, T.-G.; Wood, D.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 1. (b) Kloppenburg, L.; Petersen, J. L. *Organometallics* **1997**, *16*, 3548.

(9) See for example: (a) Jeffery, J. C.; Green, M.; Lynam, J. M. *J. Chem. Soc., Chem. Commun.* **2002**, 3056. (b) Motz, P. L.; Alexander, J. J.; Ho, D. M. *Organometallics* **1989**, *8*, 2589. (c) Bellachioma, G.; Cardaci, G.; Zanazzi, P. *Inorg. Chem.* **1987**, *26*, 84. (d) Bocarsly, J. R.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1986**, *5*, 2380.

(10) (a) Thorn, M. G.; Lee, J.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **2002**, 3398. (b) Fandos, R.; Hernandez, C.; Otero, A.; Rodriguez, A.; Ruiz, M. J.; Terreros, P. *Eur. J. Inorg. Chem.* **2003**, 493. (c) Cadierno, V.; Zablocka, M.; Donnadieu, B.; Igau, A.; Majoral, J. P.; Skowronska, A. *J. Am. Chem. Soc.* **1999**, *121*, 11086. (d) Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1977**, *16*, 3182. See also refs 6, 7a−e, and 8.

(11) (a) Alias, F. M.; Belderrain, T. R.; Paneque, M.; Poveda, M. L.; Carmona, E.; Valerga, P. *Organometallics* **1998**, *17*, 5620. (b) Tanase, T.; Fukushima, T.; Nomura, T.; Yamamoto, Y.; Kobayashi, K. *Inorg. Chem.* **1994**, *33*, 32.

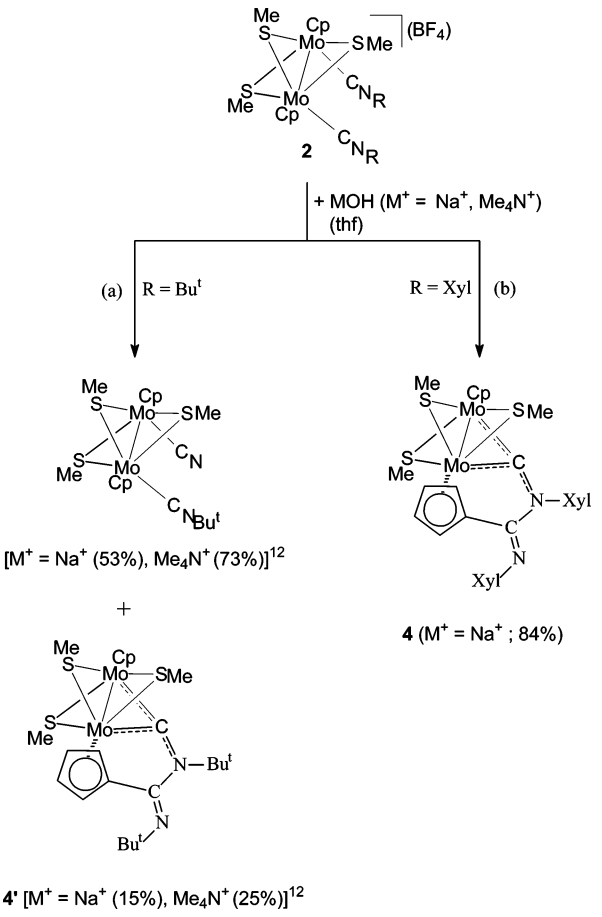
(12) Cabon, N.; Paugam, E.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Organometallics* **2003**, *22*, 4178.

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

(14) Cabon, N.; Pétillon, F. Y.; Orain, P.-Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *J. Organomet. Chem.* **2005**, *690*, 4583.

(15) Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21.

Scheme 3

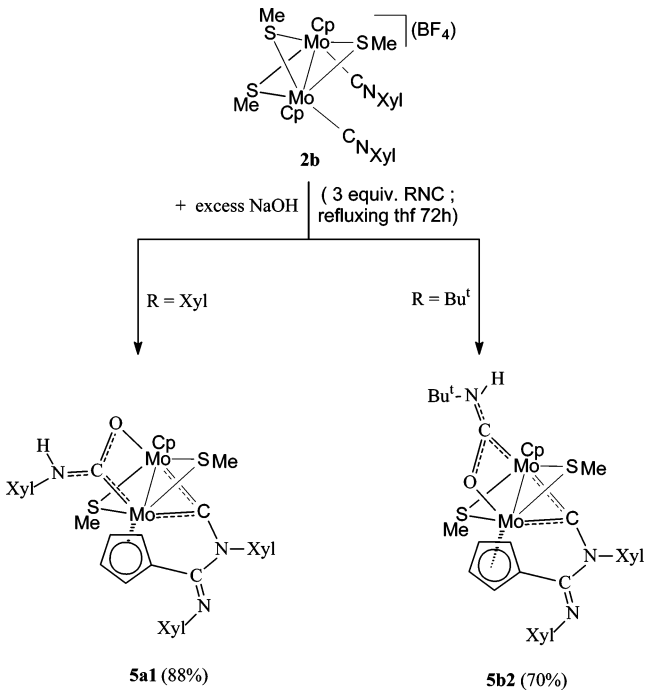


cyclopentadienyl ligand. Thus, these data are in agreement with the coupling of one cyclopentadienyl ring via one of its carbon atoms with an adjacent coordinated isonitrile. Moreover, a resonance characteristic of the Mo-bound ^{13}C atom of an *μ*-alkylidyne moiety appears at low field (δ 374.7), and a signal that could be assigned to an imine-like carbon (C═N−R) is detected at 156.5 ppm. In agreement with the presence of a C═N bond in **4**, the IR spectrum shows one absorption at 1642 cm^{-1}.

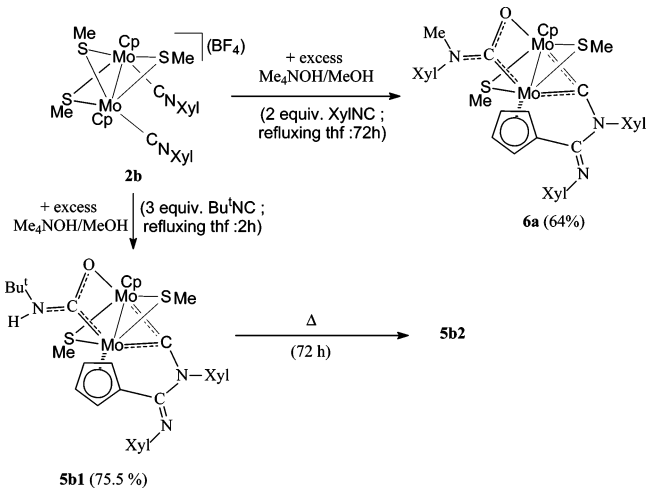
Reaction of 2b with Bases in the Presence of Isonitrile. Prolonged heating (72 h) of a THF solution of complex **2b** and NaOH (suspension) in the presence of 3 equiv of RNC (R = xyl, Bu^t) produced in high yield a *μ*-alkylidyne, *μ*-amino-oxycarbene complex, [$Mo_2Cp(\mu\text{-SMe})_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)$(xylN)CN(xyl)C}(*μ*-OCNHR)] (**5a1**, R = xyl; **5b2**, R = Bu^t), as the only Cp′Mo_2Cp species (Cp′ = η^5-C_5H_4R′; Cp = η^5-C_5H_5) detectable in the ^{1}H NMR spectrum of the crude product (Scheme 4).

X-ray analyses indicate that **5a1** and **5b2** both contain *μ*-amino-oxycarbene ligands; however, these ligands are oriented differently with respect to the Mo′−Mo units, as shown in Scheme 4. To see if a complex **5b** with a *μ*-amino-oxycarbene coordinating in a mode similar to that observed in **5a1** could be obtained, **2b** was treated with Me_4NOH in the presence of excess Bu^{t}NC under reflux in THF. Complex **5b1**, containing a *μ*-amino-oxycarbene ligand with the expected mode of coordination, was formed in good yield after only 2 h (Scheme 5). Somewhat unexpectedly, **2b** and Me_4NOH in the presence of excess xylNC under prolonged reflux (72h) in THF produced **6a**, in which a tertiary(amino)-oxycarbene ligand coordinates in the same mode as in **5b1** (Scheme 5). Contrastingly, prolonged heating of **5b1** in THF gave mainly **5b2**, together with some decomposition products. This shows clearly that **5b2** was formed via **5b1** and that it is unlikely that isomers **5b1** and **5b2** result from attacks by hydroxide ions on different atoms of **2b**. Finally, it should be noted that under similar conditions heating the xylNC compound **5a1** did not produce isomer **5a2**.

