

μ -Alkylidyne and μ -Alkylidene Complexes from a Bridging Side-on Vinylidene Sulfur-Rich Dimolybdenum Precursor

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Summary: Reaction of the μ -vinylidene complexes $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-SMe})_3(\mu\text{-}\eta^1\text{-}\eta^2\text{-C=CHR})](\text{BF}_4)$ (**1**; R = Tol (**1a**), *n*-Pr (**1b**)) with NaBH_4 produced the μ -alkylidyne derivatives $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-SMe})_3(\mu\text{-CCH}_2\text{R})]$ (**2**; R = Tol (**2a**), *n*-Pr (**2b**)) in good yields. Upon treatment with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ **2a** and **2b** were readily converted into the μ -alkylidene species $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-SMe})_3(\mu\text{-}\eta^1\text{-}\eta^2\text{-CHCH}_2\text{R})](\text{BF}_4)$ (R = Tol (**3a**), *n*-Pr (**3b**)). NMR studies on these μ -alkylidene complexes revealed α -agostic interactions.

The bis(cyclopentadienyl) bimetallic auxiliary fragment $\{\text{M}_2\text{Cp}'_2\}$ ($\text{Cp}' = \eta^5\text{-C}_5\text{R}_5$) continues to attract interest.¹ For example, we have recently shown that terminal alkynes $\text{HC}\equiv\text{CR}$ can be activated by the $\{\text{Mo}^{\text{III}}_2\text{Cp}_2\}$ compound $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\text{MeCN})_2](\text{BF}_4)$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) and that the key isomerization process is the conversion of the terminal alkyne into a $\text{C}=\text{CHR}$ vinylidene ligand. This process is recognized as an important mode of activation of terminal alkynes by metallic species.^{2,3} Moreover, we reported that this tris(thiolato)-bridged compound induced C–C and C–S couplings in the presence of excess alkyne and that a thio-alkenyl species, namely $\{[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_2(\mu\text{-CR}'=\text{CRSMe})]^+\}$, was the most probable intermediate in these transformations, rather than the well-defined $\eta^1\text{-}\eta^2$ -vinylidene derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\mu\text{-}\eta^1\text{-}\eta^2\text{-C=CHR})](\text{BF}_4)$ (**1**), which appears to be a more stable species than its alkyne adduct precursor $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\mu\text{-HC}\equiv\text{CR})](\text{BF}_4)$.³ The relative scarcity of complexes featuring $\{\text{M}_2(\mu\text{-}\eta^1\text{-}\eta^2\text{-C=CHR})\}$ groups⁴ and the small number of systematic studies of their behavior prompted us to investigate the reactivity of the readily

accessible vinylidene derivatives $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\mu\text{-}\eta^1\text{-}\eta^2\text{-C=CHR})](\text{BF}_4)$ (**1**) to see if $\eta^1\text{-}\eta^2$ coordination induces original reactivity in the vinylidene moiety or is instead a dead end in its transformation pathway. Accordingly, we are currently studying reactions of **1** with various electrophilic or nucleophilic reagents. We describe here our preliminary results concerning the formation of μ -alkylidyne derivatives $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\mu\text{-CCH}_2\text{R})]$ (**2**; R = Tol (**2a**), *n*-Pr (**2b**)) through formal addition of hydride to the outer carbon atom of the vinylidene bridge in **1** (R = Tol (**1a**), *n*-Pr (**1b**)). Furthermore, *face* protonation⁵ of the alkylidyne bridge in **2** results in the formation of μ -alkylidene derivatives $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\mu\text{-}\eta^1\text{-}\eta^2\text{-CHCH}_2\text{R})](\text{BF}_4)$ (**3**; R = Tol (**3a**), *n*-Pr (**3b**)).

