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Article

Adducts of Acetylene and Dimethylacetylenedicarboxylate at Sulfurs in Sulfur-Bridged Incomplete Cubane-Type Tungsten Clusters

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Reactions are reported of sulfur-bridged incomplete cubane-type tungsten clusters having $W_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cores with acetylene and its derivative dimethylacetylenedicarboxylate (DMAD). The reaction of the isothiocyanate tungsten cluster $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(NCS)_9]^{5-}$ (**5**) with acetylene in 0.1 M HCl afforded a novel complex having two acetylene molecules in different adduct formation 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**) was observed. The reaction of the diethyldithiophosphate (dtp) tungsten cluster $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(\mu\text{-}OAc)(dtp)_3(CH_3CN)]$ (**10**) with DMAD in acetonitrile containing acetic acid resulted in the formation of another complex having two DMAD molecules of different adduct formation modes, $[W_3(\mu_3\text{-}S)(\mu\text{-}SC(CO_2){=}CH(CO_2CH_3))(\mu_3\text{-}SC(CO_2CH_3){=}C(CO_2CH_3)S)(\mu\text{-}OAc)(dtp)_3]$ (**11**), where hydrolysis of one of the four ester groups of the two DMAD groups occurred and the resultant carboxylic group coordinated to tungsten. The conformation of the μ-SCH═CH$_2$ moiety in **6** is different from that of the corresponding moiety in $[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]^{4-}$ (**4**). Introduction of the second acetylene molecule to the intermediate $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_2(\mu\text{-}SCH{=}CH_2)(NCS)_9]^{4-}$ (**8**) resulted in the formation of **6**. The clusters were characterized by UV–vis spectroscopy, ^{1}H NMR spectroscopy, and X-ray crystallography (for $(Hpy)_4\cdot$**6**$\cdot 1.33py\cdot 0.5H_2O$ and **11**$\cdot CH_3CN$), and the formation of **6** and **11** was examined in detail from a mechanistic point of view.

Introduction

The formation and scission of carbon−sulfur bonds are interesting and important in the field of pure and applied chemistry, and a considerable effort has been made to achieve the synthesis and to understand the mechanism of metal complexes with C−S bonds. A variety of complexes have been reported over the past few decades, most of them being mono- or dinuclear molybdenum complexes.[1] Complexes having C−S bonds are divided into several categories, though some of them overlap with each other: (a) dinuclear molybdenum or tungsten complexes formed by the reaction of dinuclear complexes having terminal/bridging sulfur or sulfur-ligating ligands with acetylene or its derivatives;[2] (b) dinuclear molybdenum complexes with Mo−C bonds in addition to C−S bonds;[3] (c) mononuclear complexes having M−SCH═CH$_2$ moieties obtained by the ring opening of the [9]aneS$_3$ ligand in the complexes $[M([9]aneS_3)_2]^{3+}$ and

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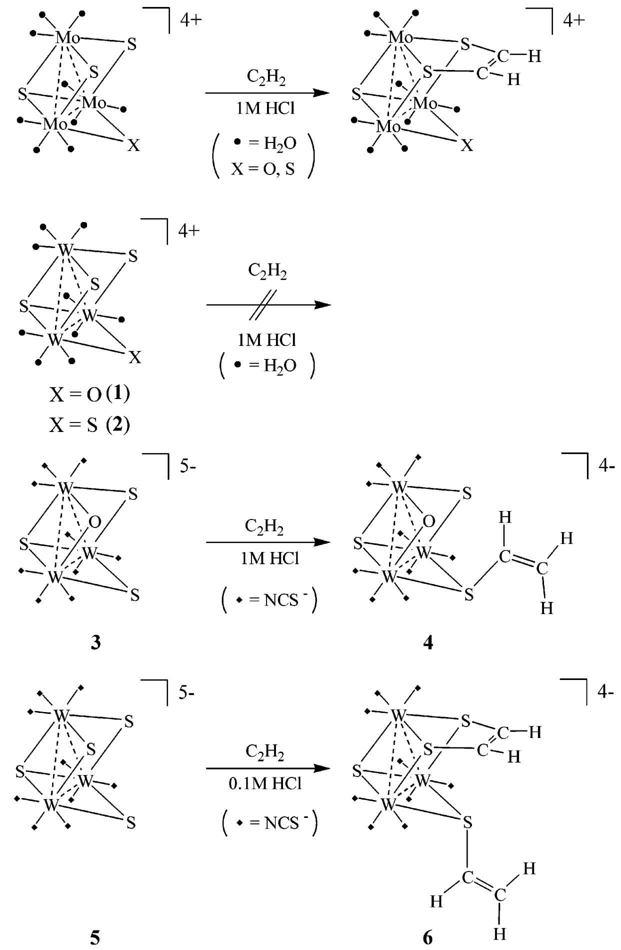
related ones (M = Co, Ru, Rh, Ir);[4] (d) mononuclear molybdenum, tungsten, or niobium complexes obtained by the reaction of complexes having sulfur-containing ligands with acetylene derivatives;[5] and (e) other types of monomeric or dimeric complexes with vinyl thiolate ligands and vinyl sulfide metallacycle complexes.[6] So far, the research of the formation and/or scission of carbon−sulfur bonds has almost been limited to mono- or di- nuclear complexes as described above. We think it is significant to extend the chemistry to trinuclear complexes.

We have explored sulfur-bridged complexes and reported some characteristics of the trinuclear complexes, such as metal incorporation reactions and acetylene adduct formation of molybdenum and tungsten clusters with incomplete cubane-type $W_3(\mu_3\text{-S})(\mu\text{-S})_3$ cores (M = Mo, W),[7] where molybdenum clusters are more reactive with acetylene than the corresponding tungsten ones (i.e., molybdenum aqua 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 (Scheme 1a),[8] 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 (Scheme 1b)).[9] However, we found that the isothiocyanate tungsten 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 (Scheme 1c).[9] The reaction of trinuclear complexes having $RhMo_2(\mu_3\text{-S})(\mu\text{-S})_3$ cores with phenylacetylene was recently reported.[10]

Scheme 1. Reaction of Sulfur-Bridged Clusters with Acetylene[a]



[a] (a) $[Mo_3(\mu_3\text{-S})(\mu\text{-X})(\mu\text{-S})_2(H_2O)_9]^{4+}$ (X = O, S), (b) $[W_3(\mu_3\text{-S})(\mu\text{-X})(\mu\text{-S})_2(H_2O)_9]^{4+}$ (X = O, S), (c) $[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})_2(NCS)_9]^{5-}$, and (d) $[W_3(\mu_3\text{-S})(\mu\text{-S})_3(NCS)_9]^{5-}$.

We here report the reaction of sulfur-bridged incomplete cubane-type tungsten clusters having $W_3(\mu_3\text{-S})(\mu\text{-S})_3$ cores with acetylene or its derivative, dimethylacetylenedicarboxylate (DMAD). We will describe the reaction of an isothiocyanate tungsten cluster $[W_3(\mu_3\text{-S})(\mu\text{-S})_3(NCS)_9]^{5-}$ (**5**) in 0.1 M HCl with acetylene to afford 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**) (Scheme 1d), and suggest 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**) having two C−S bonds and $[W_3(\mu_3\text{-S})(\mu\text{-S})_2(\mu\text{-SCH{=}CH_2})(NCS)_9]^{4-}$ (**8**) having one C−S bond. The configurations of the μ-SCH=CH₂ moieties in **4** and **8** will be compared. In addition, we report here the reaction of the diethyldithiophosphate (dtp)

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tungsten cluster $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(\mu\text{-}OAc)(dtp)_3(CH_3CN)]$ (**10**) with DMAD in acetonitrile containing acetic acid to result in the formation of another complex having two DMAD molecules in different coordination modes, $[W_3(\mu_3\text{-}S)(\mu\text{-}SC(CO_2){=}CH(CO_2CH_3))(\mu_3\text{-}SC(CO_2CH_3){=}C(CO_2CH_3)S)(\mu\text{-}OAc)(dtp)_3]$ (**11**), where the hydrolysis of one of the four ester groups of the two DMAD moieties occurred and the resultant carboxylate group coordinated to tungsten. A preliminary report of portions of this work has appeared.[11]

Experimental Section

Materials and Reagents. All chemicals were obtained from commercial sources and used as received.