Scheme 4



Scheme 5



All the new complexes, **5a1**, **5b1**, **5b2**, and **6a**, have been characterized by elemental analysis and conventional spectroscopic measurements, and for some species by mass spectroscopy (see the Experimental Section). As the NMR data alone cannot discriminate with assurance between possible adducts, X-ray analyses (see below) have established that all these complexes are formed via similar condensation reactions, initiated by base and excess isonitrile. The presence in all the complexes of a *μ*-alkylidyne ligand, (η^5-C_5H_4)(xylN)CN(xyl)C, derived from the condensation of a cyclopentadienyl and two isonitrile units, can be deduced from the NMR spectra, which closely resemble that of **4**, except that the amino-oxycarbene derivatives show only two Cp′ ^{1}H NMR signals, rather than the four observed for complex **4**. This difference may be ascribed to the orientations of the bridging SMe groups: *syn* in the amino-oxycarbene products (see crystallographic section) and *anti* in **4**.[12] The most distinctive features of the ^{1}H NMR

spectra of the μ-amino-oxycarbene complexes are the ligand N−H resonances: these appear in the 7.36−5.65 range for **5a1** and **5b** and are absent for **6a**. A downfield signal (δ 7.36) is observed for **5a1**, which contains a NH−xyl unit, whereas **5b1** and **5b2**, which have a NH−Bu^t group, exhibit upfield N−H signals (δ ∼5.65). Salient characterization features of **5a1** and **5b** include also ^{1}H−^{13}C HMBC experiments that reveal the expected correlations ($^2J_{C-H}$) of the N−H signals with both the carbene carbon resonances and also with the signals for either the C_{ipso} (xyl) or CMe_3 (Bu^t) carbon atoms. For the methyl-amino-derived complex **6a** the methyl resonance (δ 3.09) correlates with both the C_{ipso} (xyl) (δ 146.8) and carbene carbon (δ 242.4) signals. Interestingly, these experiments also show an apparent correlation between the signals for the Cp C−H and carbene carbon atom in the 2D spectrum of **5b2**, but not in those of **5b1** and **5a1**. This is further evidence that the mode of coordination of the amino-oxycarbene group to the Mo′−Mo unit in **5b2** differs from that in **5b1** and **5a1**.

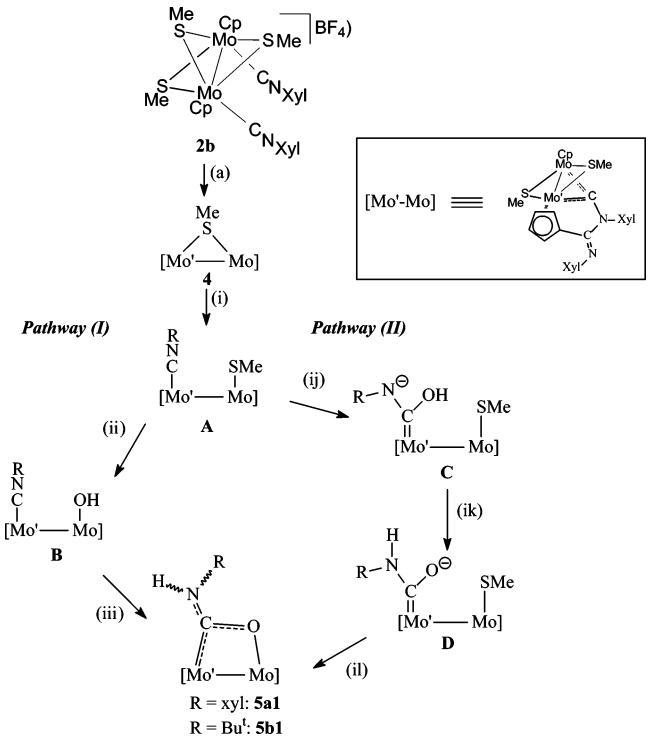
It should also be noted that a ^{1}H−^{15}N HMBC experiment ($CDCl_3$; RT) for **5b1** shows correlations ($^3J_{N-H}$) between ^{15}N and methyl resonances (δ 1.33); the ^{15}N chemical shift (δ −214.1) is observed in the range (δN −200 to −300) expected for an amide-like compound.[16] Finally, no fluxionality is apparent in the ^{1}H and ^{13}C NMR spectra of complexes **5b1** and **5b2** (Experimental Section).

Syntheses of Amino-oxycarbene Compounds 5a1 and 5b via the μ-Alkylidyne Derivative 4 and Mechanistic Considerations. Independent preparations of **5a1** and **5b2** verified that the reaction of complex **4** with NaOH and excess isonitrile RNC also produces complexes **5a1** (R = xyl) and **5b2** (R = Bu^t) in good yield.

These results indicate clearly that the formation of μ-amino-oxycarbene derivatives **5a1** and **5b** by reaction of the bis-isonitrile tris(μ-thiolato) compound **2b** with bases (see previous section) proceeds through the μ-alkylidyne derivative **4**, as shown in Scheme 6. The mechanism of formation of compound **4** has been previously discussed.[12] **4** can react to give either **5a1** (R = xyl) directly or **5b2** (R = Bu^t) via **5b1** by nucleophilic addition of hydroxide to a Mo atom (pathway I) or to the carbon atom of an additional coordinated isocyanide group (pathway II) with retention of the μ-alkylidyne ligand.

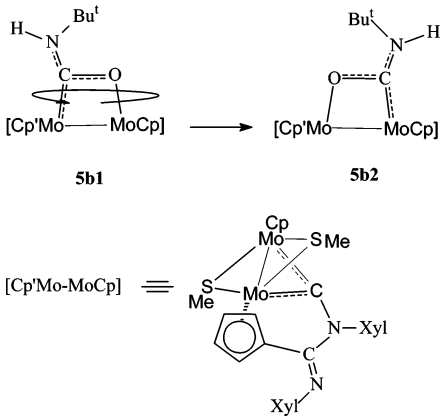
As no intermediate except **4** has been detected, the mechanism of the reaction can only be a matter of speculation at present. However, there are precedents for several steps in both possible mechanisms depicted in Scheme 6. The first step is common to paths I and II: it involves thiolate substitution promoted by addition of an excess of RNC (R = xyl, Bu^t) to **4** giving intermediate **A**. It is followed in path I by nucleophilic (OH^-) substitution at a molybdenum atom with elimination of the thiolate group as NaSMe, yielding hydroxide intermediate **B**. Concerted nucleophilic addition of the coordinated hydroxide group to the isonitrile carbon atom and a tautomeric hydrogen shift[15] finally leads to the formation of a bridging amino-oxycarbene ligand in the two complexes **5**. The available evidence does not allow us to exclude the existence of a second pathway to **5a1** or **5b1** via direct hydroxide addition to the carbon atom of the coordinated isonitrile intermediate **A**, affording amide transient **C**. As one might suspect, the amide nitrogen in this intermediate is basic and can be protonated via tautomeric hydrogen transfer,[17] giving an amidate derivative **D** that by further nucleophilic substitution yields the final product

Scheme 6. Alternative Pathways for the Formation of Complexes 5a1 and 5b1 from 2b[a]



[a] (a) + base; (i) + RNC, thiolate substitution; (ii) + NaOH, − NaSMe, nucleophilic substitution; (iii) internal rearrangement (tautomeric hydrogen shift and nucleophilic addition); (ij) + OH^- (NaOH), nucleophilic addition; (ik) tautomeric hydrogen shift; (il) − SMe^- (NaSMe), nucleophilic substitution.

