A μ-η^1-Azavinylidene Complex: Intramolecular Condensation of Two Acetonitrile Ligands at a Dinuclear Molybdenum(III) Site

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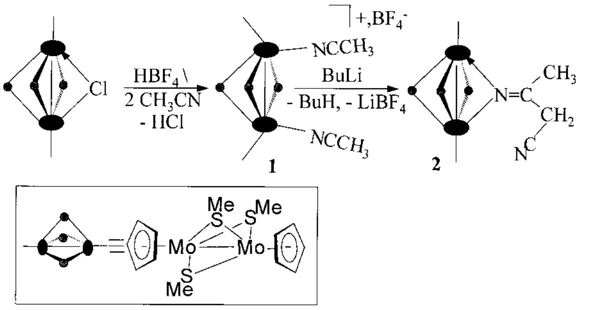
Removal of a proton from one of the two coordinated acetonitrile ligands in $[Mo_2Cp_2(\mu\text{-}SMe)_3(CH_3CN)_2](BF_4)$ (**1**) initiates its intramolecular condensation with the second of the acetonitrile ligands attached to the bimetallic $[Mo_2Cp_2(\mu\text{-}SMe)_3]$ core, thereby giving rise to the novel μ-η^1-azavinylidene complex $\{Mo_2Cp_2(\mu\text{-}SMe)_3[\mu\text{-}\eta^1\text{-}N{=}C(CH_3)CH_2CN]\}$ (**2**). Complex **2** has been characterized by NMR and X-ray methods.

Bimetallic complexes with direct M−M bonds permit the simultaneous activation of neighbouring ligands. The ensuing reactions are often different from those that occur with polymetallic systems[1] or with bimetallic species in which there is little or no direct communication between the metal atoms.[1−3] Here, we show that a well-known organic reaction, the self-condensation of an alkyl cyanide, can still occur when both substrate molecules are attached to the neighbouring metal atoms of a binuclear complex. Moreover, the product represents a new type of N-donor bridging ligand.

We are currently extensively developing the chemistry of bimetallic complexes with an $[Mo_2Cp_2(\mu\text{-}SMe)_3]$ core by using the bis(acetonitrile) compound $[Mo_2Cp_2(\mu\text{-}SMe)_3(CH_3CN)_2](BF_4)$ (**1**) as a starting material for the coordination of other substrates, such as alkynes and hydrazines, at the bimetallic site. However, we have found that the coordinated nitriles can themselves undergo reaction. We report here their transformation into a novel bridging azavinylidene ligand in the presence of a base.

Electrophilic abstraction of the chloride bridge in the complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ by HBF_4 proceeded in acetonitrile solution and was followed by the coordination of one acetonitrile molecule to each molybdenum atom (Scheme 1).[4] Reaction of the resulting bis(acetonitrile) compound $[Mo_2Cp_2(\mu\text{-}SMe)_3(CH_3CN)_2](BF_4)$ (**1**) with butyllithium in THF afforded the complex $\{Mo_2Cp_2(\mu\text{-}SMe)_3[\mu\text{-}\eta^1\text{-}N{=}C(CH_3)CH_2CN]\}$ (**2**) which was isolated in good yield (Scheme 1). Complex **2** was characterized by IR, one- and two-dimensional NMR, mass spectrometry, and elemental analysis.

The IR stretching frequency of the C≡N bond was detected at 2220 cm^{-1}, while the ^1H-NMR spectrum exhibited a set of resonances characteristic of the $[Mo_2Cp_2(\mu\text{-}SMe)_3]$ core. Two additional signals, a single resonance at $\delta = 2.05$ and an AB spin system at $\delta = 3.02$, could be attributed to the CH_3 and CH_2 groups, respectively, of a fourth bridging ligand. Two-dimensional heteronuclear ^1H-^{15}N and ^1H-^{13}C inverse-correlation experiments were carried out to further characterize **2**. The correlation peaks in the HMBC ^1H-^{15}N spectrum were characteristic of $^3J(^1H\text{-}^{15}N)$ couplings. This spectrum showed the AB pattern at $\delta = 3.02$ to be coupled with two nitrogen atoms with signals at $\delta = -132.5$ and $\delta = -14.2$, relative to nitromethane, and the methyl group with signal at $\delta = 2.05$ to be correlated only with the second nitrogen atom with signal at $\delta = -14.2$. The signal at $\delta = -132.5$ suggested the presence of a free nitrile group in the molecule (see Experimental Section).[5] Such a pattern was consistent with an $N{\equiv}C{-}CH_2{-}C(CH_3){=}N$ backbone. Full assignment of the ^{13}C chemical shifts was achieved by means of HMQC ^1H-^{13}C and HMBC ^1H-^{13}C experiments, which were also in accord with an $N{\equiv}C{-}CH_2{-}C(CH_3){=}N$ ligand.



