

Aminomethylene Complexes of Divalent Tungsten and Molybdenum

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Summary: Convenient routes are reported to aminomethylene complexes of divalent molybdenum and tungsten: $[M(=CHN^iPr_2)(CO)_2(S_2CA)_2]$ ($M = Mo, W$; $A = NMe_2, NEt_2, N(CH_2)_4, OEt$).

Aminomethylene complexes of the group 6 metals are confined to zerovalent metal centers or divalent metals coligated by cyclopentadienyl or poly(pyrazolyl)borate ligands.¹ Early indications that amino substituents could stabilize carbene ligands bound to mid-valent group 6 metal centers were provided by the observations of Kreissl: while $[W(=CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ reacts with hydrogen chloride to provide the acyl complex $[W(\eta^2-OCCH_2C_6H_4Me-4)Cl_2(CO)(\eta-C_5H_5)]$,² the same reagent with $[W(=CNET_2)(CO)_2(\eta-C_5H_5)]$ provides the aminomethylene complex $[W(=CHNET_2)Cl(CO)_2(\eta-C_5H_5)]$.³ Similar results have been recently obtained by Filippou for chromium.⁴ Continuing our studies on the reactivity of aminomethyldiyne complexes of groups 6⁵ and 8,⁶ we have now investigated the reactions of the complexes $[M(=CN^iPr_2)Cl(CO)_3L]$ ($M = Mo, W$; $L = CO, PPh_3$)⁵ with dithiocarbamate and xanthate salts. Herein, we wish to report that these reactions provide convenient access to a range of stable aminomethylene complexes of divalent molybdenum and tungsten.

The reactions of alkylidyne complexes of tungsten with dithiocarbamates have already been shown by Mayr to be complex, providing either ketenyl⁷ or thioaldehyde⁸ complexes, depending on the nature of the carbamate counteranion (Scheme 1). For the latter outcome, $[R_2NH_2][S_2CNR_2]$ is employed as the dithiocarbamate source and it is reasonable to postulate benzylidene intermediates resulting from the protonation of an anionic alkylidyne complex, although such intermediates have yet to be observed in this case. The complexes $[M(=CN^iPr_2)Cl(CO)_3(PPh_3)]$ ($M = Mo$ (**1a**), **W** (**1b**)) are conveniently obtained^{5b} from the reactions

of $[M(CO)_6]$ with LiN^iPr_2 , Cl_2PPh_3 , and PPh_3 (Scheme 2). These complexes react with $[Et_2NH_2][S_2CNET_2]$, $[NH_4][S_2CN(CH_2)_4]$, or hydrated $Na[S_2CNMe_2]$ to provide the neutral red aminomethylene complexes $[M(=CHN^iPr_2)(CO)_2(S_2CNR_2)_2]$ ($M = W, NR_2 = NMe_2$ (**2a**), NEt_2 (**2b**), $N(CH_2)_4$ (**2c**); $M = Mo, NR_2 = N(CH_2)_4$ (**2d**)) in high yields.⁹ Alternatively, the same complexes result in moderate yields in a direct "one-pot" synthesis from the successive treatment of $[M(CO)_6]$ with LiN^iPr_2 , $(CF_3CO)_2O$, and the appropriate dithiocarbamate salt. It is noteworthy that both approaches fail for chromium, providing only $[Cr(S_2CNR_2)_3]$, while *all-trans*- $[W(=CN^iPr_2)(O_2CCF_3)(CO)_2(PPh_3)_2]$ fails to react with a variety of dithiocarbamate salts. Xanthate-coordinated analogues, e.g., $[W(=CHN^iPr_2)(CO)_2(S_2COEt)_2]$ (**2e**), are however accessible in a similar manner directly from $[W(CO)_6]$ (or from preformed (**1a**)) if $K[S_2COEt]$ is employed in addition to NH_4Cl (as a proton source). The tungsten complexes are comparatively robust; however, the molybdenum complexes are decomposed rapidly by air to provide $[Mo(=O)_2(S_2CNR_2)_2]$.

The formulation of the complexes **2** rests on elemental microanalytical, spectroscopic, and FAB-MS data.⁹ While FAB-MS data confirm the gross formulation, the most informative spectroscopic data are associated with the aminomethylene ligand: $^{13}C\{^1H\}$ resonances are observed in the region 233.1–249.5 ppm for each of the complexes and for the pyrrolidynyl dithioate examples **2c** and **2d** proton-coupled spectra revealed $J(CH)$ to be 139.2 and 141.0 Hz, respectively. The 1H NMR data for the complexes **2** include singlet resonances in the low-field region of δ 11.85–12.35 ppm. The iPr resonances (two heptets and two doublets) confirm that the