Scheme 7



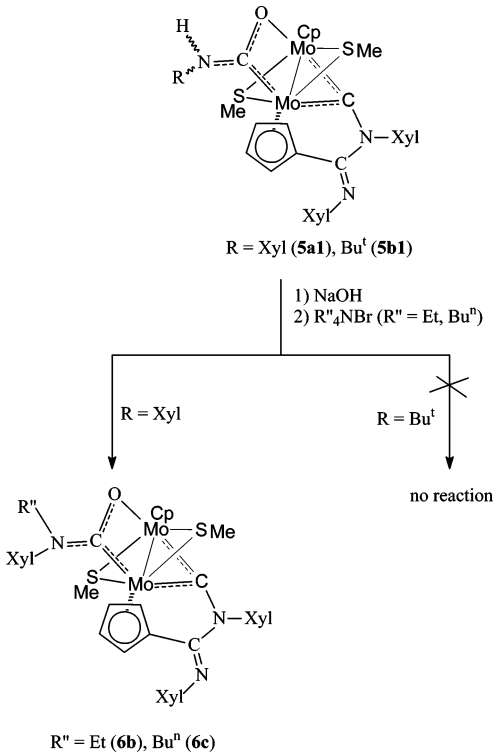
5a1 or **5b**. It is interesting to observe that **4′**, which has aliphatic (e.g., Bu^t) instead of aromatic groups (e.g., xylyl) in the μ-alkylidyne ligand, is inert to thiolate substitution reactions; thus, no amino-oxycarbene complex was formed when **4′** reacted with an excess of NaOH and isonitrile. We conclude that the presence in **4** of a μ-alkylidyne ligand with aromatic groups (e.g., xylyl) labilizes the *trans*-thiolate ligand, facilitating the transformation of **4** into **5a1** or **5b**.

As suggested above, alternative attack of OH^- at either MoCp or MoCp′ would be an attractive way to account for the formation of isomers **5b1** and **5b2**. However, it is not consistent with our observation that **5b2** is formed from **5b1**. X-ray

(16) Berger, S.; Braun, S.; Kalinowski, H.-O. In *NMR Spectroscopy of the Non-Metallic Elements;* John Wiley & Sons: Chichester, 1997; Chapter 4.

(17) See for example: (a) Schollhammer, P.; Le Hénanf, M.; Le Roy-Le Floch, C.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **2001**, 1573, and references therein. (b) Treichel, P. M.; Knebel, W. J. *Inorg. Chem.* **1972**, *11*, 1285.

Scheme 8

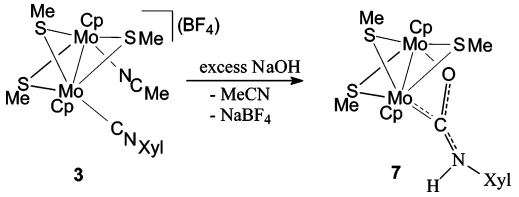


analyses of **5b1** and **5b2** (see below) show that the isomers differ only in the mode of coordination of the C(NHBu^t)−O ligand to the Mo atoms: in **5b1** the linkage to MoCp is through oxygen, whereas in **5b2** it is through the carbon atom. In both isomers the C−O bond axis is nearly parallel to the Mo−Mo axis and the dimetallacyclo-oxycarbene μ-η^1(O):η^1(C) coordination mode is comparable with that of the μ-η^1:η^1-dimetallacyclobutene ligand in $[Mo_2Cp_2(\mu\text{-SMe})_3(RCCH)](BF_4)$.[18] An exchange of alkyne from one molybdenum site to the other has been suggested to account for the fluxionality of these alkyne derivatives.[18] Here, a similar exchange process would explain the transformation of **5b1** into **5b2** (Scheme 7). Thus, **5b1** and **5b2** are respectively the kinetic and thermodynamic products of the reaction of **2** or **4** with an excess of base and isonitrile. Finally, it should be noted that when an aromatic group (e.g., xylyl) is bound to the amine nitrogen atom, only one isomer, **5b1**, could be obtained as a stable species. In contrast, two isomers, **5b1** and **5b2**, are formed when an alkyl group (e.g., Bu^t) is linked to the amine nitrogen atom.

Reaction of μ-Amino-oxycarbene Complexes with NaOH and Tetraalkylammonium Bromide. Complexes **5a1** and **5b** would seem to be suitable substrates for reaction with base, followed by an alkylating agent, to give the corresponding tertiary(amino)-oxycarbene derivatives. Indeed, reaction of **5a1** with NaOH and tetraalkylammonium bromide, R″$_4$NBr (R″ = Et, Bu^n), proceeds with high selectivity, and the targeted alkylated derivative **6b** (R″ = Et) or **6c** (R″ = Bu^n) is obtained. However, similar reactions involving complexes **5b1** and **5b2** do not give the desired products. The presence of a Bu^t group at the nitrogen atom probably lessens the acidic character of the geminal hydrogen atom relative to that observed in the related xylyl compound **5a1** and thus prevents the acid−base reaction (Scheme 8).

Complexes **6b** and **6c** have been successfully characterized from analytical and NMR data. Their NMR spectroscopic characteristics closely match those of the methyl analogue **6a**. Complexes **6b** and **6c** are therefore formulated as μ-alkylidyne, μ-tertiary(amino)-oxycarbene derivatives, consistent with X-ray analysis of single crystals of **6b** (see below). The tertiary amine nature of the amino-oxycarbene ligand in **6b** and **6c** is deduced from the presence of additional ^{1}H NMR resonances in the alkyl region [**6b**: 3.70 (intensity 2) and 1.02 (intensity 3) ppm; **6c**: 3.56 (intensity 2) [1.41 (intensity 2) and 0.83 (intensity 3) ppm] relative to those of the mother compound **5a1**. All other ^{1}H NMR resonances observed for **6b** and **6c** are in full agreement with the structure proposed above, particularly the presence of two resonances both of intensity 2 at 5.14 and 4.34 ppm (**6b**) and at 5.14 and 4.32 ppm (**6c**), which can be assigned to the modified cyclopentadienyl ligand, C_5H_4R'.

Scheme 9



Reaction of 3 with a Base. We have shown above that formation of an amino-oxycarbene ligand by addition of OH$^-$ to a coordinated isonitrile is only observed when the transition metal complex contains labile ancillary ligands. Therefore, it could reasonably be expected that the mixed isonitrile−nitrile compound **3**, which contains a labile MeCN group, will undergo a similar reaction. Indeed, refluxing **3** with NaOH in THF gave high yields of the target amino-oxycarbene complex **7** (Scheme 9). **3** is derived from **2** by replacing a terminal isonitrile by acetonitrile. This replacement changes the regiochemistry of the reaction and precludes formation of a μ-alkylidyne unit by coupling the isonitrile, nitrile, and cyclopentadienyl ligands. Consistent with the structure depicted in Scheme 9 for **7**, the ^{1}H NMR spectrum displays two cyclopentadienyl resonances at δ 5.42 and 5.15 and a singlet at δ 6.70 (intensity 1) assigned to the N−H group. The presence of an amino-oxycarbene ligand in **7** is supported both by the carbene ^{13}C chemical shift (δ 240.8), similar to values (∼244 ppm) for the related complexes **5** and **6**, and by an X-ray structure analysis (see next section).

It is likely that **7** is formed by processes such as those proposed above for **5a1** and **5b1**: alternative pathways involving hydroxide attack at either Mo or the C atom of the coordinated isonitrile, followed by an internal rearrangement, can be envisaged.

Molecular Structures of 5a1, 5b1, 5b2, 6a, 6b, and 7. The compounds **5a1**, **5b1**, **5b2**, **6a**, and **6b** (Figures 1−4, Table 1) share a common structural architecture: an $Mo_2(\mu\text{-SMe})_2Cp$ moiety is stabilized by bridging $(\eta^5\text{-}C_5H_4)$(xylN)CN(xyl)C alkylidyne and R′R″NCO amino-oxycarbene ligands. The S-methyl groups are invariably *syn* to the Mo_2S_2 plane and enfold the R′R″NCO ligand. However, in **6a** disorder of a methyl group suggests that the *anti* form may also be present as a minor component. In **7** (Figure 5) where a xylHNCO ligand bridges a $Cp_2Mo_2(\mu\text{-SMe})_3$ unit and in **4′** where the same unit is bridged by a $(\eta^5\text{-}C_5H_4)$(Bu^{t}N)CN(Bu^t)C alkylidyne an *anti* arrangement of S-methyl groups is also found.[12] In the following discussion less weight is given to the markedly less precise results for **5a1** and **6b** (see below).