Syntheses of Compounds. $K_{0.5}(Hpy)_{4.5}[W_3(\mu_3\text{-}S)\mu\text{-}S)_3(NCS)_9]\cdot H_2O$ (5′). The same procedures as those in the synthesis of $(Hbpy)_5[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(NCS)_9]\cdot 3H_2O$[12] were used except for the use of pyridine instead of bipyridine. To a conical flask containing the aqua cluster **2** (3.32×10^{-3} M in 0.1M HCl, 100 mL) was added KSCN to make a 1.5 M KSCN solution. The resultant purple solution was then heated in a water bath for 90 min at 50 °C. The color of the solution turned to green. Addition of pyridine (0.50 mL, 6.21×10^{-3} mol) to the solution and allowing the solution to stand at room temperature for a few days gave green crystals of **5′**; yield, 0.402 g (75%). Anal. of **5′** Found (Calcd for $W_3S_{13}K_{0.5}ON_{13.5}C_{31.5}H_{29}$): N, 11.96 (11.81); C, 23.72 (23.64); H, 1.86 (1.83).

$K_{0.3}(Hpy)_{3.7}[W_3(\mu_3\text{-}S)(\mu_3\text{-}SCH{=}CHS)(\mu\text{-}SCH{=}CH_2)(NCS)_9]$ (6′). To a conical flask containing **2** (3.04×10^{-3} M in 0.1 M HCl, 100 mL) was added KSCN to make a 1.5 M KSCN solution through which a stream of acetylene gas was passed for 15 min; the flask was then sealed at room temperature (1 atm). The resultant solution was kept at 50 °C for 3 days in a water bath. The color turned to brownish green. Addition of pyridine (0.30 mL, 3.72×10^{-3} mol) to the solution and allowing the solution to stand at room temperature for a few days gave brown needlelike crystals of **6′**; yield, 0.313 g (65%). Anal. of **6′** Found (Calcd for $W_3K_{0.3}S_{13}N_{12.7}C_{31.5}H_{27.2}$): N, 11.50 (11.38); C, 24.59 (24.19); H, 1.68 (1.75).

$(Hpy)_4[W_3(\mu_3\text{-}S)(\mu_3\text{-}SCH{=}CHS)(\mu\text{-}SCH{=}CH_2)(NCS)_9]\cdot 1.33py\cdot 0.5H_2O$ (6″). Crystals of **6″** suitable for X-ray crystallography were obtained by the recrystallization of **6′**. The cluster **6′** (50 mg, 3.20×10^{-5} mol) was dissolved in a 1.5 M KSCN solution (15 mL), and the mixture was filtered. To the filtrate were added a few drops of a mixture of 1.0 M HCl and pyridine (1: 1 by volume), and the resultant solution was allowed to stand at room temperature for a few days. Platelike crystals of **6″** were obtained together with a small amount of **6′**; **6″** and **6′** were separated from each other manually. Anal. of **6″** Found (Calcd for $W_3S_{13}O_{0.5}N_{14.33}C_{39.65}H_{36.65}$): N, 11.68 (11.87); C, 28.00 (28.17); H, 2.22 (2.19)%.

$[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(\mu\text{-}dtp)(dtp)_3(CH_3CN)]$ (9). Similar procedures were applied to those of the preparation of the corresponding molybdenum complex $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(\mu\text{-}dtp)(dtp)_3(CH_3CN)]$.[13] To a conical flask containing **2** (5.41×10^{-2} M in 1.0 M HCl, 100 mL) was added an ethanolic solution of Hdtp (ca. 1.8 M, 40 mL). A black oily material deposited immediately and solidified overnight and was then filtered. For recrystallization, the precipitate was dissolved in acetonitrile (35 mL), and the resultant solution was kept in a freezer for a week. Green platelike crystals of **9**·CH_3CN were obtained; yield, 1.98 g (24%). Anal. Found (Calcd for $W_3S_{12}P_4O_8NC_{18}H_{43}$): N, 0.99 (0.96); C, 14.58 (14.76); H, 2.68 (2.97).[14]

$[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(\mu\text{-}OAc)(dtp)_3(CH_3CN)]$ (10). The cluster **10** having μ-OAc was obtained by similar procedures to those for the preparation of $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(\mu\text{-}OAc)(dtp)_3(py)]$.[15] To a solution of **9**·CH_3CN (500.1 mg, 3.33×10^{-4} mol) in CH_3CN (25 mL) was added acetic acid (6.0 mL, 1.05×10^{-1} mol, 300 equiv). Immediate color change of the solution from green to brown was observed. The solution was kept in a freezer (−20 °C) for a week, and brown platelike crystals of **10**·CH_3CN deposited; yield, 0.387 g (84%). Anal. Found (Calcd for $W_3S_{10}P_3O_8NC_{16}H_{36}$): N, 0.99 (1.05); C, 13.98 (14.39); H, 2.66 (2.72).[14]

$[W_3(\mu_3\text{-}S)(\mu\text{-}SC(CO_2){=}CH(CO_2CH_3))(\mu_3\text{-}SC(CO_2CH_3){=}C(CO_2CH_3)S)(\mu\text{-}OAc)(dtp)_3]$ (11). To a solution of **10**·CH_3CN (99.8 mg, 7.25×10^{-2} mmol) in CH_3CN (1.0 mL) were added acetic acid (1.25 mL, 21.8 mmol) and DMAD (0.90 mL, 7.32 mmol) under a dinitrogen atmosphere. The mixture was stirred continuously overnight. Then, the following procedures were done in the air. To the resultant brownish green solution was added water (ca. 50 mL). The oily product separated by decantation was dissolved in acetone (ca. 20 mL). Then, the solvent (acetone) was removed using a flash evaporator. The resultant solid was dissolved in acetonitrile (2.0 mL), and the solution was kept in a freezer (−20 °C) for a few days to give black-green platelike crystals of **11**·CH_3CN; yield, 46.1 mg (40%). Anal. Found (Calcd for $W_3S_{10}P_3O_{16}C_{25}H_{43}$): C, 19.36 (19.19); H, 2.62 (2.77).[14]

Structural Determination 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″) and $[W_3(\mu_3\text{-}S)(\mu\text{-}SC(CO_2){=}CH(CO_2CH_3))(\mu_3\text{-}SC(CO_2CH_3){=}C(CO_2CH_3)S)(\mu\text{-}OAc)(dtp)_3]\cdot CH_3CN$ (11·CH_3CN). X-ray diffraction data were collected with a Rigaku CCD diffractometer and analyzed using the teXsan System. The crystal dimensions of the analyzed crystals **6″** and **11**·CH_3CN were $0.23 \times 0.18 \times 0.13$ mm^3 and $0.53 \times 0.49 \times 0.10$ mm^3, respectively. Single crystals were mounted on the tips of glass fibers and cooled to −160 °C. The structures of **6″** and **11**·CH_3CN were solved by the direct methods (SIR92)[16] and Patterson methods (DIRDIF94),[17] respectively, and all the remaining non-hydrogen atoms were located from difference maps.

