Reaction of a Sulfur Bridged Incomplete Cubane-Type Tungsten Cluster with Acetylene: Formation of Three Carbon–Sulfur Bonds

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The reaction of sulfur-bridged isothiocyanate tungsten cluster $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(NCS)_9]^{5-}$ (**5**) with acetylene affords a novel complex having two acetylene molecules of different coordination modes, $[W_3(\mu_3\text{-}S)(\mu_3\text{-}SCH{=}CHS)(\mu\text{-}SCH{=}CH_2)(NCS)_9]^{4-}$ (**6**), and the presence of two kinds of intermediates $[W_3(\mu_3\text{-}S)(\mu\text{-}S)(\mu_3\text{-}SCH{=}CHS)(NCS)_9]^{5-}$ (**7**) and $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_2(\mu\text{-}SCH{=}CH_2)(NCS)_9]^{4-}$ (**8**) are suggested. They are characterized by X-ray crystallography (for **6**) and ^1H NMR spectroscopy (for **6**, **7**, and **8**).

The formation and scission of carbon–sulfur bonds are interesting and important in the field of pure and applied chemistry. Rakowski DuBois and her colleagues reported that the reaction of the dinuclear molybdenum complex $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ with acetylene or phenyl acetylene gave the complexes with $Mo_2(\mu\text{-}SCH{=}CH_2)$[1] or $Mo_2(\mu\text{-}SC(Ph){=}CH_2)_2$ moieties, respectively. The complexes $[M([9]aneS_3)_2]^{3+}$ (M = Co, Ru, Rh, Ir) having $M\text{–}SCH{=}CH_2$ moieties are known,[3–6] and other types of complexes with vinyl thiolate ligands and vinyl sulfide metallacycle complexes have also been reported.[7–12]

We have recently reported the reaction of sulfur/oxygen-bridged incomplete cubane-type molybdenum or tungsten clusters with acetylene or acetylene derivatives.[13,14] The molybdenum clusters are more reactive with acetylene than the corresponding tungsten ones, that is, molybdenum clusters $[Mo_3(\mu_3\text{-}S)(\mu\text{-}X)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (X = O, S) in 1 M HCl react with acetylene to afford clusters with alkenedithiolate ligands $[Mo_3(\mu_3\text{-}S)(\mu\text{-}X)(\mu_3\text{-}SCH{=}CHS)(H_2O)_9]^{4+}$ (X = O, S), each having two C–S bonds,[13] while $[W_3(\mu_3\text{-}S)(\mu\text{-}X)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (X = O, **1**; X = S, **2**) in the same media do not react with acetylene. However, we found that isothiocyanate cluster $[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(NCS)_9]^{5-}$ (**3**) obtained from **1** and NCS^- reacted with acetylene to give $[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]^{4-}$ (**4**) having one C–S bond.[14]

Here we report the reaction of sulfur-bridged isothiocyanate tungsten cluster $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(NCS)_9]^{5-}$ (**5**),[15] obtained from **2** and NCS^-, with acetylene to give the complex having three C–S bonds, $[W_3(\mu_3\text{-}S)(\mu_3\text{-}SCH{=}CHS)(\mu\text{-}SCH{=}CH_2)(NCS)_9]^{4-}$ (**6**). No complexes, to our knowledge, have been reported that have two acetylene molecules (or derivatives) of different coordination modes, though complexes having two acetylene molecules of the same coordination mode are known.[16] We also report the presence of two kinds of intermediates $[W_3(\mu_3\text{-}S)(\mu\text{-}S)(\mu_3\text{-}SCH{=}CHS)(NCS)_9]^{5-}$ (**7**) and $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_2(\mu\text{-}SCH{=}CH_2)(NCS)_9]^{4-}$ (**8**).