(9) Selected data for new complexes are as follows: (25 °C; IR, $\nu(CO)$, CH_2Cl_2 ; NMR, $CDCl_3$; satisfactory microanalytical data obtained). **2a**: $[W(CO)_6]$ (4.3 mmol) in diethyl ether (30 mL) was treated with LDA (4.3 mmol) and cooled (0 °C). Ph_3PCl_2 (4.3 mmol) was added, and the suspension was stirred for 5 min. $Na[S_2CNMe_2] \cdot 2H_2O$ (9.0 mmol) was then added, and after stirring for 1 h, the supernatant was chromatographed (alumina, 10 °C, Et_2O). Addition of ethanol and concentration of the eluate resulted in deep orange-red microcrystals. Yield: 1.42 g (51%). IR: 1914, 1817 cm^{-1} . NMR: 1H , δ 1.19, 1.33 [$d \times 2$, 12 H, CH_2F_3], 3.25 [s, 12 H, NCH_3], 3.84, 4.44 [$h \times 2$, 2 H, $CHCH_3$], 11.95 [s, 1 H, $W=CHN$]; $^{13}C\{^1H\}$ δ 248.7 [WCO , $J(WC)$ 132 Hz], 236.4 [$W=CH$, $J(WC)$ 84 Hz], 209.2 [S_2CNMe_2], 60.8, 51.2 [$CHCH_3$], 39.2 [NCH_3], 23.9, 21.1 [$CHCH_3$]. FAB-MS: m/z 594 [M]⁺, 565 [$M - CO$]⁺, 537 [$M - 2CO$]⁺. **3**: yield 44% directly from $[W(CO)_6]$. IR: 1987, 1897 cm^{-1} . NMR: 1H , δ 2.29 [s, 6 H, CCH_3], 2.84, 2.92 [$s \times 2$, 6 H, NCH_3], 6.83 [d , 2 H, $H^{3,5}(C_6H_3)$], 7.04 [t, 1 H, $H^4(C_6H_3)$]; $^{13}C\{^1H\}$, 284.1 [$W=C$, $J(PC)$ 10 Hz], 226.8 [2 C, CO , $J(PC)$ 5 Hz], 213.6 [CO , $J(PC)$ 52 Hz], 207.7 [S_2C], 139.9–126.8 [C_6H_3 and C_6H_5], 39.7, 39.4 [NCH_3], 20.9 [CCH_3]. FAB-MS: m/z 739 [M]⁺, 711 [$M - CO$]⁺, 682 [$M - 2CO$]⁺, 420 [$M - PPh_3 - 2CO$]⁺. **4a**: yield 39% directly from $[W(CO)_6]$. IR: 1922 cm^{-1} . NMR: 1H , δ 3.30, 3.32, 3.34, 3.72 [$s \times 4$, 12 H, NCH_3], 3.79 [s, 3 H, OCH_3], 5.50 [s, 1 H, CHS], 6.82, 7.07 [$d \times 2$, 4 H, C_6H_4]; $^{13}C\{^1H\}$, δ 259.2 [NCS], 217.9 [CO], 215.9 [NCS_2], 159.0 [SCH], 139.7–113.0 [C_6H_4], 56.7, 55.3, 40.7, 39.6 [NCH_3], 48.2 [OCH_3]. FAB-MS: m/z 574 [M]⁺, 544 [$M - CO$]⁺.

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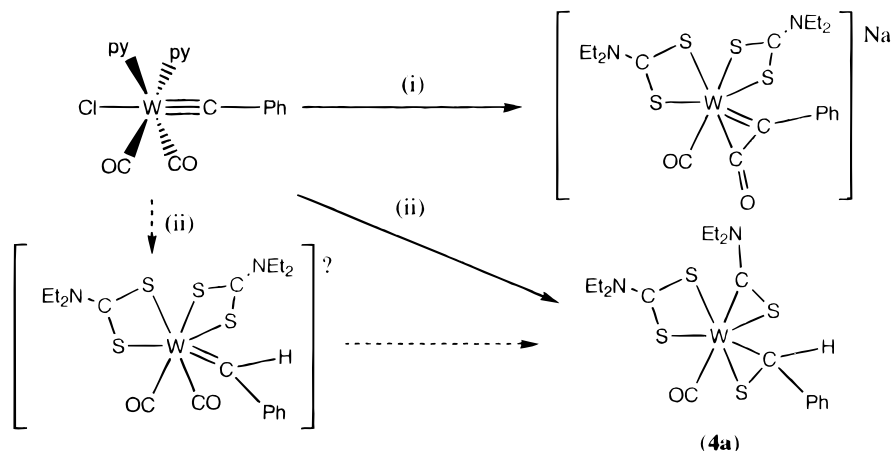
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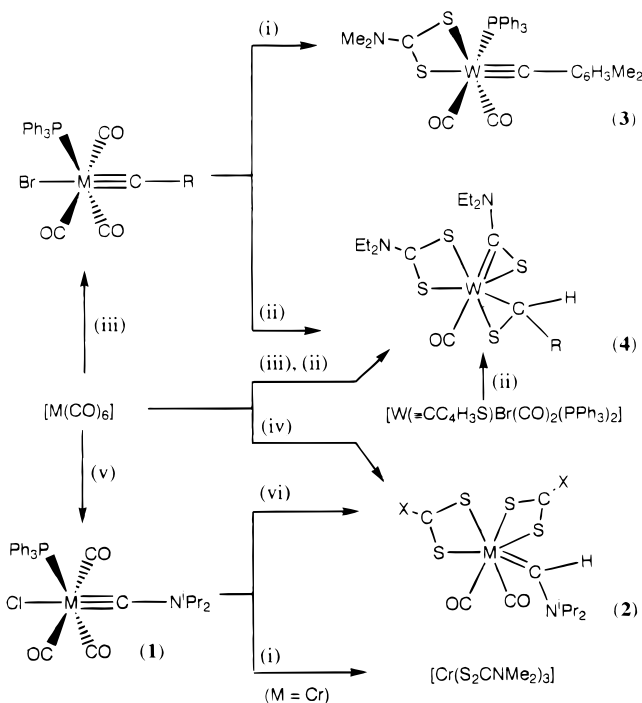
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Scheme 1. Ketenyl vs Thioaldehyde Formation^{a,8a}