The η^5-(C_5H_4)(xylN)CN(xyl)C alkylidyne ligands in **5a1**−**6b** arise from condensation of a Cp and two xylNC ligands: C49, originally the donor atom of an isonitrile, has detached from Mo1 and is now bonded through C21 to a

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

Table 1. Selected Bond Lengths (Å) and Bond and Torsion Angles (deg) for the [$Mo_2Cp(\mu\text{-}SMe)_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)(xylN)CN(xyl)C\}\{\mu\text{-}OCNRR'\}$] Complexes 5a1 (R = H, R′ = xyl), 5b1/b2 (R = H, R′ = Bu^t), 6a (R = Me, R′ = xyl), and 6b (R = Et, R′ = xyl) and for 7

(a) μ-(η^5-C_5H_4)(xylN)CN(xyl)C Ligands

	5a1	5b1	5b2	6a	6b	7
Mo1−Mo2	2.654(2)	2.649(1)	2.654(1)	2.660(1)	2.652(1)	2.666(1)
Mo1−C39	1.99(2)	2.012(6)	1.976(4)	2.019(5)	2.00(1)	
Mo2−C39	1.97(2)	1.993(6)	2.053(4)	2.004(5)	2.00(1)	
N3−C39	1.44(2)	1.386(7)	1.358(5)	1.370(6)	1.38(1)	
N3−C49	1.39(2)	1.386(7)	1.400(6)	1.409(6)	1.39(1)	
N3−Cxyl	1.46(2)	1.453(7)	1.460(6)	1.436(6)	1.42(1)	
N4−C49	1.29(2)	1.278(7)	1.257(5)	1.262(6)	1.27(1)	
N4−Cxyl	1.44(2)	1.416(8)	1.423(6)	1.427(6)	1.45(1)	
C49−C21	1.46(2)	1.473(8)	1.509(6)	1.498(7)	1.51(1)	
Mo1−C39−N3	124.3(10)	123.4(4)	126.0(3)	125.7(3)	125.5(6)	
Mo2−C39−N3	151.3(10)	153.4(5)	151.7(3)	151.2(4)	151.3(7)	
C39−N3−C49	115.0(11)	118.2(5)	117.4(4)	116.5(4)	117.8(8)	
N3−C49−C21	113.9(12)	112.3(5)	111.0(3)	111.7(4)	111.1(8)	
N3−C49−N4	118.9(13)	117.6(5)	120.7(4)	119.6(4)	120.0(9)	
N4−C49−C21	127.2(14)	130.2(6)	128.3(5)	128.7(4)	128.9(9)	
C49−N4−C41	115.4(13)	120.2(5)	122.5(4)	119.8(4)	118.2(8)	
C39−N3−C49−N4	−176(1)	−179.6(5)	179.5(4)	168.1(4)	−179(1)	
N3−C49−N4−C41	180(1)	−175.3(5)	−177.6(6)	−179.8(4)	179(1)	

(b) μ-OCNRR′ Ligands

	5a1	5b1	5b2	6a	6b	7
Mo1−O1			2.167(3)			2.161(3)
Mo2−O1	2.20(1)	2.171(4)		2.181(3)	2.166(6)	
Mo1−C50	2.14(2)	2.165(6)		2.168(5)	2.15(1)	
Mo2−C50			2.148(4)			2.140(4)
O1−C50	1.29(2)	1.304(7)	1.287(5)	1.291(6)	1.30(1)	1.294(5)
N5−C50	1.36(2)	1.340(8)	1.352(6)	1.363(6)	1.38(1)	1.358(6)
N5−C51	1.43(2)	1.488(7)	1.486(6)	1.440(7)	1.41(1)	1.438(6)
N5−C3				1.489(7)	1.50(1)	
Mo−O1−C50	103.5(9)	102.7(3)	102.6(2)	104.9(3)	104.7(6)	102.8(3)
Mo−C50−O1	113.2(10)	113.5(4)	114.5(3)	111.8(3)	111.9(7)	114.4(3)
O1−C50−N5	115.1(12)	116.7(6)	117.0(4)	116.7(4)	115.6(9)	114.2(4)
Mo−C50−N5	131.7(11)	129.6(5)	128.5(3)	131.6(4)	132.6(7)	131.4(4)
C50−N5−C3				119.8(4)	120.9(8)	
C50−N5−C51	123.3(11)	132.3(5)	130.8(4)	123.4(4)	119.7(8)	124.8(4)
C51−N5−C3				116.8(4)	119.0(8)	
Mo−C50−O1−Mo	−1(1)	−2.5(4)	0.7(3)	2.3(3)	1.2(7)	5.1(3)

cyclopentadienyl ring, displacing a hydrogen atom, and through N3 to the second isonitrile ligand. The resulting μ-alkylidyne uses C39 to bridge the two molybdenum atoms but also engages in a conventional η^5-cyclopentadienyl interaction with Mo1. C39 is virtually equidistant from the metal atoms in **5a1**, **5b1**, **6a**, and **6b** (see Table 1): the Mo−C39 bond distances [1.976(4)−2.019(5) Å] in these four complexes lie between the value of 1.894(5) Å for the formally double bond Mo=C in the vinylidene compound [$Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{=}CHTol)$]-($BF_4$) and that of 2.068(3) Å for the single Mo−C bond in the acetylide derivative [$Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}C{-}Ph)$];[18] they thus indicate a symmetrical coordination of the alkylidyne group through Mo−C bonds of order 1.5. However, the Mo−C39 distances differ in **5b2**, where the amino-oxycarbene C50 is bonded to Mo2 rather than Mo1, by 0.077(6) Å and in **4′** by 0.111(3) Å, indicating sensitivity to the nature of the ancillary ligands. Otherwise, as may be seen from Table 1, the μ-alkylidyne ligands of **5a1**−**6b** are remarkably similar. The bonds radiating from C39, N3, C49, and N4 are nearly coplanar; compared with the single N−Cxyl bonds the N3−C39, N3−C49, and N4−C49 show conjugative shortening, with N4−C49 aproaching a bond order of 2. The conjugation does not extend to the xyl and C_5H_4 ring π-systems because of their unfavorable orientation.The angles at C39 show severe deviations (see Table 1) from sp^2 hybridization but broadly agree with those found in the μ-alkylidyne derivative [$Mo_2Cp_2(\mu$-

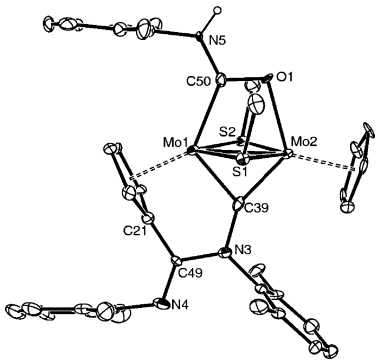


Figure 1. Molecular structure of complex **5a1**. Non-hydrogen atoms are shown with 20% probability ellipsoids, and H atoms bonded to C atoms are omitted for clarity.

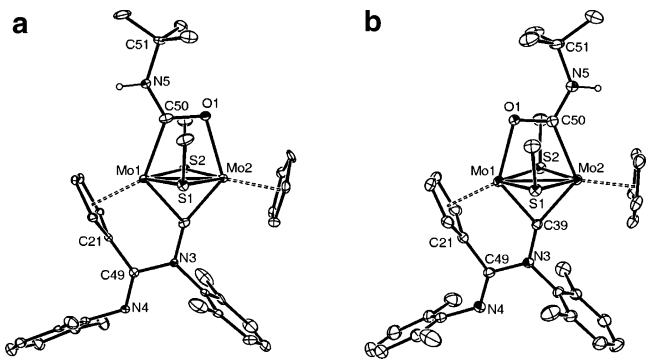


Figure 2. Molecular structure of complexes **5b1** (a) and **5b2** (b).