Acetylene gas was passed through a green solution of **5** (3.04×10^{-3} M in 0.1 M HCl containing 1.5 M KSCN, 100 mL). The resultant solution was then sealed (one atmosphere) and kept at 50 °C for three days. The color of the solution turned to brown-green. Addition of a small amount of pyridine (0.30 mL, 3.72×10^{-3} mol) and allowing the solution to stand at room temperature for three days gave brown needle-like crystals. Crystals suitable for X-ray crystallography were obtained by the recrystallization: to an aqueous solution of **6'** containing 1.5 M KSCN, a few drops of a mixture of 1 M HCl and pyridine (1:1 by volume) was added, and the resultant solution was allowed to stand at room temperature to give brown plate like crystals of $(Hpy)_4[W_3(\mu_3\text{-}S)(\mu_3\text{-}SCH{=}CHS)(\mu\text{-}SCH{=}CH_2)(NCS)_9]\cdot 1.33py\cdot 0.5H_2O$ (**6''**); yield, 5 mg (9%). Anal. Found: N, 11.68; C, 28.00; H, 2.22%. Calcd for $W_3S_{13}O_{0.5}N_{14.33}C_{39.65}H_{36.65}$: N, 11.87; C, 28.17; H, 2.19%.

The X-ray structural analysis[17] of **6''** revealed that two acetylene molecules attached to three μ-sulfur atoms (Figure 1). One molecule links with two μ-sulfur atoms and the other does with one μ-sulfur atom, a proton attaching to the latter molecule.

In order to elucidate the reaction mechanism from **5** to **6**, we followed the ^1H NMR spectral change (Figure 2). The reaction mixture of **5** and acetylene was kept at 50 °C. After 3 h, a small portion of the solution was taken out of the solution, to which a small amount of pyridine was added and the resultant solution was allowed to stand at room temperature for 3 days. The pow-

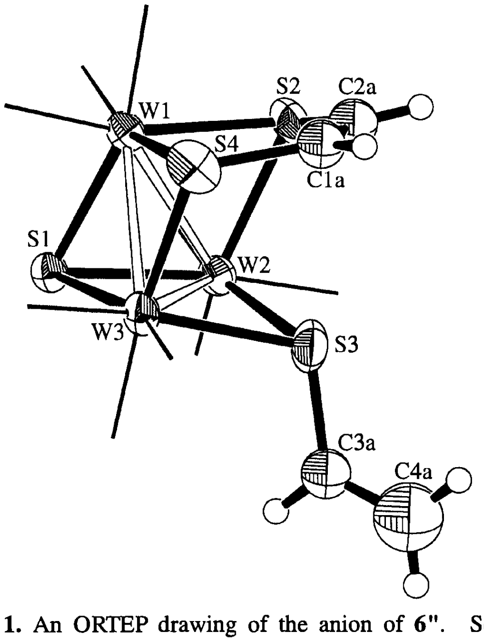

Figure 1. An ORTEP drawing of the anion of **6''**. Selected atomic distances(Å): W1-W2, 2.7252(4); W1-W3, 2.7218(4); W2-W3, 2.7079(4); W1-S1, 2.363(2); W1-S2, 2.402(2); W1-S4, 2.405(2); W2-S1, 2.353(2); W2-S2, 2.419(2); W2-S3, 2.404(2); W3-S1, 2.365(2); W3-S3, 2.441(2); W3-S4, 2.412(2); C1a-C2a, 1.33(2); C1b-C2b, 1.30(2); C3a-C4a, 1.34(3); C3b-C4b, 1.34(4). One set of the attached acetylene molecules is shown for clarity. See References and Notes 17.

der precipitated from the solution was filtered with suction. The same procedures were carried out after 12 h, 1 day, and 2 days. Each powder was dissolved in CD_3CN for the measurement of ^{1}H NMR at 20 °C, 400 MHz. Figure 2d shows four distinct signals assignable to **6**: δ 5.22 (1H, d, J = 9.0 Hz), δ 5.69 (1H, d, J = 16.7 Hz), δ 6.13 (1H, dd, J = 9.0, 16.7 Hz), and δ 6.42 (2H, s). The HH COSY spectrum shows spin couplings of the signal at *d* 6.13 with each of the two signals at *d* 5.22 and *d* 5.69. If the relationship "J_{trans}>J_{cis}" holds in this species,[18] the three protons H1 (δ 6.13), H2 (δ 5.22), and H3 (δ 5.69), are assigned to the moiety μ-SCH=CH_2 (see the top of Figure 2). No geminal coupling between H2 and H3 was observed. The remaining signal at δ 6.42 is assigned to the moiety of μ_3-SCH=CHS. Signals at ca. δ 2.0 and δ 8–9 (not shown) are due to CH_3CN and Hpy^+, respectively.