^a Reagents: (i) Na[S₂CNEt₂] \cdot 2H₂O; (ii) [Et₂NH₂][S₂CNEt₂].

Scheme 2^a

^a Reagents: (i) Na[S₂CNMe₂] \cdot 2H₂O, R = C₆H₃Me₂-2,6; (ii) [Et₂NH₂][S₂CNEt₂], R = C₆H₄OMe-2, C₄H₃S-2, C₁₀H₇-1; (iii) LiR, LiBr, (CF₃CO)₂O, PPh₃, R = C₆H₃Me₂-2,6, C₆H₄OMe-2, C₄H₃S-2, C₁₀H₇-1; (iv) LiNⁱPr₂, Cl₂PPh₃, Na[S₂CNMe₂] \cdot 2H₂O (X = NMe₂); (v) LiNⁱPr₂, Cl₂PPh₃, PPh₃; (vi) M = Mo, W, Na[S₂CNMe₂] \cdot 2H₂O, NH₄[S₂CN(CH₂)₄], [Et₂NH₂][S₂CNEt₂], or NH₄Cl + K[S₂COEt].

NⁱPr₂ group is no longer coordinated to a linear sp-hybridized carbon. These data are all consistent with the presence of the aminomethylene ligand. Signals due to the carbamate substituents in both the ¹³C and ¹H NMR spectra indicate a fluxional time averaging of their chemical environments in the seven-coordinate complexes.

Given the remarkable stability of the aminomethylene complexes, the reactivity of the related arylmethylidyne complexes [M(=C₆H₃Me₂-2,6)Br(CO)₃(PPh₃)] (M = Mo, W; Ar = C₆H₃Me₂-2,6, C₆H₄OMe-4, C₁₀H₇-1) and *all-trans*-[M(=CC₄H₃S-2)Br(CO)₂(PPh₃)₂] toward dithiocarbamate salts was also investigated. For the molybdenum complexes, the only isolable products were [Mo(=O)₂(S₂CNR₂)₂]. For the tungsten examples, however, the

alkylidyne complex [W(=CC₆H₃Me₂-2,6)(S₂CNMe₂)(CO)₂(PPh₃)] (**3**) or the thioaldehyde complexes [W(η²-SCHAr)(CO)(η²-SCNEt₂)(S₂CNEt₂)] (R = C₆H₄OMe-4 (**4b**), 2-C₄H₃S (**4c**), 1-C₁₀H₇ (**4d**)) are obtained, which are analogous to the previously reported complexes [W(η²-SCHAr)(CO)(η²-SCNEt₂)(S₂CNEt₂)] (Ar = Ph (**4a**),^{8a} C₅H₄Mn(CO)₃ (**4e**)^{8b}). In direct reactions beginning with [W(CO)₆] the same thioaldehyde complexes are obtained. The alkylidyne complex **3** is obtained by sequential treatment of [W(CO)₆] with LiC₆H₃Me₂-2,6, (CF₃CO)₂O, PPh₃, and Na[S₂CNMe₂]. Thus, it has not been possible to isolate either benzylidene or ketenyl complexes from these reactions and it appears that the unique electronic properties of the amino substituent are crucial for the stabilization of the aminomethylene complexes **2**. Similarly, the dithiocarbamate-induced progress from alkylidyne to alkylidene to thioaldehyde appears to be intercepted at the dithiocarbamate-alkylidyne stage by inclusion of sterically cumbersome substituents in the case of **3**.

Aminomethylene complexes of zerovalent group 6 metals have increasingly attracted attention for use in organic synthesis.¹⁰ The reactivity of the alkylidene ligand may, in principle, be modified by the nature of the metal center (oxidation state, coordinative saturation, *d* configuration, and chirality). The convenient and large-scale access to aminomethylene complexes of divalent group 6 metals offered by the present strategies makes the complexes **2** intriguing candidates for further reactivity studies, which we are currently pursuing.

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Supporting Information Available: Synthetic details, spectroscopic data, and elemental analyses for all new compounds (9 pages). Ordering information is given on any current masthead page.

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