As to **6″**, both acetylene moieties were disordered, and each was modeled over two positions: (C1a, C2a; C3a, C4a) and (C1b, C2b; C3b, C4b), the rotation of the former group by 120° giving the latter group (see Supporting Information). The occupancy factors of the carbon atoms of the former group were assigned to be 0.55, and those of the latter groups, 0.45, which resulted in fairly similar temperature factors of the corresponding carbon atoms. The bridging sulfur-acetylenic carbon distances were fixed to 1.77 Å, which was referred to the S−C distances determined by the X-ray crystallography of **4′**. Two of the nine NCS^- ligands in **6″** were disordered, and each of the disordered ones was split into two. According to the elemental analysis and charge balance, there must be four pyridinium ions and one and one-third pyridine molecules. No

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Chart 1. Abbreviations and Formula Numbers of Stable Products

dtp	dietyldithiophosphate anion
DMAD	dimethylacetylenedicarboxylate
HOAc	acetic acid

$[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})_2(H_2O)_9]^{4+}$ (**1**)
$[W_3(\mu_3\text{-S})(\mu\text{-S})_3(H_2O)_9]^{4+}$ (**2**)
$[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})_2(NCS)_9]^{5-}$ (**3**)
$[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})(\mu\text{-SCH=CH}_2)(NCS)_9]^{4-}$ (**4**)
$K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})(\mu\text{-SCH=CH}_2)(NCS)_9]$ (**4'**)
$[W_3(\mu_3\text{-S})(\mu\text{-S})_3(NCS)_9]^{5-}$ (**5**)
$K_{0.5}(Hpy)_{4.5}\,[W_3(\mu_3\text{-S})(\mu\text{-S})_3(NCS)_9]\cdot H_2O$ (**5'**)
$[W_3(\mu_3\text{-S})(\mu_3\text{-SCH=CHS})(\mu\text{-SCH=CH}_2)(NCS)_9]^{4-}$ (**6**)
$K_{0.3}(Hpy)_{3.7}[W_3(\mu_3\text{-S})(\mu_3\text{-SCH=CHS})(\mu\text{-SCH=CH}_2)(NCS)_9]$ (**6'**)
$(Hpy)_4[W_3(\mu_3\text{-S})(\mu_3\text{-SCH=CHS})(\mu\text{-SCH=CH}_2)(NCS)_9]\cdot 1.33py\cdot 0.5H_2O$ (**6"**)
$[W_3(\mu_3\text{-S})(\mu\text{-S})(\mu_3\text{-SCH=CHS})(NCS)_9]^{5-}$ (**7**)
$[W_3(\mu_3\text{-S})(\mu\text{-S})_2(\mu\text{-SCH=CH}_2)(NCS)_9]^{4-}$ (**8**)
$[W_3(\mu_3\text{-S})(\mu\text{-S})_3(\mu\text{-dtp})(dtp)_3(CH_3CN)]$ (**9**)
$[W_3(\mu_3\text{-S})(\mu\text{-S})_3(\mu\text{-OAc})(dtp)_3(CH_3CN)]$ (**10**)
$[W_3(\mu_3\text{-S})(\mu\text{-SC(CO}_2\text{)=CH(CO}_2\text{CH}_3\text{)})(\mu_3\text{-SC(CO}_2\text{CH}_3\text{)=C(CO}_2\text{CH}_3\text{)S})(\mu\text{-OAc})(dtp)_3]$ (**11**).

attempt, however, was made to distinguish between pyridinium ions and pyridine molecules. Further, it was difficult to distinguish between nitrogen and carbon atoms in the pyridinium ions and pyridine molecules. In the initial stage, all the atoms in the pyridinium and pyridine groups were tentatively assigned to carbon atoms. Then, the atom having the smallest temperature factor in each group was assigned to the nitrogen atom. Thus, five nitrogen atoms were determined (atom label and occupancy factor: N81, 1.0; N82, 1.0; N83, 1.0; N84, 1.0; N85, 0.333). As to the remaining one pyridinium ion (or one pyridine molecule), two groups were found, each of them residing at or near a center of symmetry. Since it was impossible to distinguish between nitrogen and carbon atoms in the groups, each atom position was assigned to have occupancy factors of 5/6 for C and 1/6 for N, and the positions and temperature factors of the carbon atoms were refined, those of the nitrogen atoms being fixed (N861, N862, N863, C861, C862, C863; N871, N872, N873, C871, C872, C873). One of the methyl groups of the dtp's in **11**$\cdot$$CH_3CN$ was disordered and modeled over two positions, each with 50% occupancy.

All hydrogen atoms in **6″** and **11**$\cdot$$CH_3CN$ were assigned to idealized positions with thermal parameters that were 1.2 times the thermal parameters of the carbon atoms to which each was attached. All the calculations for the refinement of **6″** and **11**$\cdot$$CH_3CN$ were performed using the teXsan crystallographic software package.[18] Although the residual electron densities were not small in **6″** and **11**$\cdot$$CH_3CN$, they were near the tungsten atoms.

The crystal data and structure refinement parameters for **6″** and **11**$\cdot$$CH_3CN$ are listed in Table 1. All pertinent crystallographic information for each complex, including bond distances and angles, atomic coordinates, and equivalent isotropic displacement parameters, is provided in the Supporting Information.

Measurements of NMR Spectra. Spectra from ^1H NMR, ^{13}C NMR, and HH correlation spectroscopy (COSY) were obtained with a Bruker ARX-400R spectrometer.

Table 1. Crystallographic Data for$(Hpy)_4[W_3(\mu_3\text{-S})(\mu\text{-SCH=CH}_2)(\mu_3\text{-SCH=CHS})(NCS)_9]\cdot 1.33py\cdot 0.5H_2O$ (**6″**) and $[W_3(\mu_3\text{-S})(\mu\text{-SC(CO}_2\text{)=CH(CO}_2\text{CH}_3\text{)})(\mu_3\text{-SC(CO}_2\text{CH}_3\text{)=C(CO}_2\text{CH}_3\text{)S})(\mu\text{-OAc})(dtp)_3]\cdot CH_3CN$ (**11**$\cdot$$CH_3CN$)

	6″	**11**$\cdot$$CH_3CN$
formula	$W_3S_{13}O_{0.5}N_{14.33}C_{39.65}H_{36.65}$	$W_3S_{10}P_3O_{16}NC_{27}H_{46}$
fw	1690.22	1605.73
cryst syst	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No.2)
a (Å)	14.725(1)	13.163(2)
b (Å)	15.259(1)	14.100(3)
c (Å)	26.033(1)	14.663(2)
α (deg)		102.606(2)
β (deg)	105.3243(2)	100.461(2)
γ (deg)		108.053(3)
V (Å^3)	5641.3(4)	2432.4(7)
Z	4	2
R1^a	0.039	0.031
R, R_w^{b}	0.065, 0.098	0.059, 0.088
μ (cm^{-1})	66.36	76.74
T (°C)	−160.0	−160.0
GOF^c	1.00	1.07

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $1 > 2\sigma(I)$. [b] $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$, $R_w(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [c] Goodness of fit indicator $= [\Sigma w(F_o^2 - F_c^2)^2/(N_{\text{observations}} - N_{\text{variables}})]^{1/2}$.

Expt 1. ^{1}H NMR of 6′. The cluster **6′** (204.0 mg, 1.20×10^{-4} mol) was dissolved in CD_3CN (1.0 mL) for the measurement of ^1H NMR and HH COSY at 20 °C, 400 MHz, TMS = 0.0 ppm.

Expt 2. ^{1}H NMR Spectral Change from 5 to 6 in 0.1 M HCl Containing 1.5 M KSCN. A stream of acetylene gas was passed through the cluster **5** (2.27×10^{-3} M) in 0.1 M HCl (500 mL) containing 1.5 M KSCN for 15 min, and the solution was sealed and then heated at 50 °C. After 3 h, 12 h, 1 day, and 2 days, portions (each 50 mL) of the solution were removed, and pyridine (each 0.30 mL, 3.72×10^{-3} mol) was added to it. Resultant powder samples (3 h, 148.2 mg; 12 h, 145.8 mg; 1 day, 134.8 mg; 2 days, 148.6 mg) were separated by filtration, 3 days after the addition of pyridine.[19] Each sample was dissolved in CD_3CN for the measurement of ^1H NMR at 20 °C, 400 MHz, TMS = 0.0 ppm.