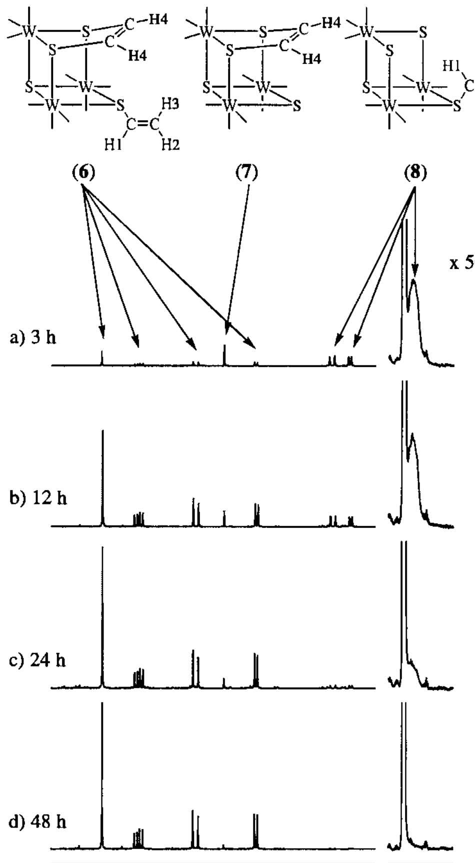

Figure 2. The time-course ^{1}H NMR signals of the reaction mixture of **5** and acetylene in CD_3CN.

The signals arising from the moiety μ-SCH=CH_2 of **6** appear in the region (δ 5–7) and the signal of H1 is at lower magnetic field than those of H2 and H3 (δ (H1) > δ (H2), δ (H3)), as were reported on the complexes with M_2(μ-SCH=CH_2) or M–SCH=CH_2 moieties.[3–6,11] On the other hand, the signals of **4** appear at much higher magnetic field, and the signal of H1 (δ 2.42 (1H, s)) is at higher magnetic field than those of H2 (δ 4.84 (1H, d, J = 8.7 Hz)) and H3 (δ 4.89 (1H, d, J = 16.1 Hz)), that is, (δ (H1) < δ (H2), δ (H3)). When the structures of **4** and **6** are compared, the μ-SCH=CH_2 moiety in **4** is close to the center line perpendicular to the plane defined by W_3 or W_3(μ-O)(μ-S)$_2$ ring, while the moiety in **6** is away from the line. Therefore, the protons, especially H1, in **4** sense a shielding effect due to the W and the NCS moiety, while H1 of **6** does not sense the shielding effect to the contrary. Ring current due to the W_3, W_3OS_3, or W_3S_4 groups also explains the shielding effect, if any.[19,20]

Each of Figures 2a and 2b shows eight signals, four of which are assignable to **6**, and one signal at δ 5.47 (s) of the four remaining ones is assignable to **7**. Of the three remaining signals the HH COSY spectrum shows spin couplings of the signal at δ 1.91 (br) with the signals at δ 4.50 (d, J = 8.5 Hz) and δ 4.64 (d, J = 15.9 Hz), respectively, and the relation "δ (H1) < δ (H2), δ (H3)" hold. Therefore, the three signals are assignable to **8**. The time-course of signals (see Figure 2) indicates that those due to **7** and **8** decrease and those due to **6** increase instead. We are trying to find out the reaction mechanism in detail.

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17 Crystal data: Formula $W_3S_{13}O_{0.5}N_{14.33}C_{39.65}H_{36.65}$, MW = 1690.26, monoclinic, space group $P\ 2_1/c$, a = 14.742(3) Å, b = 15.272(4) Å, c = 26.012(7) Å, β = 105.34(1)°, V = 5648(3) Å^3, Z = 4, D_{calc} = 1.988 g cm^{-3}, $R(R_w)$ = 0.047(0.088) for 8813 reflections (I > 1.50σ(I)). The carbon and bridging sulfur bond lengths were fixed: S3–C3a and S4–C3b, 1.79 Å; S2–C2a, S4–C1a, S2–C1b, and S3–C2b, 1.77 Å.
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