The reaction of $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\mu\text{-}\eta^1\text{-}\eta^2\text{-C=CHR})](\text{BF}_4)$ (R = Tol (**1a**), *n*-Pr (**1b**)) with NaBH_4 (excess) in acetonitrile at room temperature readily afforded deep blue solutions from which the compounds $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\mu\text{-CCH}_2\text{R})]$ (**2**; R = Tol (**2a**), *n*-Pr (**2b**)) were isolated in good yields as blue powders (Scheme 1).⁶ Compounds **2** were characterized by elemental analyses and NMR spectroscopy. Their ¹H NMR (CDCl_3) spectra were typical for complexes with a $\{\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3\}$ core; they exhibited a single resonance for the two cyclopentadienyl ligands and three peaks for the three

(5) Torraca, K. E.; Ghiviriga, I.; McElwee-White, L. *Organometallics* **1999**, *18*, 2262 and references therein.

(6) Preparation of **2**: a solution of complex **1** (0.2 g; 0.30 mmol of **1a**, 0.32 mmol of **1b**) in acetonitrile (10 mL) was stirred in the presence of an excess of NaBH_4 (3 equiv; 0.034 g (**2a**), 0.037 g (**2b**)) for a few minutes at room temperature. The solution turned readily from blue to deep blue. The solvent was then removed, and the residue was extracted with diethyl ether (40 mL). The extracts were evaporated to dryness, and the residue was chromatographed on a silica gel column. Elution with hexane– CH_2Cl_2 (4:1) afforded a blue solution of **2**, which was evaporated under vacuum. After they were washed with cold pentane, **2a** and **2b** were obtained as blue powders (**2a**, 0.148 g, 85% yield; **2b**, 0.111 g, 65% yield). **2a** (R = Tol): ¹H NMR (CDCl_3 , 25 °C; δ): 7.10, 6.90 (2 × d, $J_{\text{HH}} = 7.8$ Hz, 2 × 2H, $\text{CH}_3\text{C}_6\text{H}_4$), 5.33 (s, 10H, C_5H_5), 5.00 (s, 2H, CCH_2R), 2.36 (s, 3H, $\text{CH}_3\text{C}_6\text{H}_4$), 1.78 (s, 3H, SCH_3), 1.70 (s, 3H, SCH_3), 1.41 (s, 3H, SCH_3); ¹³C{¹H} NMR (CDCl_3 , 25 °C; δ): 445.1 (CCH_2R), 129.1, 129.3, 135.8, 140.4 ($\text{CH}_3\text{C}_6\text{H}_4$), 95.5 (C_5H_5), 65.4 (CCH_2R), 31.9 (SCH_3), 21.6 ($\text{CH}_3\text{C}_6\text{H}_4$), 8.3 (SCH_3), 7.2 (SCH_3). Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{Mo}_2\text{S}_3$: C, 45.5; H, 4.8. Found: C, 45.2; H, 4.6. **2b** (R = *n*-Pr): ¹H NMR (CDCl_3 , 25 °C; δ): 5.49 (s, 10H, C_5H_5), 3.92 (m, 2H, CCH_2R), 1.78 (s, 3H, SCH_3), 1.59 (s, 3H, SCH_3), 1.35–1.45 (m, 4H, $(\text{CH}_2)_2$), 1.39 (s, 3H, SCH_3), 0.95 (t, $J_{\text{HH}} = 7.1$ Hz, 3H, $(\text{CH}_2)_2\text{CH}_3$); ¹³C{¹H} NMR (CDCl_3 , 25 °C; δ): 449.0 (CCH_2R), 93.2 (C_5H_5), 60.0 (CCH_2R), 30.7 (CH_2), 22.5 (CH_2), 30.6 (SCH_3), 14.1 ($(\text{CH}_2)_2\text{CH}_3$), 7.9 (SCH_3), 6.7 (SCH_3). Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{Mo}_2\text{S}_3$: C, 40.6; H, 5.2. Found: C, 40.9; H, 5.4.