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(18) *Crystal structure Analysis Package*; Molecular Structure Corporation: The Woodlands, TX, 1985 and 1992.

Expt 3. ^{1}H NMR Spectral Change from 5 to 6 in a Mixture of 1.0 M DCl Containing 1.5 M KSCN and CD_3CN (1:1). Cluster **5′** (100.02 mg, 6.40×10^{-5} mol) was dissolved in a mixture (1.0 mL) of 1.0 M DCl containing 1.5 M KSCN and CD_3CN (1:1), through which a stream of acetylene gas was passed for 5 min. The flask was then sealed and kept at room temperature. ^{1}H NMR spectra were taken after 1, 7, 14, and 21 days at 20 °C, 400 MHz, $CD_3CN = 1.95$ ppm.

Expt 4. ^{1}H NMR of 11·CH_3CN. Cluster **11**·CH_3CN (11.2 mg, 6.98×10^{-3} mmol) was dissolved in CD_3CN (1.0 mL) for the measurement of ^{1}H NMR at 20 °C, 400 MHz, TMS = 0.0 ppm.

Expt 5. ^{1}H NMR Spectral Change from 10 to 11 in CH_3CN. Cluster **10**·CH_3CN (50.0 mg, 3.63×10^{-2} mmol) was dissolved in CH_3CN(1.0 mL), to which acetic acid (0.63 mL, 11.0 mmol; 300 equiv) and DMAD (0.45 mL, 3.66 mmol; 100 equiv) were added, and the mixture was stirred for 17 h under a dinitrogen atmosphere. Then, in the air, water was added to the mixture to give a precipitate, which was filtered and air-dried. A portion (10 mg) of the precipitate was dissolved in CD_3CN (1.0 mL) for the measurement of ^{1}H NMR at 20 °C, 400 MHz, TMS = 0.0 ppm.

Measurements of Electronic Spectra. Electronic spectra were measured using a Hitachi U-2000 double-beam spectrophotometer.

Expt 6. An electronic spectrum of **10** (19.7 mg, 1.43×10^{-2} mmol) in CH_3CN (3.0 mL) was taken. Then, to the solution was added excess DMAD (100 equiv; 0.18 mL, 1.46 mmol) in a dinitrogen atmosphere; the electronic spectra were taken immediately and after 1, 2, 3, 4, 5, and 17 h using a 1 mm cell.

Expt 7. An electronic spectrum of **10** (19.7 mg, 1.43×10^{-2} mmol) in CH_3CN was taken. Then, to the solution were added excess HOAc (300 equiv; 2.5×10^{-1} mL, 4.36 mmol) and excess DMAD (100 equiv; 0.18 mL, 1.46 mmol) in a dinitrogen atmosphere, and the electronic spectra were taken immediately and every hour using a 1 mm cell.

Thin-Layer Separation. The precipitate obtained by the addition of water (see synthesis of **11**) was dissolved in CH_2Cl_2 and separated by thin-layer chromatography (Whatman, PLK 5 SILICA GEL 150A; $CH_2Cl_2/C_6H_{14} = 4$).

Results and Discussion

The abbreviations and formula numbers of stable products are summarized in Chart 1.

Synthesis of $[W_3(\mu_3\text{-}S)(\mu_3\text{-}SCH{=}CHS)(\mu\text{-}SCH{=}CH_2)(NCS)_9]^{4-}$ (6). Previously, we reported that an oxygen- and sulfur-bridged tungsten aqua cluster **1** did not react with acetylene but that the thiocyanate cluster **3** did react with acetylene to give **4** having one S−C bond.[9] Similarly, we found that a sulfur-bridged tungsten aqua cluster **2** did not react with acetylene but that the thiocyanate cluster **5** did react with acetylene to give **6**, which was isolated as potassium pyridinium salt, **6′**. Since we have reported the synthesis and X-ray structure of bipyridinium salt of **5**, $(Hbpy)_5[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(NCS)_9]\cdot 3H_2O$,[12b] we tried to isolate crystals of bipyridinium salt of **6** suitable for X-ray crystallography; however, we were unsuccessful. Instead, we succeeded in isolating crystals of pyridinium salt **6″**.

The reaction of **5** with acetylene to give **6** was performed in 0.1 M HCl rather than in 1 M HCl, while that of **3** with acetylene to give **4** was done in 1 M HCl.[9] The rate of the former reaction was fast enough in 0.1 M HCl. A lower HCl concentration is preferred because, at higher acid concentrations, the decomposition of NCS^- ion occurs more rapidly to give white precipitates. Cluster **5** is stable in the air, and the spectrum does not change for more than a month in either 0.1 M HCl containing 1.5 M KSCN or acetonitrile.

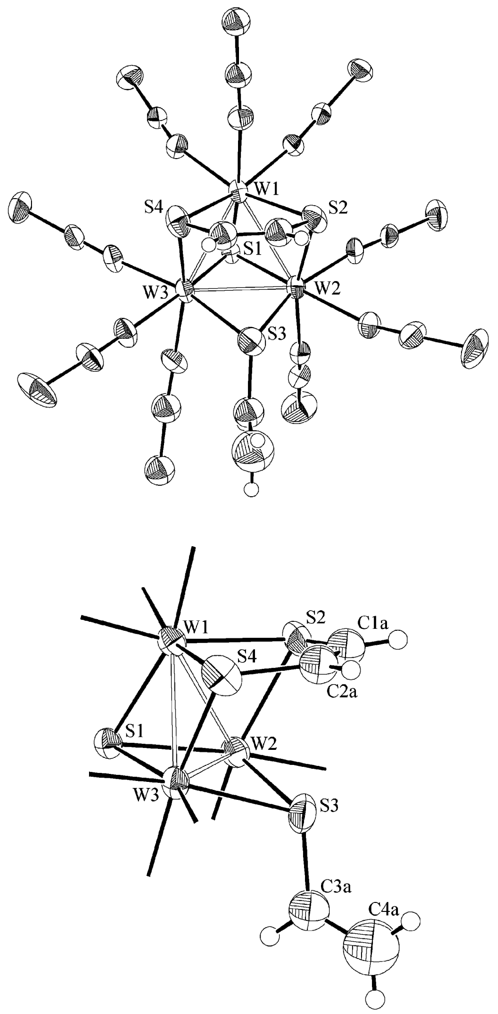

Figure 1. ORTEP drawings of the anion of **6″** at the 50% probability level. One of the two sets of the disordered acetylene molecules and each one of the two disordered NCS groups are shown for clarity. Top: whole structure. Bottom: the moiety of the W_3S_4 core and acetylene molecules.

Synthesis of $[W_3(\mu_3\text{-}S)(\mu\text{-}SC(CO_2){=}CH(CO_2CH_3))(\mu_3\text{-}SC(CO_2CH_3){=}C(CO_2CH_3)S)(\mu\text{-}OAc)(dtp)_3]$ (11). Cluster **11** was synthesized from **2** via **9** and **10**. After the reaction of **10** with a large excess of DMAD was completed in acetonitrile containing acetic acid, a large amount of water was added to the reaction mixture, and the resultant precipitate was separated from the excess DMAD and acetic acid by filtration. The precipitate containing **11** was dissolved in acetone, and the solution was evaporated to dryness and then dissolved in acetonitrile to give crystals of **11**·CH_3CN. Although clusters **10** and **11** are stable to air oxidation, the reaction of **10** with DMAD that took place in the air gave a much smaller amount (6.8%) of **11** compared to the amount (40%) that took place in a dinitrogen atmosphere, which

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(19) A large excess of pyridine was added to obtain as much product as possible. Each filtrate was pale in color, indicating that most of the clusters in the solution were precipitated by the addition of pyridine.