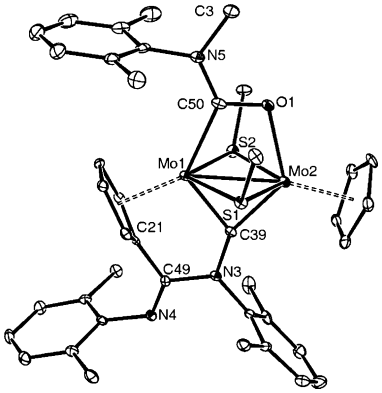


Figure 3. Molecular structure of **6a**. Disorder of the methyl group attached to S2 is not shown.

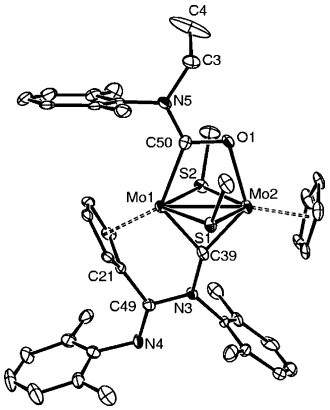


Figure 4. Molecular structure of complex **6b**.

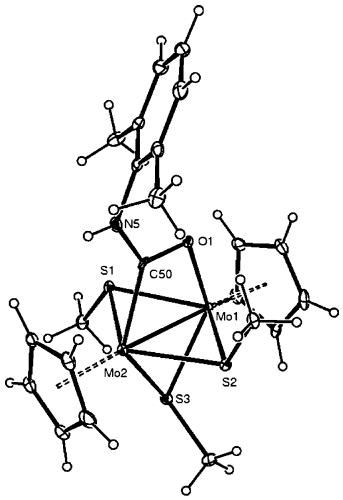


Figure 5. Molecular structure of **7**. Selected bonds lengths (Å), angles (deg), and torsion angles (deg): Mo1−S1 2.466(1), Mo1−S2 2.453(1), Mo1−S3 2.443(1), Mo2−S1 2.449(1), Mo2−S2 2.458(1), Mo2−S3 2.480(1), C50−N5−Cxyl 124.8(4), C50−N5−H1 115(5), Cxyl−N5−H1 120(5), Cxyl−N5−C50−Mo2 177.9(4), Cxyl−N5−C50−O1 −4.5(7). Also see Table 1.

$SMe)_3(\mu\text{-}CCH_2Pr^n)]$.[19] Trends in bond angles at C39, N3, and C49 (Table 1) reflect the constraint imposed by the attachment of the alkylidyne to Mo1 through both C39 and the η^5-C_5 ring.

Complexes **5**−**7** also contain *μ*-amino-oxycarbene ligands: in **5** and **7** they are the result of C−O and N−H bond formation between incoming isonitrile and hydroxide ligands; in **6** H is replaced by alkyl at N5. The Mo−O and Mo−C distances fall in narrow ranges of 2.161(3)−2.20(1) and 2.140(4)−2.168(5) Å, respectively. The C50−N5 and C50−O1 distances imply some multiple character. The former are more than 0.1 Å shorter than the N5−C3 distances in **6**, a difference too great to be explained by the difference in C hybridization, while the latter are ca. 0.15 Å shorter than, for example, the single C−O bond of 1.451(9) Å in $[\{Fe(CO)_3\}_2\{\mu\text{-}S(Me)C(CF_3)C(NHNHC(O)OMe)C\ (NHNHC(O)OMe)\}]$.[20] As previously noted, **5b1** and **5b2** can be regarded as novel linkage isomers: in **5b1** O1 bonds to Mo2 (which carries the η^5-C_5H_5 ring) and C50 to Mo1, while in **5b2** O1 is attached to Mo1 and C50 to Mo2. It is striking that the N5 Bu^t substituent in **5b1** and **5b2** bends away from the adjacent Cp or Cp′ ligand, whereas the corresponding xyl groups in **5a1**, **6a**, and **6b** (but, surprisingly, not in **7**) bend toward the adjacent Cp′ ring. This feature appears to have a steric origin.

The dimensions of the $Mo_2(\mu\text{-}SMe)_2Cp$ moieties in **5**−**7** agree with results of many previous studies on related compounds.[21] The single Mo−Mo bonds show remarkably little variation in length [from 2.649(1) to 2.666(1) Å]. Finally, we note that, while structurally characterized alkylidyne−transition metal complexes $M_2(\mu_2\text{-}C-Csp^3)$ (e.g., M = W, Mo)[22] are well-known, the new *μ*-alkylidyne derivatives **5a1**, **5b1**, **5b2**, **6a** and **6b**, and **4′**,[12] with a Mo_2 (μ_2-C−N) core, are without precedent.

Concluding Remarks

The bis-isonitrile dimolybdenum complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(xylNC)_2](BF_4)$ (**2b**), containing labile bridging groups, has been shown to be an excellent starting point for the construction of new bridging alkylidyne and amino-oxycarbene ligands. These ligands are formed by coupling reactions of an unprecedented nature: when base is added to the molybdenum complex in the presence of excess isonitrile, a new alkylidyne ligand is first formed by linking a cyclopentadienyl and two isonitrile ligands; subsequently, a second isonitrile and hydroxide link to give an amino-oxycarbene. When the added isonitrile is Bu^tNC, the kinetic adduct **5b1** transforms by heating into the thermodynamic isomer **5b2**; when the added isonitrile is xylNC, only **5a1**, an analogue of **5b1**, is isolated.

Addition of a base and excess isonitrile to the mixed isonitrile−nitrile derivative $[Mo_2Cp_2(\mu\text{-}SMe)_3(MeCN)(xylNC)](BF_4)$ (**3**), containing labile acetonitrile, leads only to the formation of an amino-oxycarbene ligand by coupling between additional isonitrile and hydroxide.

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 $[Mo_2Cp_2(\mu\text{-}SMe)_3\ L_2](BF_4)$ [L = MeCN (**1**),[13] xylNC (**2b**)[14]]. 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 mass spectra were measured with a LC-MS Thermo-Finnigan spectrom-

(19) Cabon, N.; Schollhammer, P.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W. *Organometallics* **2002**, *21*, 448.

(20) Guennou-de Cadenet, K.; Rumin, R.; Pétillon, F. Y.; Yufit, D. S.; Muir, K. W. *Eur. J. Inorg. Chem.* **2002**, 639.

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

(22) See for example ref 19, and: Liu, A.-H.; Murray, R. C.; Dewan, J. C.; Santarsiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282.

eter at the Laboratoire de Biochimie, Faculté de Médecine (Brest, France). The NMR spectra (^{1}H, ^{13}C) were recorded at room temperature in $CDCl_3$, C_6D_6, or $(CD_3)_2CO$ solutions with a Bruker AMX 400 spectrometer and were referenced to $SiMe_4$. ^{1}H−^{13}C and ^{1}H−^{15}N 2D experiments were carried out on a Bruker DRX 500 spectrometer.

Synthesis of [$Mo_2Cp_2(\mu$-SMe)$_3$(MeCN)(xylNC)](BF$_4$) (3). A solution of complex **1** (200 mg, 0.317 mmol) in dichloromethane (30 mL) was stirred in the presence of 1 equiv of xylNC (41.5 mg) for 4 h at room temperature. The color of the solution turned from red to orange. The volume of the solution was reduced under vacuum, and diethyl ether (50 mL) was added to precipitate a maroon powder that was washed twice with pentane (2 × 15 mL). After drying, compound **3** was obtained; its NMR spectra were those expected of a pure sample (163 mg, 71% yield) and gave its structure without ambiguity. IR (KBr, cm^{-1}): ν(CN) 2075 (s), ν(BF) 1150−1050 (s). ^{1}H NMR [$(CD_3)_2CO$]: δ 7.28−6.82 (m, 3H, $C_6H_3(CH_3)_2$), 5.64 (s, 5H, C_5H_5), 5.41 (s, 5H, C_5H_5), 2.45 (s, 6H, $C_6H_3(CH_3)_2$), 2.20 (s, 3H, CH_3CN), 1.81 (s, 3H, SCH_3), 1.80 (s, 3H, SCH_3), 1.56 (s, 3H, SCH_3).