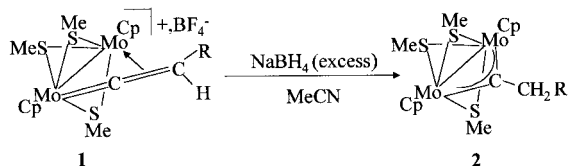
(1) For recent examples and reviews: (a) Bridgeman, A. J.; Mays, M. J.; Woods, A. D. *Organometallics* **2001**, *20*, 2076. (b) Hobert, S. E.; Bruce, C.; Noll, B. C.; Rakowski DuBois, M. *Organometallics* **2001**, *20*, 1370. (c) Takagi, Y.; Matsuzaka, H.; Ishii, Y.; Hidai, M. *Organometallics* **1997**, *16*, 4445. (d) Alvarez, M. A.; Garcia, G.; Garcia, M. E.; Riera, V.; Ruiz, M. A.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1999**, *18*, 4509. (e) Adams, H.; Allott, C.; Bancroft, M. N.; Morris, M. J. *J. Chem. Soc., Dalton Trans.* **2000**, 4145. (f) Curtis, M. D. *Polyhedron* **1987**, *6*, 759. (g) Winter, M. J. *Adv. Organomet. Chem.* **1989**, *29*, 101. (h) Rakowski DuBois, M. *Polyhedron* **1997**, *16*, 3089. (i) Hidai, M.; Mizobe, Y.; Matsuzaka, H. *J. Organomet. Chem.* **1994**, *473*, 1.

(2) *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; Wiley-VCH: Weinheim, Germany, 1995.

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

(4) (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) El Amouri, H.; Gruselle, M. *Chem. Rev.* **1996**, *96*, 1077.

Scheme 1



SMe bridges.⁷ Instead of the characteristic ¹H NMR signal of the =C_βHR group in **1**, between 6 and 8 ppm,³ two protons were detected as a singlet (**2a**) or a multiplet (**2b**) between 4 and 5 ppm, suggesting that a hydride anion had been added to the outer carbon atom (C_β) of the vinylidene group (=C_α=C_βHR) to give a new hydrocarbyl bridge. The ¹³C NMR spectra of **2** displayed a resonance at extreme low field, ca. 445–450 ppm, which was assigned to the carbon atom bonded to the two molybdenum atoms.⁸ Two-dimensional heteronuclear inverse-correlation ¹H–¹³C experiments (HMQC, HMBC) allowed further characterization of **2**. Correlation peaks between the CH₂ protons at 5.00 ppm and both the carbon atom at 445.1 ppm (²J_{CH}) and the carbon atoms at 140.4 ppm (²J_{CH}) and 129.1 ppm (³J_{CH}) of the tolyl group were detected for **2a**, in agreement with a CCH₂R backbone. The equivalence of Cp groups suggested that the alkylidyne bridge is symmetrically bonded to the two molybdenum atoms and that the π-Mo–C overlap, required by electron-counting rules, is delocalized through the Mo–C–Mo bridge. These conclusions were confirmed by X-ray analysis of a single crystal of **2b**, obtained by cooling a pentane solution to –15 °C (Figure 1).⁹ This showed that **2b** contains a μ-CCH₂-*n*-Pr group which is bonded through one carbon atom, C(4), to the two molybdenum atoms of a {Mo₂Cp₂(μ-SMe)₃} core. The Mo–C(4) distances (1.994(2) and 1.996(2) Å) are equal to within experimental error. They lie between the value of 1.894(5) Å for the formally double Mo=C in the vinylidene compound [Mo₂Cp₂(μ-SMe)₃(μ-η¹:η²-C=CHTol)](BF₄) (**1a**) 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)].³ The Mo–C(4) lengths therefore are in accord with a symmetrical coordination of the alkylidyne group through Mo–C bonds of order 1.5. The C(4)–C(5) bond length (1.492(2) Å) is close to that expected for a C_{sp}²–C_{sp}³ single bond and is substantially longer than corresponding distances in