Table 2. Interatomic Distances (Å) and Angles (deg) in $(Hpy)_4[W_3(\mu_3\text{-}S)(\mu\text{-}SCH{=}CH_2)(\mu_3\text{-}SCH{=}CHS)(NCS)_9]\cdot 1.33py\cdot 0.5H_2O$ (**6″**)

Distances

atom	atom	distance	atom	atom	distance
W1	W2	2.7251(3)	W1	W3	2.7217(4)
W2	W3	2.7078(3)	W1	S1	2.362(1)
W1	S2	2.400(2)	W1	S4	2.406(2)
W1	N11	2.139(6)	W1	N12	2.099(5)
W1	N13	2.117(5)	W2	S1	2.352(1)
W2	S2	2.419(2)	W2	S3	2.404(2)
W2	N21	2.147(5)	W2	N22	2.111(6)
W2	N23	2.093(6)	W3	S1	2.365(1)
W3	S3	2.441(2)	W3	S4	2.412(2)
W3	N31	2.143(6)	W3	N32	2.101(5)
W3	N33	2.086(6)			
C1a	C2a	1.37(2)	C1b	C2b	1.30(2)
C3a	C4a	1.36(3)	C3b	C4b	1.29(3)

Angles

atom	atom	atom	angle	atom	atom	atom	angle
W2	W1	W3	59.620(9)	W1	W2	W3	60.126(9)
W1	W3	W2	60.253(9)	S2	W1	S4	87.29 (6)
S2	W2	S3	87.48(7)	S3	W3	S4	89.60(7)
W2	S3	W3	67.96(5)				
W1	S2	C1a	99.8(5)	W1	S4	C2a	104.6(5)
W2	S3	C3a	112.1(5)	W3	S3	C3a	109.4(5)
S2	C1a	C2a	129.2(9)				
S3	C3a	C4a	119(1)				
S4	C2a	C1a	117.8(9)				

suggests the presence of air-unstable intermediate species. We have not succeeded in identifying any intermediate.

As was revealed by the X-ray analysis of **11**·CH_3CN, one of the four ester groups originating from two DMAD molecules was hydrolyzed to give a carboxylic group, which was coordinated to tungsten. Probably, hydrolysis had occurred before the addition of water, since the addition of water caused immediate precipitation, and the time was too short for hydrolysis to have been the result of the addition of water. The water in the acetic acid might be responsible.

X-ray Structures 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″) and $[W_3(\mu_3\text{-}S)(\mu\text{-}SC(CO_2){=}CH(CO_2CH_3))(\mu_3\text{-}SC(CO_2CH_3){=}C(CO_2CH_3)S)(\mu\text{-}OAc)(dtp)_3]\cdot CH_3CN$ (11·CH_3CN). The X-ray structural analysis of **6″** revealed two acetylene molecules attached to the three μ-S atoms (Figure 1). The interatomic distances and angles are listed in Table 2. Although the two acetylene molecules are disordered (see Experimental Section), it is clear that the two molecules exist in different adduct-formation modes. It should be noted that the conformation of the μ-S(3)C(3a)H═C(4a)H_2 moiety in **6″** is different from that of the corresponding moiety in **4′**. The moiety in **6″** is far from the line perpendicular to the plane defined by the tungsten triangle and passing through the center of gravity of the triangle, while the corresponding moiety in **4′** is close to the line (see also Scheme 1c). The reason for the difference between the two conformations will be discussed later in the description of the reaction mechanism.

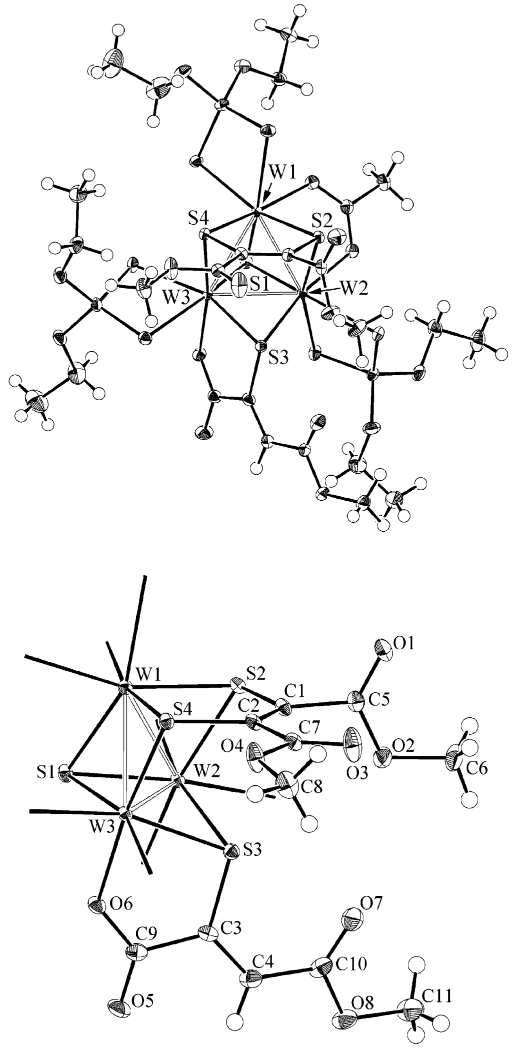

Figure 2. ORTEP drawings of **11** in **11**·CH_3CN at the 50% probability level. Top: whole structure. Bottom: the moieties of the W_3S_4 core and DMAD molecules.

The ORTEP view of **11** is shown in Figure 2. The interatomic distances and angles are listed in Table 3. Of the four ester-groups originating from two DMAD molecules, one group (bonding to C1) was hydrolyzed to give a carboxylic group, which was then coordinated to tungsten (W1). The μ-SC(CO_2)═CH(CO_2CH_3) moiety was also far from the line, as defined above, and it should also be noted that the hydrogen atom originated by proton addition was trans to S4. This will also be discussed in the section describing the reaction mechanism. The distances in **11**, C1−C2 and C6−C7, are closer to that of ethylene (1.339 Å) than to that of acetylene (1.203 Å), and the bond angles about C1, C2, C6, and C7 are close to 120°. In addition, the atoms C1, C2, C3, C4, and S4 in the moiety μ-SC(CO_2)═CH(CO_2CH_3) are on the same plane, and the atoms C6, C7, C9, C10, S2, and S3 in the moiety μ_3-SC(CO_2CH_3)═C(CO_2CH_3)S are on the same plane. These all indicate the sp^2 character of the orbitals of the carbon atoms.

Reaction Mechanism of $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(NCS)_9]^{5-}$ (5) to $[W_3(\mu_3\text{-}S)(\mu_3\text{-}SCH{=}CHS)(\mu\text{-}SCH{=}CH_2)(NCS)_9]^{4-}$ (6), and ^1H NMR and Electronic Spectra of the Relevant Clusters. We propose the reaction mechanism of **5** to **6** in Scheme 2, where the presence of intermediates **7**, **8**, **8a**, and **8b** is postulated, and a conformational change of the μ-SCH═CH_2 moiety is supposed to occur between **8** and **6**, which will be discussed in detail.