Reaction of [$Mo_2Cp_2(\mu$-SMe)$_3$(xylNC)$_2$](BF$_4$) (2b) with NaOH: Synthesis of [$Mo_2Cp(\mu$-SMe)$_3$\{μ-(η^5-C$_5$H$_4$)(xylN)CN(xyl)C\}] (4). The complex **2b** (400 mg, 0.492 mmol) and a large excess of NaOH (201 mg, 5 mmol) were heated in tetrahydrofuran (30 mL) at reflux for 24 h. After filtration, the solvent was removed under vacuum and one organometallic product was extracted with diethyl ether (3 × 10 mL). Evaporation of volatiles afforded complex **4** as a red powder, which was washed twice with pentane (2 × 15 mL) (300 mg, 84% yield). Anal. Calcd for $C_{31}H_{36}Mo_2N_2S_3$: C, 51.4; H, 5.0; N, 3.9. Found: C, 51.7; H, 5.0; N, 3.9. IR (KBr, cm^{-1}): ν(CN) 1642 (m). ^{1}H NMR [$(CD_3)_2CO$]: δ 7.17−6.96 (m, 6H, $C_6H_3(CH_3)_2$), 6.00 (m, 1H, C_5H_4), 5.66 (m, 1H, C_5H_4), 5.29 (m, 1H, C_5H_4), 5.10 (s, 5H, C_5H_5), 5.00 (m, 1H, C_5H_4), 2.29 (s, 3H, CH_3(xyl)), 2.27 (s, 3H, CH_3(xyl)), 2.17 (s, 6H, CH_3(xyl)), 1.89 (s, 3H, SCH_3), 1.82 (s, 3H, SCH_3), 1.60 (s, 3H, SCH_3). ^{13}C{^{1}H}NMR (C_6D_6): δ 374.7 (Mo_2C), 156.5 (C═N), 147.3, 143.1, 137.2, 134.2, 128.8, 128.6, 123.4 ($C_6H_3(CH_3)_2$), 105.9, 103.6, 95.9 (C_5H_4), 92.0 (C_5H_5), 90.6, 84.3 (C_5H_4), 29.2 (SCH_3), 20.3, 19.4 ($C_6H_3(CH_3)_2$), 8.0 (SCH_3), 6.6 (SCH_3).

Reaction of [$Mo_2Cp_2(\mu$-SMe)$_3$(xylNC)$_2$](BF$_4$) (2b) with Hydroxide in the Presence of Excess RNC: Preparation of [$Mo_2Cp(\mu$-SMe)$_2$ \{μ-(η^5-C$_5$H$_4$)(xylN)CN(xyl)C\}\{μ-OCNHR\}] [R = xyl (5a1), Bu^t (5b1, 5b2)]. Method A. Complex **2b** (500 mg, 0.615 mmol) was treated with an excess of NaOH (201 mg) in the presence of 3 equiv of xylNC (242 mg) in refluxing tetrahydrofuran (50 mL) for 72 h. Then NaOH in excess and Na(BF$_4$) were eliminated by filtration, and the solvent was removed under reduced pressure. The resulting residue was washed three time with cold diethyl ether (3 × 15 mL), affording complex **5a1** as an orange powder (449 mg, 88% yield).

Complex **5b** (**5b2**) was obtained by a procedure like that described for the synthesis of **5a1**, by reacting **2b** (600 mg, 0.738 mmol) with an excess of NaOH (201 mg) in the presence of 3 equiv of Bu^{t}NC (V = 253 μL) in tetrahydrofuran (50 mL) and extracting compound **5b2** from the residue with diethyl ether (3 × 15 mL) at room temperature. Evaporation of the solvent afforded **5b2** as an orange powder (401 mg, 70% yield).

Method B. Complex **5b** can also be prepared as a mixture of two isomers, **5b1** and **5b2**, by a process like that described above, but using Me_4NOH in MeOH (2.2 M) instead of NaOH.

In a typical procedure, a mixture of **2b** (100 mg, 0.123 mmol) and an excess of Me_4NOH (V = 168 μL) in the presence of 3 equiv of Bu^{t}NC (V = 42 μL) in tetrahydrofuran (20 mL) was refluxed for 2 h. Insoluble materials were eliminated by filtration, the solvent was removed under pressure, and the residue was washed with cold (−60 °C) diethyl ether (3 × 15 mL) to give orange powders of **5b** (78.5 mg, 82% yield) as a mixture of two inseparable isomers, **5b1** and **5b2**, in a 11:1 ratio by chromatography. When the reaction was conducted under reflux for 72 h, compound **5b** was recovered in lower yields (71 mg, 74.5%), but isomers **5b1** and **5b2** were then obtained in a 1:10 ratio (^{1}H NMR analysis).

Method C. Complex **5b2** can also be synthesized in moderate yields (48%) by refluxing a tetrahydrofuran solution of the above mixture of **5b1** (92%) and **5b2** (8%) for 72 h (^{1}H NMR analysis only). However, this thermal reaction gave rise to appreciable decomposition of **5b** into an unidentified product (∼31%).

Orange crystals of **5a1**, **5b1**, and **5b2**, suitable for X-ray analysis, were obtained by crystallization at room temperature from a CH_2Cl_2 solution layered with diethyl ether. Analytical data for **5a1** have been confirmed by electrospray mass spectroscopy. The observed characteristic multiplets, caused by the polyisotopic nature of Mo, N, and S, allowed an unambiguous assignment of the detected signals: in particular, the upper parts of the spectrum of **5a1** were dominated by the molecular ion $[M]^+$. Full ^{13}C NMR assignments of compounds **5a1** and **5b** were based on ^{1}H−^{13}C and ^{1}H−^{15}N HMBC experiments.

5a1. Anal. Calcd for $C_{39}H_{43}Mo_2N_3OS_2$: C, 56.7; H, 5.25; N, 5.0. Found: C, 55.7; H, 5.4; N, 4.5. ESI-MS (*m*/*z*): 825.6 $[M]^+$. IR (KBr, cm^{-1}): ν(NH) 3412 (s), ν(CN) 1637 (s). ^{1}H NMR ($CDCl_3$): δ 7.36 (s, 1H, N*H*), 7.17−6.72 (m, 9H, $C_6H_3Me_2$), 5.22 (*p*t, J_{H-H} = 2.0 Hz, 2H, C_5H_4), 4.98 (s, 5H, C_5H_5), 4.49 (*p*t, J_{H-H} = 2.0 Hz, 2H, C_5H_4), 2.26, 2.21, 2.07 (s, 6H, CH_3(xyl)), 1.81 (s, 6H, SCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 369.3 (Mo_2C), 248.4 (Mo*C*O), 155.5 (C═N), 146.4, 141.8, 138.0, 135.5, 128.4, 128.3, 127.7, 127.4, 122.4, 122.2 ($C_6H_3Me_2$), 98.6 (C_5H_4), 92.8 (*Ci*(C_5H_4)), 92.7 (C_5H_5), 87.4 (C_5H_4), 20.5, 19.1, 18.3 (CH_3(xyl)), 15.3 (SCH_3).