Scheme 1. Synthesis of complex **2**

The structure of the new complex was confirmed by X-ray analysis of the orange crystals of **2**, which were obtained by cooling a dichloromethane/pentane/carbon disulfide (1:1:1, v/v/v) solution to −15°C (Figure 1). It was found to consist of a typical $[Mo^{III}{}_2Cp_2(\mu\text{-}SMe)_3]$ unit[6] bridged by the nitrogen atom of the 3-iminobutyronitrile ligand $N{\equiv}C{-}CH_2{-}C(CH_3){=}N$, namely an η^1-azavinylidene group. The p orbitals on sp^2-hybridized N1 and C5 are seen to overlap [Mo1−N1−C5−C6 = −5.4(5)°], so that the C5−N1

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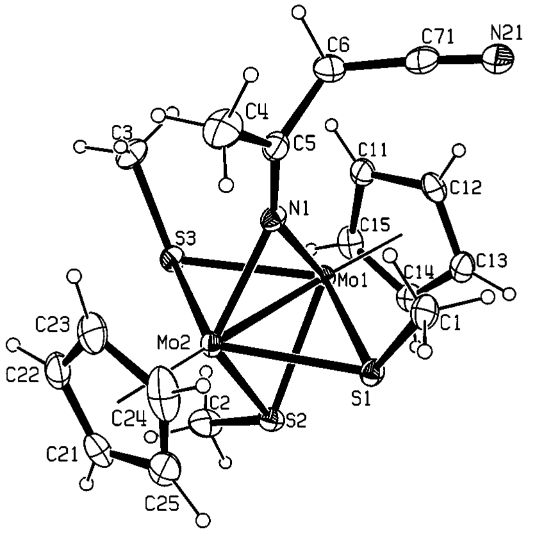
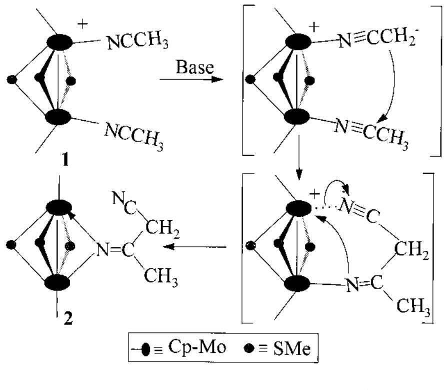


Figure 1. A view of the $\{Cp_2Mo_2(\mu\text{-}SMe)_3[\mu\text{-}\eta^1\text{-}N{=}C(Me)\text{-}CH_2CN]\}$ molecule showing 20% probability ellipsoids; hydrogen atoms are shown as spheres of arbitrary radius; the CN group attached to C6 adopts two orientations with equal probability [N1−C5−C6−C71 92.5(8), N1−C5−C6−C72 −169.6(8)°]; this disorder is not shown for the sake of clarity; selected distances [Å] and angles [°]: Mo1−Mo2 2.574(1), Mo1−N1 2.101(4), Mo1−S1 2.479(1), Mo1−S2 2.448(1), Mo1−S3 2.458(1), Mo2−N1 2.114(4), Mo2−S1 2.466(1), Mo2−S2 2.458(2), Mo2−S3 2.450(1), N1−C5 1.266(6), C5−C6 1.507(8), C6−C71 1.430(13), C6−C72 1.468(13), C71−N21 1.142(14), C72−N22 1.161(14); Mo2−S1−Mo1 62.7(1), Mo2−S2−Mo1 63.3(1), Mo2−S3−Mo1 63.3(1), Mo1−N1−Mo2 75.3(1), Mo1−N1−C5 142.8(4), Mo2−N1−C5 142.0(4), C4−C5−C6 116.1(5), C71−C6−C5 116.3(7), C6−C71−N21 175.5(1)

bond [1.266(6) Å] has appreciable multiple character. The Mo−N1 bond lengths [2.101(4) and 2.114(4) Å] are nearly equal.

A mechanism involving an intramolecular carbon−carbon attack accounts for the formation of the 3-iminobutyronitrile ligand in this reaction (Scheme 2). Initial deprotonation of the methyl group of one of the coordinated acetonitriles by a strong base leads to a resonance-stabilized $[Mo{-}N{\equiv}C{-}CH_2^-]$ carbanion.[7] This is then attacked by the electrophilic nitrile carbon atom of the second acetonitrile ligand $[Mo{-}N{\equiv}C{-}CH_3]$. The imino nitrogen atom moves to a bridging position as the second C≡N group decoordinates, finally giving the bridging azavinylidene ligand $[\mu\text{-}\eta^1\text{-}N{=}C(CH_3)CH_2CN]$ present in **2**. Evidently, coordination to molybdenum does not impair the ability of acetonitrile to undergo Thorpe−Ziegler-type activation through α-hydrogen abstraction, while the electronic and geometric properties of the bimetallic site ensure a specific intramolecular condensation in preference to an intermolecular reaction[2] or other types of coupling.[8] Moreover, the two bonded metal atoms confer stability on the azavinylidene ligand.