Scheme 2. Reaction of **5** with Acetylene to Give **6** via Intermediates **7**, **8**, **8a**, and **8b**

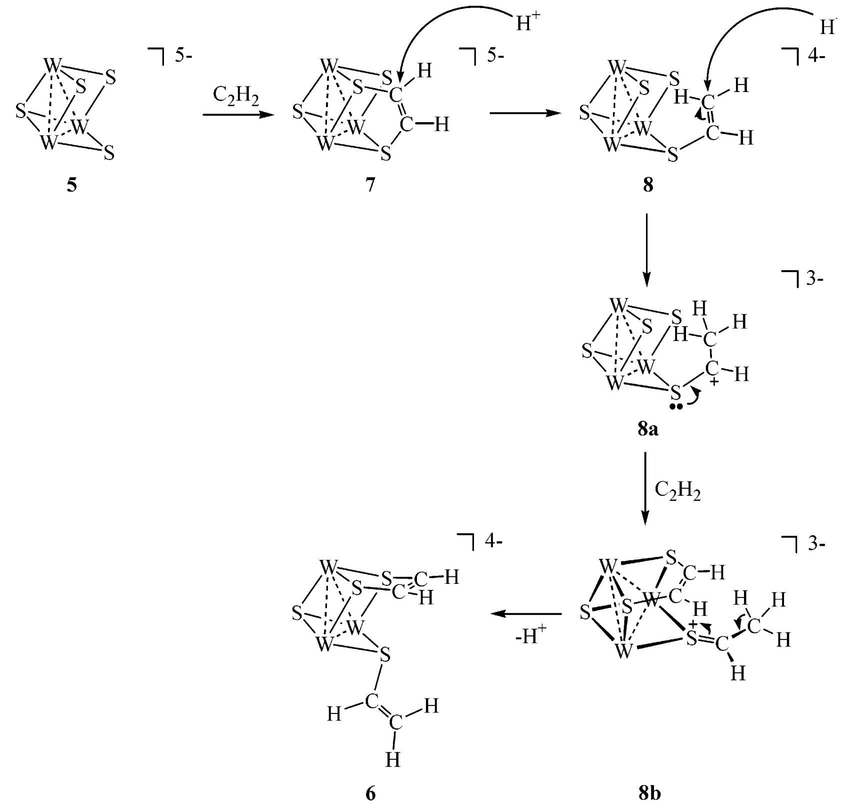

Table 3. Interatomic Distances (Å) and Angles (deg) in $[W_3(\mu_3\text{-}S)(\mu\text{-}SC(CO_2){=}CH(CO_2CH_3))(\mu_3\text{-}SC(CO_2CH_3){=}C(CO_2CH_3)\text{-}S)(\mu\text{-}OAc)(dtp)_3]\cdot CH_3CN$ (**11**·CH_3CN)

Distances

atom	atom	distance	atom	atom	distance
W1	W2	2.6509(2)	W1	W3	2.7276(3)
W2	W3	2.6895(2)	W1	S1	2.358(1)
W1	S2	2.4021(8)	W1	S4	2.3845(8)
W1	S11	2.579(1)	W1	S12	2.5008(9)
W1	O41	2.135(3)	W2	S1	2.3598(8)
W2	S2	2.440(1)	W2	S3	2.4527(9)
W2	S21	2.5759(9)	W2	S22	2.488(1)
W2	O42	2.135(3)	W3	S1	2.3615(8)
W3	S3	2.4175(9)	W3	S4	2.4308(9)
W3	S31	2.5812(9)	W3	S32	2.4772(9)
W3	O6	2.073(3)			
S2	C1	1.809(4)	S3	C3	1.790(4)
S4	C2	1.789(4)			
C1	C2	1.325(5)	C3	C4	1.336(5)

Angles

atom	atom	atom	angle	atom	atom	atom	angle
W2	W1	W3	59.987(6)	W1	W2	W3	60.423(7)
W1	W3	W2	58.590(5)	S2	W1	S4	85.07(3)
S2	W2	S3	91.05(3)	S3	W3	S4	95.34(3)
W2	S3	W3	67.04(2)				
W1	S2	C1	104.8(1)	W1	S4	C2	105.9(1)
W2	S3	C3	106.3(1)	W3	S3	C3	97.5(1)
S2	C1	C2	122.2(3)				
S3	C3	C4	123.1(3)				
S4	C2	C1	122.0(3)				

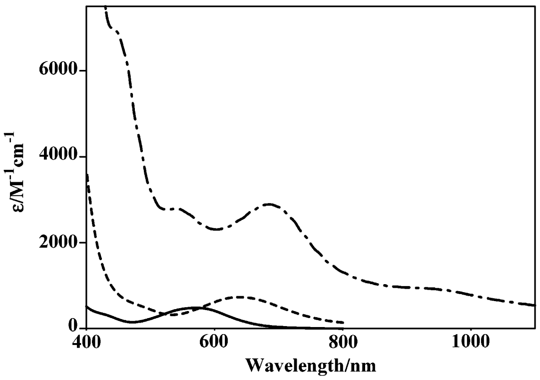

Figure 3. Electronic spectra of (—) **2**, (- - -) **5**, and (— · —) **6**.

Table 4. Electronic Spectral Data of $K_{0.3}(Hpy)_{3.7}[W_3(\mu_3\text{-}S)(\mu_3\text{-}SCH{=}CHS)(\mu\text{-}SCH{=}CH_2)(NCS)_9]$ (**6′**), $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(\mu\text{-}dtp)(dtp)_3(CH_3CN)]\cdot CH_3CN$ (**9**·CH_3CN), $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(\mu\text{-}OAc)(dtp)_3(CH_3CN)]\cdot CH_3CN$ (**10**·CH_3CN), and $[W_3(\mu_3\text{-}S)(\mu\text{-}SC(CO_2){=}CH(CO_2CH_3))(\mu_3\text{-}SC(CO_2CH_3){=}C(CO_2CH_3)S)(\mu\text{-}OAc)(dtp)_3]\cdot CH_3CN$ (**11**·CH_3CN)

compd	λ_{max}, nm (ϵ/M^{-1} cm^{-1})	solvent
6′	440sh (6980), 538 (2790), 684 (2890)	0.1M HCl containing 1.5 M KSCN
9·CH_3CN	567 (473), 610sh (388)	CH_3CN
10·CH_3CN	552 (421), 670 (247)	CH_3CN
11·CH_3CN	523 (2060), 628 (1780), 746 (1340)	CH_3CN

Electronic Spectra of **2**, **5**, and **6** are shown in Figure 3. The cluster **6** shows a much more stronger absorbance than **5** all over the region measured. Observation of electronic spectral changes of the reaction of **5** with acetylene to give the final product **6** indicated that it took approximately 2 days for the reaction to complete either in 1 or 0.1 M HCl, while it took more than four weeks for the reaction to complete at pH 3. Electronic spectral data of these and related clusters are listed in Table 4.

^1H NMR and HH correlation spectra of **6′** are shown in Figures 4 and 5, respectively; these spectra are in good agreement with the result of the X-ray structural analysis.

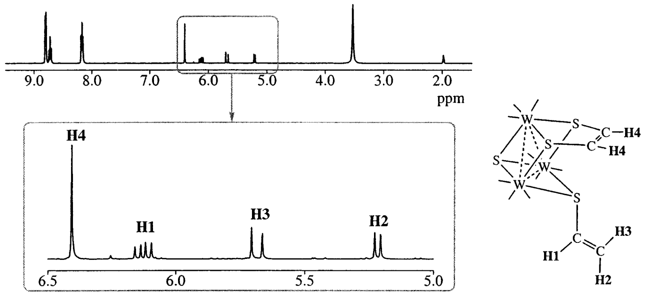

Figure 4. ^{1}H NMR spectrum of **6′** (20 °C, 400 MHz, CD_3CN).