5b. Anal. Calcd for $C_{35}H_{43}Mo_2N_3OS_2$: C, 54.05; H, 5.6; N, 5.4. Found: C, 54.5; H, 5.3; N, 4.8. IR (KBr, cm^{-1}), **5b1**: ν(NH) 3424 (s), ν(CN) 1643 (m); **5b2**: ν(NH) 3456 (vs), ν(CN) 1654 (s). ^{1}H NMR ($CDCl_3$), **5b1**: δ 7.11, 6.91, and 6.80 (m, 6H, $C_6H_3Me_2$), 5.65 (s, br, 1H, N*H*), 5.45 (s, 4H, C_5H_4), 4.93 (s, 5H, C_5H_5), 2.20, 2.15 (s, 6H, $C_6H_3Me_2$), 1.81 (s, 6H, SCH_3), 1.33 (s, 9H, CMe_3); **5b2**: δ 7.11, 6.85, and 6.77 (m, 6H, $C_6H_3Me_2$), 5.72 (*p*t, J_{H-H} = 2.2 Hz, C_5H_4), 5.65 (s, br, N*H*), 5.48 (*p*t, J_{H-H} = 2.2 Hz, 2H, C_5H_4), 4.77 (s, 5H, C_5H_5), 2.14 (s, 12H, $C_6H_3Me_2$), 1.80 (s, 6H, SCH_3), 1.34 (s, 9H, CMe_3). ^{1}H NMR (C_6D_6), **5b1**: δ 6.97, 6.87, and 6.79 (m, 6H, $C_6H_3Me_2$), 5.57 (*p*t, J_{H-H} = 2.2 Hz, 2H, C_5H_4), 5.55 (s, 1H, N*H*), 5.15 (*p*t, J_{H-H} = 2.2 Hz, 2H, C_5H_4), 5.00 (s, 5H, C_5H_5), 2.39, 2.20 (s, 6H, $C_6H_3Me_2$), 1.98 (s, 6H, SCH_3), 1.24 (s, 9H, CMe_3); **5b2**: δ 6.99, 6.95, and 6.84 (m, 6H, $C_6H_3Me_2$), 5.50 (*p*t, J_{H-H} = 2.2 Hz, 2H, C_5H_4), 5.50 (s concealed, 1H, N*H*), 5.38 (*p*t, J_{H-H} = 2.2 Hz, 2H, C_5H_4), 4.82 (s, 5H, C_5H_5), 2.34, 2.18 (s, 6H, $C_6H_3Me_2$), 1.98 (s, 6H, SCH_3), 1.25 (s, 9H, CMe_3). ^{13}C{^{1}H} NMR ($CDCl_3$), **5b1**: δ 362.7 (Mo_2C), 242.9 (Mo*C*O), 155.3 (C═N), 146.9, 142.1 (*Ci* (xyl)), 135.4, 128.2, 128.1, 127.8, 127.75, 127.6, 122.6 ($C_6H_3Me_2$), 112.5 (*Ci* (C_5H_4)), 100.2 (C_5H_4), 92.5 (C_5H_5), 85.0 (C_5H_4), 53.5 (CMe_3), 30.6 (CMe_3), 19.2, 18.25 (CH_3(xyl)), 15.3 (SCH_3); **5b2**: 366.4 (Mo_2C), 242.7 (Mo*C*O), 156.0 (C═N), 147.2, 142.9 (*Ci* (xyl)), 135.7 ($C_6H_3Me_2$), 128.0−127.5 ($C_6H_3Me_2$), 106.6 (*Ci* (C_5H_4)), 100.1 (C_5H_4), 91.6 (C_5H_5), 88.4 (C_5H_4), 53.7 (CMe_3), 30.3 (CMe_3), 19.0, 18.5 (CH_3(xyl)), 15.4 (SCH_3).

Reaction of [$Mo_2Cp(\mu$-SMe)$_3$\{μ-(η^5-C$_5$H$_4$)(xylN)CN(xyl)C\}] (4) with Sodium Hydroxide in the Presence of RNC (R = xyl, Bu^t): Formation of 5a1 and 5b2. Complex **4** (100 mg, 0.138 mmol) was treated with an excess of NaOH (201 mg) in the presence of 2 equiv of RNC [R = xyl (32.5 mg), Bu^t (V = 31 μL)] in refluxing tetrahydrofuran (30 mL) for 24 h. After filtration the solvent was removed under reduced pressure and the residue washed three time with cold diethyl ether (3 × 15 mL), affording orange powders of **5a1** (60.5 mg, 53% yield) or **5b2** (50 mg, 55% yield).

Reaction of 2b with Tetramethylammonium Hydroxide in the Presence of xylNC: Preparation of [$Mo_2Cp(\mu$-SMe)$_2$\{μ-(η^5-C$_5$H$_4$)(xylN)CN(xyl)C\}\{μ-OCNMe xyl\}] (6a). To a tetrahydrofuran solution (50 mL) of [$Mo_2Cp_2(\mu$-SMe)$_3$(xylNC)$_2$](BF$_4$) (**2b**)

Table 2. Crystallographic Data for Complexes 5a1, 5b1, 5b2, 6a, 6b, and 7

	5a1	5b1	5b2	6a	6b	7
formula	$C_{39}H_{43}Mo_2N_3OS_2$	$C_{35}H_{43}Mo_2N_3OS_2$	$C_{35}H_{43}Mo_2N_3OS_2$	$C_{40}H_{45}Mo_2N_3O_{1.14}S_2$	$C_{41}H_{47}Mo_2N_3OS_2$	$C_{22}H_{29}Mo_2NOS_3$
M_r	825.76	777.72	777.72	842.10	853.82	611.52
cryst size/mm	0.30 × 0.23 × 0.03	0.08 × 0.06 × 0.04	0.50 × 0.40 × 0.05	0.40 × 0.10 × 0.08	0.20 × 0.20 × 0.05	0.60 × 0.20 × 0.05
syst	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$Pca2_1$ (see note b)	$P2_1/c$	$P2_1/c$	$P2_1/a$
a/Å	15.8718 (15)	9.9768(9)	16.2946(8)	8.3600 (1)	12.9957 (10)	15.6163 (3)
b/Å	14.3618 (9)	13.2860(16)	13.4907(6)	16.9560(2)	18.5383(14)	8.9018(2)
c/Å	16.2998(16)	13.9137(18)	16.0487(7)	26.1569(4)	16.2894(15)	16.8896(4)
α/deg		77.796(11)				
β/deg	95.892(9)	86.048(9)		94.300(1)	95.627(7)	93.291(1)
γ/deg		68.941(10)				
V/Å	3695.9(6)	1682.2(3)	3527.9(3)	3697.36(8)	3905.5(6)	2344.01(9)
Z	4	2	4	4	4	4
D_c/Mg m^{-3}	1.484	1.535	1.464	1.513	1.452	1.351
T/K	170	170	300	120	170	120
μ/mm^{-1}	0.826	0.902	0.860	0.827	0.784	1.351
range of θ/deg	3.1−20.6	3.3−26.4	3.3−31.2	3.0−25.0	3.3−20.8	2.6−28.5
N_{measd}[a]	9730	8920	35546	39623	19626	34466
N_{unique}[a]/N_{params}	2545/396	5516/397	8842/397	6477/451	4068/442	5842/271
R_{int}	0.080	0.052	0.048	0.148	0.107	0.116
R_1 ($I > 2\sigma(I)$], N_{obs}[a]	0.0807, 2176	0.0482, 3592	0.0427, 6223	0.0469, 4520	0.0650, 2923	0.0501, 3945
R_1 (all data)	0.0897	0.0894	0.0626	0.0799	0.106	0.0879
wR_2 (all data)	0.226	0.101	0.099	0.118	0.122	0.135
goodness of fit on F^2	1.089	0.956	0.952	1.028	1.107	1.081
$\Delta\rho_{max.}$, $\Delta\rho_{min.}$/e Å^{-3}	1.82, −0.91	1.21, −0.67	1.44, −0.53	0.70, −0.61	0.49, −0.40	1.39, −1.07

[a] N_{measd} = total number of intensity measurements; N_{unique} = number of intensity measurements after averaging according to point symmetry; N_{obs} = number of these with intensities $I > 2\sigma(I)$. [b] Flack parameter = −0.09(4).

(218 mg, 0.268 mmol) were added 3 equiv of Me_4NOH-MeOH (2.2 M) (V = 383 μL) and 2 equiv of xylNC (70 mg), and the mixture was heated under reflux for ca. 72 h. The solution was then filtered to remove $Me_4N(BF_4)$. After evaporation of the solvent (THF), **6a** was extracted from the residue with diethyl ether (3 × 15 mL). Evaporation of volatiles afforded **6a** as an analytically pure, orange solid (146 mg, 64% yield). Orange crystals of **6a**, suitable for X-ray analysis, were obtained by crystallization at −20 °C from a diethyl ether solution. Anal. Calcd for $C_{40}H_{45}Mo_2N_3OS_2$: C, 57.2; H, 5.4; N, 5.0. Found: C, 57.8; H, 5.5; N, 5.0. IR (KBr, cm^{-1}): ν(CN) 1639 (s). ^{1}H NMR ($CDCl_3$): δ 7.18−6.64 (m, 9H, $C_6H_3Me_2$), 5.15 (m, 2H, C_5H_4), 4.99 (s, 5H, C_5H_5), 4.36 (m, 2H, C_5H_4), 3.09 (s, 3H, N−CH_3), 2.20 (s, 12H, CH_3(xyl)), 2.06 (s, 6H, CH_3 (xyl)), 1.72 (s, 6H, SCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 336.8 (Mo$_2$*C*), 242.4 (Mo*C*O), 155.4 (*C*═N), 146.8, 144.9, 142.0, 137.8, 135.6, 128.8, 128.6, 128.4, 128.3, 128.2, 127.7, 127.6, 127.5, 122.6, 114.4 ($C_6H_3Me_2$), 98.3 (C_5H_4), 92.9 (C_5H_4), 92.7 (*Ci* (C_5H_4)), 87.0 (C_5H_4), 30.9 (N*C*H$_3$), 19.7, 18.9, 18.2 (*C*H$_3$(xyl)), 15.8 (S*C*H$_3$).