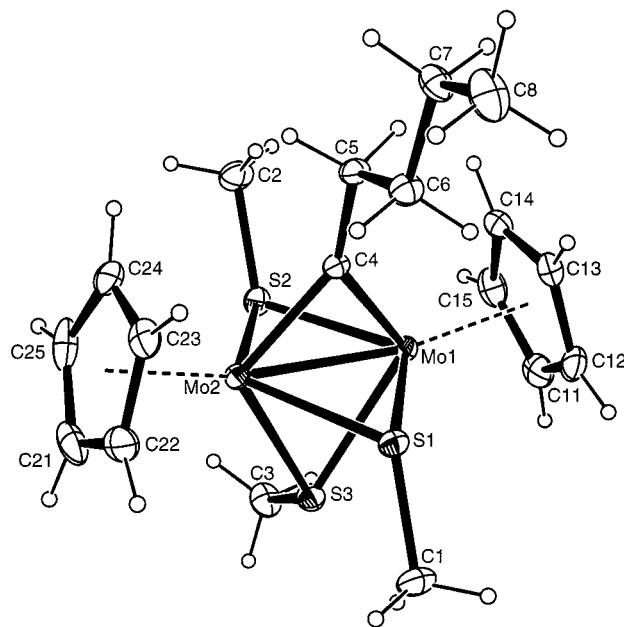


Figure 1. View of a molecule of [Mo₂Cp₂(μ-SMe)₃(μ-CCH₂-*n*-Pr)] (**2b**) showing 20% probability ellipsoids. Hydrogen atoms are drawn as spheres of arbitrary radius. Selected bond lengths (Å) and angles (deg): Mo(1)–C(4) = 1.9940(17), Mo(2)–C(4) = 1.9958(17), Mo(1)–C(14) = 2.277(2), Mo(1)–C(13) = 2.284(2), Mo(1)–C(15) = 2.343(2), Mo(1)–C(12) = 2.345(2), Mo(1)–C(11) = 2.398(2), Mo(2)–C(23) = 2.278(2), Mo(2)–C(24) = 2.279(2), Mo(2)–C(22) = 2.337(2), Mo(2)–C(25) = 2.345(2), Mo(2)–C(21) = 2.383(2), C(4)–C(5) = 1.492(5), C(5)–C(6) = 1.535(3), C(6)–C(7) = 1.516(3), C(7)–C(8) = 1.518(3), Mo(1)–Mo(2) = 2.5846(2); Mo(1)–C(4)–Mo(2) = 80.75(6), C(4)–Mo(1)–C(14) = 92.9(1), C(4)–Mo(1)–C(13) = 91.9(1), C(4)–Mo(1)–C(15) = 124.8(1), C(4)–Mo(1)–C(12) = 123.2(1), C(4)–Mo(1)–C(11) = 148.8(1), C(4)–Mo(2)–C(23) = 93.3(1), C(4)–Mo(2)–C(24) = 91.1(1), C(4)–Mo(2)–C(22) = 125.7(1), C(4)–Mo(2)–C(25) = 121.6(1), C(4)–Mo(2)–C(21) = 148.4(1), C(5)–C(4)–Mo(1) = 138.57(14), C(5)–C(4)–Mo(2) = 140.45(14), C(4)–C(5)–C(6) = 113.51(15), C(7)–C(6)–C(5) = 112.06(17), C(8)–C(7)–C(6) = 113.1(2), C(4)–C(5)–C(6)–C(7) = 174.6(2), C(5)–C(6)–C(7)–C(8) = 176.9(2)°.