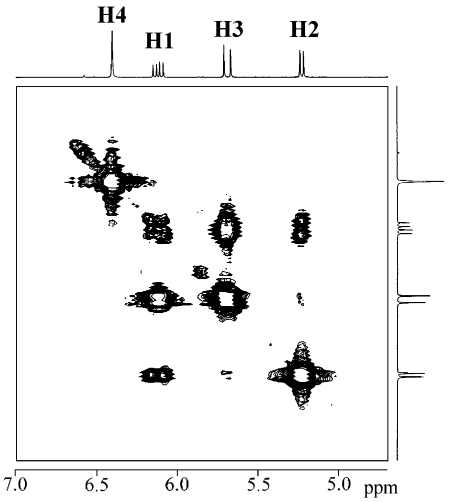

Figure 5. ^{1}H NMR and HH correlation spectra of **6′** (20 °C, 400 MHz, CD_3CN).

The four signals at 5.22 (1H, d, $J = 9.0$ Hz), 5.69 (1H, d, $J = 16.7$ Hz), 6.13 (1H, dd, $J = 9.0$, 16.7 Hz), and 6.42 (2H, s) ppm in the ^{1}H NMR spectra are assignable to either μ-SCH$=$CH$_2$ or μ_3-SCH$=$CHS moieties. The HH correlation spectrum shows spin couplings of the signal at 6.13 ppm with each of the two signals at 5.22 and 5.69 ppm. If the relationship "$J_{\mathrm{trans}} > J_{\mathrm{cis}}$" holds in this species,[20] the three protons H1 (6.13), H2 (5.22), and H3 (5.69 ppm) are assigned to the moiety μ-SCH$=$CH$_2$. No geminal coupling between H2 and H3 was observed. The remaining signal H4 at 6.42 ppm was assigned to the moiety μ_3-SCH$=$CHS. Signals at ca. 2.0 and 8−9 ppm are due to CH_3CN and Hpy$^+$, respectively. The intensity ratio of the sum of Hpy$^+$ and py groups to the sum of μ-SCH$=$CH$_2$ and μ_3-SCH$=$CHS moieties is 3.7, which is in good agreement with the theoretical value, 3.70. The ^{1}H NMR signal of H1 is at lower magnetic field than those of H2 and H3 (δ(H1) $>$ δ(H2), δ(H3)), as reported on the complexes with M$_2$(μ-SCH$=$CH$_2$) or M−SCH$=$CH$_2$ moieties (M $=$ metals).[2k,4,9] It should be noted that the corresponding signals of **4′** appear at a higher magnetic field region; furthermore, the signal of H1 (2.42 (1H, s) ppm) is at a much higher magnetic field than those of H2 (4.84 (1H, d, $J = 8.7$ Hz) ppm) and H3 (4.89 (1H, d, $J = 16.1$ Hz) ppm), 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 the tungsten triangle, while the corresponding moiety in **6** is away from the corresponding line. Therefore, the protons in **4**, especially H1, sense a shielding effect due to the W$_3$ or W$_3$(μ_3-S)(μ-O)(μ-S)$_2$ moiety, while H1 in **6** does not sense the shielding effect. The ring current due to the W$_3$ or W$_3$(μ_3-S)(μ-O)(μ-S)$_2$ will explain the shielding effect.[21,22]

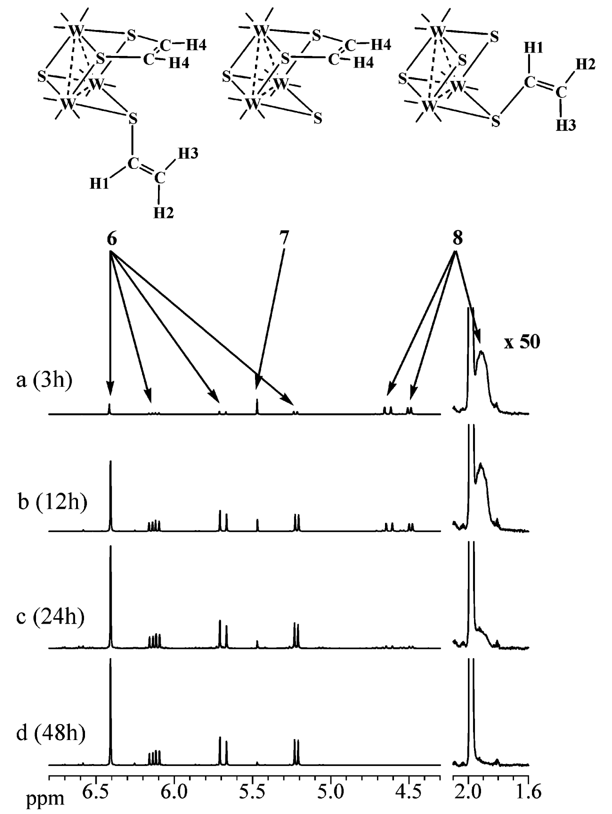

Figure 6. ^{1}H NMR spectral change during the reaction of **5** with acetylene in 1.0 M HCl: 3 and 12 h, and 1 and 2 days after mixing.

The ^{1}H NMR spectral change was followed to clarify the reaction mechanism of **5** to **6** (Figure 6). Figure 6a,b shows eight signals each; four of them are assignable to **6**, and one signal at δ 5.47 (s) of the four remaining ones is assignable to **7**. As to the remaining three signals, the HH COSY spectrum (Supporting Information) 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), and the relation δ (H1) $<$ δ (H2), δ (H3) holds. Therefore, the three signals are assignable to **8**. The time-course of signals in Figure 6 indicates that those due to **7** and **8** decrease, and those due to **6**, on the other hand, increase. The ^{1}H NMR spectrum (Figure 7) of the reaction products of **5′** with acetylene in the mixed solvent (1.0 M DCl/CD_3CN $=$ 1:1 containing 1.5 M KSCN) indicates the presence of isotopic isomers **b** and **c** in 1:1 ratio.[23] We propose the presence of intermediates **8a** and **8b** to account for the appearance of the isotopic isomers. A conformational change of the μ-SCH$=$CH$_2$ moiety is supposed to occur between **8** and **6**. It can be

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[20] Pretsch, E.; Clerc, T.; Soible, J.; Simon, W. *Table of Spectral Data for Structure Determination of Organic Compounds*, 2nd ed.; Springer: New York, 1985.

[21] Kobayashi, H.; Shibahara, T.; Uryu, N. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 799−803.

[22] Chen, Z.; Lu, J.-X.; Liu, C.-W.; Zhang, Q.-N. *Polyhedron* **1991**, *10*, 2799−2807.

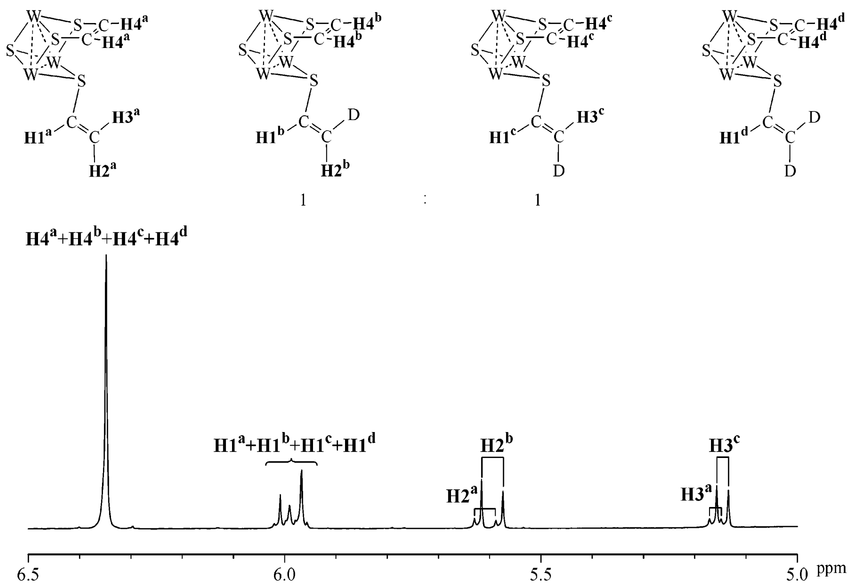

Figure 7. ^1H NMR spectrum of the reaction of **5** with acetylene in the mixture of 1.0 M DCl containing 1.5 M KSCN and CD_3CN (1:1), 21 days after mixing. Isotopic species are named **a**, **b**, **c**, and **d**.