Reaction of [Mo$_2$Cp(μ-SMe)$_2$\{μ-(η^5-C$_5$H$_4$)(xylN)CN(xyl)C\}-\{μ-OCNHxyl\}] (5a1) with an Alkylating Reagent in the Presence of Sodium Hydroxide: Synthesis of [Mo$_2$Cp(μ-SMe)$_2$\{μ-(η^5-C$_5$H$_4$)(xylN)CN(xyl)C\}\{μ-OCNRxyl\}] [R = Et (6b), Bu^n (6c)]. To a tetrahydrofuran solution (50 mL) of **5a1** (200 mg, 0.242 mmol) were added 2 equiv of R_4NBr [R = Et (102 mg), Bu^n (156 mg)] and an excess of NaOH (201 mg), and the mixture was heated under reflux for 72 h. The solution was then filtered to remove NaOH in excess. After evaporation of the volatiles the product was extracted from the oily residue with diethyl ether (3 × 15 mL) at room temperature. Evaporation of the solvent afforded **6b** or **6c** as an orange powder (**6b**: 184 mg, 89% yield; **6c**: 100 mg, 47% yield). Crystallization at −20 °C from a diethyl ether solution afforded crystals of **6b** suitable for X-ray analysis. Despite several attempts no reliable analyses are available for **6c**; however the complex has been satisfactorily characterized by its NMR spectroscopy.

6b. Anal. Calcd for $C_{41}H_{47}Mo_2N_3OS_2$: C, 57.6; H, 5.5; N, 4.9. Found: C, 56.7; H, 5.4; N, 5.1. ^{1}H NMR ($CDCl_3$): δ 7.30−6.64 (m, 9H, $C_6H_3Me_2$), 5.14 (t, 2H, C_5H_4), 4.99 (s, 5H, C_5H_5), 4.34 (t, 2H, C_5H_4), 3.70 (q, 2H, −CH_2CH$_3$), 2.25 (s, 6H, CH_3(xyl)), 2.21 (s, 6H, CH_3(xyl)), 2.06 (s, 6H, CH_3(xyl)), 1.74 (s, 6H, SCH_3), 1.02 (t, 3H, −CH$_2$CH_3).

6c. ^{1}H NMR ($CDCl_3$): δ 7.16−6.67 (m, 9H, C_6H_3), 5.14 (m, 2H, C_5H_4), 4.98 (s, 5H, C_5H_5), 4.32 (m, 2H, C_5H_4), 3.56 (t, 2H, −CH_2−(CH$_2$)$_2$−CH$_3$), 2.24 (s, 6H, CH_3(xyl)), 2.20 (s, 6H, CH_3(xyl)), 2.06 (s, 6H, CH_3(xyl)), 1.73 (s, 6H, SCH_3), 1.41 and 1.28 (m, 2H, −CH$_2$−(CH_2)$_2$−CH$_3$), 0.83 (t, 3H, −(CH$_2$)$_3$−CH_3).

Reaction of [Mo$_2$Cp$_2$(μ-SMe)$_3$(MeCN)(xylNC)](BF$_4$) (3) with Sodium Hydroxide: Preparation of [Mo$_2$Cp$_2$(μ-SMe)$_3$\{μ-(η^1-(O),η^1(C)-OCNHxyl\}] (7). Solid NaOH in excess (201 mg, 26 equiv) was added to a tetrahydrofuran solution (30 mL) of compound **3** (140 mg, 0.193 mmol). The mixture was heated under reflux for 24 h, and the solution was then filtered to remove excess NaOH. Removal of the solvent from the filtrate under vacuum yielded a red residue, from which **7** was extracted with diethyl ether (3 × 15 mL). Solvent was then evaporated to dryness and the resulting residue washed with cold pentane (3 × 15 mL) to give compound **7** (110 mg, 93% yield) as a red powder. Red crystals of the complex, suitable for X-ray analysis, were obtained by crystallization at −20 °C from a diethyl ether solution. Anal. Calcd for $C_{22}H_{29}Mo_2NOS_3$: C, 43.2; H, 4.8; N, 2.3. Found: C, 43.1; H, 4.8; N, 2.3. IR (KBr, cm^{-1}): ν(NH) 3437 (m). ^{1}H NMR ($CDCl_3$): δ 6.90 (s, 3H, $C_6H_3Me_2$), 6.70 (s, 1H, N*H*), 5.42 (s, 5H, C_5H_5), 5.15 (s, 5H, C_5H_5), 2.06 (s, 6H, CH_3(xyl)), 1.67 (s, 3H, SCH_3), 1.55 (s, 3H, SCH_3), 1.47 (s, 3H, SCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 240.8 (Mo*C*O), 135.7 (*Ci*(xyl)), 134.4 (*Co*(xyl)), 127.9 (*Cm*(xyl)), 125.5 (*Cp*(xyl)), 92.3 (C_5H_5), 90.5 (C_5H_5), 20.7 (S*C*H$_3$), 19.6 (*C*H$_3$(xyl)), 9.9 (S*C*H$_3$).

X-ray Structural Determinations. Measurements for compounds **5a1**, **5b1**, **5b2**, and **6b** were made in Brest on a Oxford Diffraction X-Calibur-2 CCD diffractometer equipped with a jet cooler device. Measurements for **6a** and **7** were made in Glasgow on a Nonius Kappa CDD diffractometer. Graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) was used in all experiments. The structures were solved and refined by standard procedures.[23] H atoms were positioned using stereochemical considerations, the orientations of methyl groups being initially obtained from difference maps; they then rode on their parent C or N atoms. In **7** the N5-bonded H atom was freely refined. For **5a1** and **6b** all crystal specimens were of poor quality and gave only weak, low-angle

diffraction patterns; the results of these analyses, in particular that of **5a1**, are in consequence appreciably less precise than the others. In **6a** an isolated site is attributed to the O atom [occupancy = 0.143(7)] of a water molecule and the CH_3 group attached to S2 is distributed over alternative sites, suggesting 0.82:0.18(1) *syn*:*anti* disorder. Selected bond lengths and angles are given in Table 1 and the caption to Figure 5; pertinent crystal data, in Table 2.

(23) Programs used: (a) Sheldrick, G. M. *SHELX 97*; University of Göttingen: Göttingen, Germany, 1998. (b) Farrugia, L. J. *WinGX*−A Windows Program for Crystal Analysis. *J. Appl. Crystallogr.* **1999**, *32*, 837. (c) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *SIR 92*−A program for crystal structure solution. *J. Appl. Crystallogr.* **1993**, *26*, 343. (d) *CrysAlis CCD and RED*, Version 1.171.28 cycle 4 beta; Oxford Diffraction Ltd, 2005.

Acknowledgment. We are grateful to Dr. F. Michaud for the crystallographic measurements of **5a1**, **5b1**, **5b2**, and **6b**, and to Dr. R. Pichon and N. Kervarec for recording two-dimensional NMR spectra on a Bruker DRX 500 (500 MHz) spectrometer. We thank the CNRS, the EPSCR, and the Universities of Glasgow and Brest for financial support. The Ministère de l'Enseignement Supérieur et de la Recherche du Gabon is acknowledged for providing studentships (W.-S.O.).

Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060383V