Scheme 2. Possible pathway to the formation of **2**

In view of the role of azavinylidene species as postulated intermediates in the reduction of nitriles to amines[9] and the importance of cyanoenamine in the synthesis of heterocycles,[10] we now intend to investigate the redox behaviour of complex **2** and to extend these preliminary results to other bis(nitrile) complexes.

Experimental Section

Experimental Procedure: At −70°C, 0.5 mL of a 2.5 M solution of butyllithium in hexane (1.25 mmol) was added to a red solution of **1** (600 mg, 0.9 mmol) in THF (50 mL). When the temperature reached 25°C, the solution became orange. After evaporation of the solvent, the product **2** was extracted with toluene (5 × 15 mL). The toluene was then removed from the pooled extracts in vacuo, and after washing of the residue with cold pentane, **2** was obtained as an orange powder (424 mg, 85%). − $C_{17}H_{24}N_2Mo_2S_3$ (544.44): calcd. C 37.5, H 4.4, N 5.1; found C 36.9, H 4.4, N 4.9. − MS; *m/z*: 544 $[M^+]$. − Selected spectroscopic data for **2**: ^1H NMR ($CDCl_3$, relative to TMS): $\delta = 5.46$ (s, 5 H, $C_5\mathit{H}_5$), 5.44 (s, 5 H, $C_5\mathit{H}_5$), 3.02 [AB, $J_{HH} = 16.7$ Hz, $N{\equiv}CC\mathit{H}_2C(CH_3){=}N$], 2.05 [s, 3 H, $N{\equiv}CCH_2C(C\mathit{H}_3){=}N$], 1.67 (s, 3 H, $SC\mathit{H}_3$), 1.28 (s, 3 H, $SC\mathit{H}_3$), 1.23 (s, 3 H, $SC\mathit{H}_3$). − ^{13}C NMR ($CDCl_3$, relative to TMS): $\delta =$ 158.8 [$N{\equiv}CCH_2\mathit{C}(CH_3){=}N$], 116.7 [$N{\equiv}\mathit{C}CH_2C(CH_3){=}N$], 91.5 ($\mathit{C}_5H_5$), 31.2 [$N{\equiv}C\mathit{C}H_2(CH_3){=}N$], 26.4 [$N{\equiv}CCH_2C(\mathit{C}H_3){=}N$], 13.9 (2 × $S\mathit{C}H_3$), 10.8 ($S\mathit{C}H_3$). − ^{15}N NMR ($CDCl_3$, relative to CH_3NO_2): $\delta = -132.5$ [$\mathit{N}{\equiv}CCH_2C(CH_3){=}N$], −14.2 [$N{\equiv}CCH_2C(CH_3){=}\mathit{N}$]. − ^{15}N NMR (CD_3COCD_3, relative to CH_3NO_2): $\delta =$ −184.9 {($Mo{-}\mathit{N}{\equiv}CCH_3$) in $[Mo_2Cp_2(\mu\text{-}SMe)_3(NCCH_3)_2]BF_4$ (**1**)}, −137 (free $\mathit{N}{\equiv}CCH_3$).

Crystal Data for 2: $C_{17}H_{24}Mo_2N_2S_3$, $M_r = 544.44$, monoclinic, space group $P2_1/c$, $a = 14.153(1)$, $b = 8.930(1)$, $c = 15.710(1)$ Å, $\beta = 95.250(6)°$, $V = 1977.1(3)$ $Å^3$, $Z = 4$, $D_c = 1.829$ Mg/m^3, $F(000) = 1088$, Mo-K_α radiation, $\lambda = 0.71073$ Å, $\mu = 1.587$ mm^{-1}, orange plate 0.28 × 0.24 × 0.04 mm, CAD4 diffractometer; 5562 absorption-corrected intensities (transmission factors 0.734−0.655) with θ(Mo-K_α) < 27° yielded the 4297 unique F_0^2 values ($R_{int} = 0.044$) that were used to refine 235 parameters (SHELXL-97). $R = 0.081$ for all unique data and 0.038 for the 2846 reflections with $I > 2\sigma(I)$. The CN group attached to C6 can adopt two equally probable orientations. H atoms were allowed to ride on their parent C atoms.

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