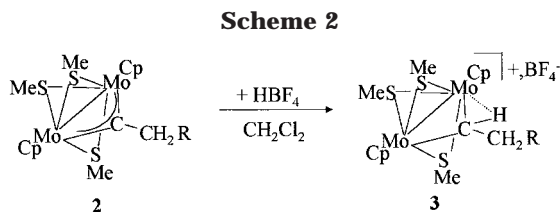
[Mo₂Cp₂(μ-SMe)₃(μ-η¹:η²-C≡CPh)] (1.238(4) Å, C≡C) and [Mo₂Cp₂(μ-SMe)₃(μ-η¹:η²-C=CHTol)](BF₄) (1.356(6) Å, C=C).³ **2b** appears to be the first structurally characterized alkylidyne–molybdenum complex; however, the geometry of the W₂(μ₂-CCR₃) unit is well-established^{10a} and the coordination of C(4) in **2b** closely resembles that of the corresponding atoms in, for example, [(C₅Me₅)WMe(μ₂-CCH₃)₂](μ-W–C, 1.95(1) and 1.97(1) Å; C–CH₃, 1.54 Å).^{10b} The angles at C(4) (C(5)–C(4)–Mo, 138.6(1) and 140.5(1)°; Mo–C(4)–Mo, 80.8(1)°) show the deviations from sp² hybridization implied by the Mo–C and Mo–Mo bond lengths and broadly agree with those found in [(C₅Me₅)WMe(μ₂-CCH₃)₂]. Addition of H[–] to the C_β atom of the C_α=C_βHR bridge in **1** gives a product where C(4) carries a staggered *n*-butyl chain of unexceptional geometry (Figure 1). It is striking that the Cp ligands bend away from S(3) to adopt a *cis* disposition relative to the Mo–Mo axis (Cp–Mo–Mo, 168.7(1) and 168.1(1)°, where Cp is the ring centroid)

(7) Pétilion, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Coord. Chem. Rev.* **1998**, *178*–180, 203.

(8) For examples of μ-alkylidyne ¹³C NMR chemical shifts: (a) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Marder, S. R.; Austin, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 4043. (b) Casey, C. P.; Gohdes, M. A.; Meszaros, M. W. *Organometallics* **1986**, *5*, 196. (c) Jeffery, J. C.; Ruiz, M. A.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1988**, 1131. (d) Chi, Y.; Shapley, J. R. *Organometallics* **1985**, *4*, 1900. (e) Farrugia, L. J.; Jeffery, J. C.; Marsden, C.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 51. (f) Green, M.; Howard, J. A. K.; James, A. P.; Jelfs, A. N. de M.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 81. (g) Byrne, P. G.; Garcia, M. E.; Tran-Huy, N. H.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 1243. (h) Delgado, E.; Hein, J.; Jeffery, J. C.; Ratermann, A. L.; Stone, F. G. A.; Farrugia, L. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1191. (i) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135.

(9) Crystallographic data for [Mo₂Cp₂(μ-SMe)₃(μ-CCH₂-*n*-Pr)] (**2b**): C₁₈H₂₈Mo₂S₃, *M*_r = 532.46, triclinic, space group *P*1, *a* = 7.9604(4) Å, *b* = 10.7934(6) Å, *c* = 12.1014(7) Å, α = 91.874(5)°, β = 102.708(4)°, γ = 90.914(5)°, *V* = 1013.5(1) Å³, *Z* = 2, *D*_c = 1.745 g cm^{–3}, μ(Mo Kα) = 1.543 mm^{–1}. For all 6148 unique, absorption-corrected intensities with θ(Mo Kα) < 30.4°, *R*(*F*) = 0.025 and *R*_w(*F*²) = 0.067 after refinement of 213 parameters. |Δρ| < 1.16 e Å^{–3}.

(10) (a) A search of the Cambridge Structural Database (version 521, 233 218 entries) revealed 13 entries for W₂(μ₂-CCR₃) complexes. (b) Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santarsiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282.



in preference to the usual linear Cp–Mo–Mo–Cp disposition.⁷ This feature does not appear to have a steric origin. It may indicate that the alkylidyne ligand exerts a weak trans influence which requires Mo(1)–C(11) and Mo(2)–C(21) to be the longest π -Mo–C(Cp) bonds. Finally, the length of the Mo–Mo single bond in **2b** (2.585(1) Å) is typical of values for other [Mo₂Cp₂(μ -SMe)₃(μ -X)] complexes⁷ and the methyl groups of the thiolate bridges have an anti orientation.

Addition of HBF₄·Et₂O to a solution of **2** in dichloromethane readily afforded brownish red solutions of the complexes [Mo₂Cp₂(μ -SMe)₃(μ - η^1 : η^2 -CHCH₂R)](BF₄) (**3**; R = Tol (**3a**), *n*-Pr (**3b**)) (Scheme 2).¹¹ The structure of **3** could not be established by X-ray analysis since, even when the counterion was varied (BF₄⁻, BPh₄⁻), single crystals of diffraction quality were not obtained. Nevertheless, the NMR data clearly indicated that **3** results from a *face-addition*⁵ of a proton to a Mo–C bond in **2**. The ¹H NMR spectra displayed, apart from features expected for a {Mo₂Cp₂(μ -SMe)₃} core, a signal attributable to a methylene group (observed between 3.0 and 5.0 ppm as a doublet with a coupling constant (*J*_{HH}) of 4.0 Hz) and a strongly shielded, high-field resonance (appearing as a broad, unresolved triplet at ca. –5.5 ppm) ascribed to a single proton. Two-dimensional ¹H–¹H experiments showed correlation peaks between these resonances. This coupling and the high-field shift strongly suggest the presence of a {RCH₂C(μ -H)Mo} backbone featuring an α -agostic interaction.^{5,12} ¹³C NMR and HMQC and HMBC ¹H–¹³C experiments yielded additional information which supports this suggestion. The HMQC ¹H–¹³C spectrum of **3a** indicated that the additional proton at –5.71 ppm was attached to a deshielded carbene-like carbon atom which resonates at 338 ppm. The value of the coupling constant ¹*J*_{CH} (66.0 Hz), determined by recording the ¹³C NMR spectrum of **3b** without ¹H decoupling, lies in the range of *J*_{CH} values typical of agostic alkylidyne complexes.^{5,12}

(11) Preparation of **3**: to a solution of **2** (0.1 g; 0.17 mmol of **2a**, 0.19 mmol of **2b**) in CH₂Cl₂ (10 mL) was added 1 equiv of H[BF₄]·Et₂O. The blue solution readily turned brownish red. The volume was then reduced under vacuum and diethyl ether was added to precipitate a brownish red powder of **3** (**3a**, 0.965 g, 85% yield; **3b**, 0.101 g, 86% yield). **3a** (R = Tol): ¹H NMR (CD₂Cl₂, –10 °C; δ) 7.08, 6.76 (2 × d, *J*_{HH} = 7.7 Hz, 2 × 2H, CH₃C₆H₄), 5.98 (s, 10H, C₅H₅), 4.51 (d, *J*_{HH} = 4.0 Hz, 2H, CHCH₂R), 2.30 (s, 3H, CH₃C₆H₄), 2.02 (s, 3H, SCH₃), 1.90 (s, 3H, SCH₃), 1.84 (s, 3H, SCH₃), –5.71 (t, br, 1H, CHCH₂R); ¹³C{¹H} NMR (CD₂Cl₂, –10 °C; δ) 338.0 (CHCH₂R), 137.8, 137.5, 129.9, 128.3 (CH₃C₆H₄), 98.7 (C₅H₅), 61.0 (CCH₂R), 37.9 (SCH₃), 21.1 (CH₃C₆H₄), 13.1 (SCH₃), 10.5 (SCH₃). Elemental analyses for **3a** were obtained under argon on four independently prepared samples (NMR grade) and allowed to obtain reproducible values, showing the presence of dichloromethane in the microcrystalline powder of **3a**. Anal. Calcd for C₂₂H₂₉BF₄Mo₂S₃·0.75CH₂Cl₂: C, 37.3; H, 4.2. Found: C, 37.4; H, 4.2. **3b** (R = *n*-Pr): ¹H NMR (CDCl₃, 25 °C; δ) 6.16 (s, 10H, C₅H₅), 3.45 (m, 2H, CHCH₂R), 2.01 (s, 3H, SCH₃), 1.89 (s, 3H, SCH₃), 1.47 (s, 3H, SCH₃), 1.5–1.0 (m, 2 × 2H, (CH₂)₂CH₃), 0.86 (t, *J*_{HH} = 7.2 Hz, 3H, (CH₂)₂CH₃), –5.41 (1H, m, CHCH₂R); ¹³C{¹H} NMR (CDCl₃, 25 °C; δ) 340.1 (CHCH₂R), 99.5 (C₅H₅), 56.9 (CHCH₂R), 37.1 (SCH₃), 33.4 (CH₂), 22.2 (CH₂), 9.9, 12.5, 13.7 (SCH₃, (CH₂)₂CH₃, SCH₃).

(12) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

Finally, expected correlation peaks between the protons of the CH₂ group at 4.51 ppm and carbon atoms at 338.0 ppm (CH) and at 137.8 and 128.3 ppm (tolyl) were observed in the HMBC ¹³C–¹H spectrum of **3a**, in accordance with the proposed structure [Mo₂Cp₂(μ -SMe)₃(μ - η^1 : η^2 -CHCH₂R)]⁺. It must be emphasized here that the more commonly observed β -agostic structure¹³ is not adopted by **3**, probably because the crowded thiomethyl environments would prevent such an interaction. Observation of a single resonance for the Cp groups in the ¹H NMR spectra of **3**, down to 213 K, suggested that compounds **3** are fluxional on the NMR time scale.

The β -addition of electrophiles to vinylidene ligands is a well-established synthetic path to alkylidyne groups.¹⁴ In contrast, there are very few reports of the formation of alkylidyne ligands by formal addition of a nucleophile to the outer carbon atom of a vinylidene moiety. This is in keeping with the nucleophilic character of the β -carbon atom of vinylidene ligands.¹⁵ As far as we know, the closest parallel to such an addition is the reaction of the monometallic complex [Mo(C=CHPh)Br{P(OMe)₃}₂Cp] with Li[CuPh₂] or K[BH(*s*-Bu)₃] to give the carbyne species [Mo(≡CCHRPh){P(OMe)₃}₂Cp] (R = H, Ph) through a proposed S_N2' substitution of the bromide ligand.¹⁶ A second example which may involve hydride addition at the β -carbon of a vinylidene involves the solution equilibrium between hydrido–vinylidene [IrHCl(C=CHR)(P-*i*-Pr)₃]⁺ and alkylidyne [IrCl(C–CH₂R)(P-*i*-Pr)₃]⁺ isomers, which has been rationalized in terms of a 1,3-hydride shift.¹⁷ The versatile behavior which can be exhibited by binuclear complexes containing side-on vinylidene bridges is illustrated by the charge-controlled protonation and frontier-orbital-controlled addition of nucleophiles to the α -carbon atom of the neutral vinylidene species [Mo₂Cp₂(CO)₄(μ - η^1 : η^2 -C=CR'R)]⁺.¹⁸ No evidence for the formation of an intermediate arising from the addition of H⁻ to sites in **1** other than C _{β} (e.g. metal or C _{α}) has been found. Further experiments are now planned to extend the scope of the reactivity of these side-on vinylidene species and to understand better the factors which govern their behavior.

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Supporting Information Available: For **2b**, tables giving details of the structure determination, non-hydrogen atomic positional parameters, all bond distances and angles, anisotropic displacement parameters, and hydrogen atomic coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) Jaffart, J.; Etienne, M.; Maseras, F.; McGrady, J. E.; Eisenstein, O. *J. Am. Chem. Soc.* **2001**, *123*, 6000.

(14) (a) Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 227. (b) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N. *J. Am. Chem. Soc.* **1993**, *115*, 4683.

(15) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.

(16) Beevor, R. G.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1319.

(17) Höhn, A.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 737.

(18) (a) Bamber, M.; Conole, G. C.; Deeth, R. J.; Froom, S. F. T.; Green, M. *J. Chem. Soc., Dalton Trans.* **1994**, 3569. (b) Bamber, M.; Froom, S. F. T.; Green, M.; Schulz, M.; Werner, H. *J. Organomet. Chem.* **1992**, *434*, C19.