concluded that the replacement of μ-O in **3** with μ-S to give **5** prompted the scission of the C−S bond, for the reaction rate of **3** with acetylene to give **4** in 0.1 M HCl was slower than that in 1 M HCl, and a C−S scission was not observed at pH 3.[9]

Reaction Mechanism of $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(\mu\text{-}OAc)(dtp)_3(CH_3CN)]$ (10) to $[W_3(\mu_3\text{-}S)(\mu\text{-}SC(CO_2){=}CH(CO_2CH_3))(\mu_3\text{-}SC(CO_2CH_3){=}C(CO_2CH_3)S)(\mu\text{-}OAc)(dtp)_3]$ (11), and ^1H NMR and Electronic Spectra of the Relevant Clusters. Taking into account the reaction mechanism of **5** to **6**,[24] we propose the reaction mechanism of **10** to **11** in Scheme 3, where the presence of intermediates **12**, **13**, **13a**, **13b**, and **13c** is postulated, which will be discussed in detail.

The electronic spectra of **10** and **11** are shown in Figure 8; the latter shows much stronger absorption over the range measured. Electronic spectral changes of the reaction of **10** with DMAD in CH_3CN with and without HOAc are shown in Figure 9a,b, respectively, each figure showing the spectrum of **10** for comparison. The strong absorption at ca. 700 nm in Figure 9b is most probably due to an intermediate with one molecule of DMAD having two C−S bonds. The intermediate is unstable even in a dinitrogen atmosphere: addition of HOAc to the resultant solution (i.e., after 17 h) did not give **11**. In Figure 9a, the strong peak at ca. 700 nm that appeared immediately after the reaction had started disappeared completely in an hour, and an entirely different spectrum started to appear. The peak in Figure 9a is weaker than that in Figure 9b, which indicates that the C−S bond cleavage of the intermediate is rapid and that a part of the intermediate has already changed to the final product **11**: the second addition reaction of DMAD also seems rapid.

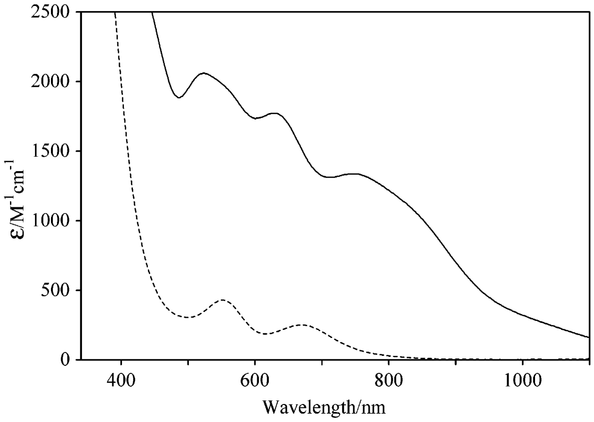

Figure 8. Electronic spectra of (- - -) **10**·CH_3CN and (—) **11**·CH_3CN in CH_3CN.

The final spectrum (after 17 h) in Figure 9a is not identical to the spectrum of **11** shown in Figure 8, though they are close to each other. The application of thin-layer chromatography revealed the presence of some byproducts, the yield of **11** in solution being 57%.

Figure 10 shows the ^1H NMR spectrum of **11**·CH_3CN. The following chemical shift values (ppm) were obtained: H^a, 6.76 (1H, s); dtp-CH_2, 4.28−4.04 (12H, broad-m); dtp-CH_3, 1.37−1.15 (18H, m); μ-OAc−CH_3, 2.03 (3H, s); H^b, 3.95 (3H, s), 3.84 (3H, s), 3.79 (3H, s). The chemical shift, 6.76 ppm, of the ethylenic proton H^a is not so different from that (5.23 ppm) of the corresponding proton H2 in **6′** when the effects of the substituents are taken into consideration.[25]

Although attempts to find any intermediates by ^1H NMR spectroscopy were unsuccessful, the reaction mechanism of **10** with DMAD to give **11** would be described temporarily

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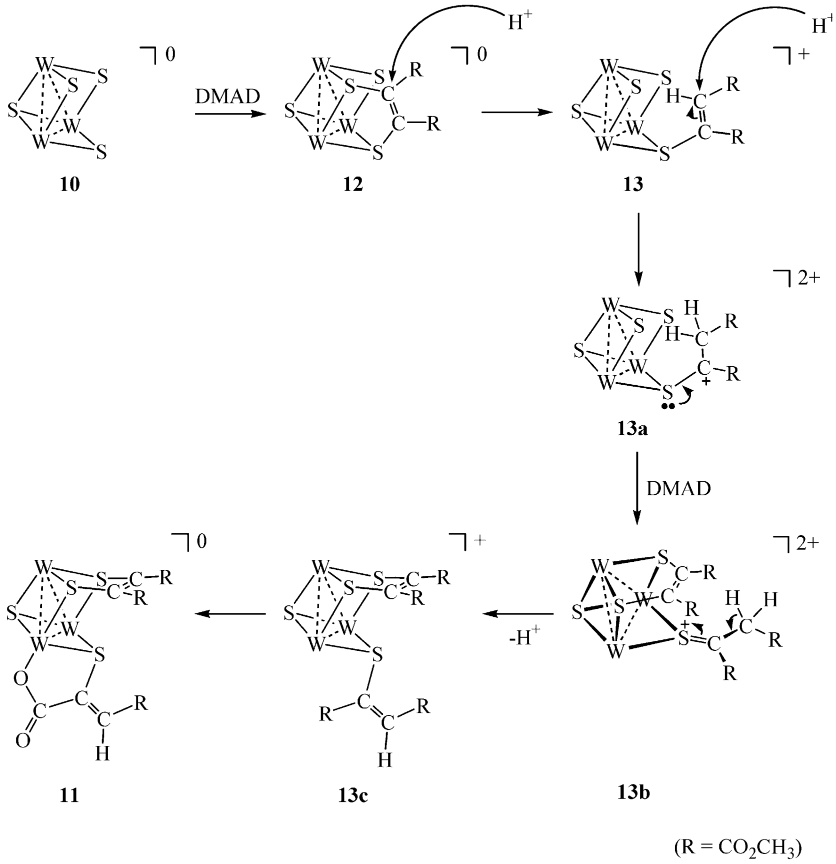
(23) Isotopic species are named **a**, **b**, **c**, and **d**. The species **a** should be minor. The ratio (1:1) of species **b** and **c** was calculated from the signal intensity ratio of $H2^b$ and $H3^c$. Signals due to H1 protons overlapped with each other and could not be assigned individually, and the amount of species **d** could not be determined.

(24) Attempts to find any intermediates of **10** to **11** were unsuccessful by ^1H NMR spectroscopy.

(25) For example: Pascual, C.; Meier, J.; Shimon, W. *Helv. Chim. Acta* **1965**, *49*, 164−168. **11**: H^a, measured 6.76 ppm, calcd 7.33 ppm (=5.28 + 0.90 (gem COOR) + 1.20 (cis COOR) − 0.05 (trans SR)). **6′**: H1, measured 6.13 ppm, calcd 6.28 ppm (=5.28 +1.0 (gem SR)); H2, measured 5.22 ppm, calcd 5.23 (=5.28 − 0.05 (trans SR)); H3, measured 5.69 ppm, calcd 5.03 (=5.28 − 0.25 (cis SR)); H4, measured 6.42 ppm, calcd 6.23 ppm (=5.28 + 1.0 (gem SR) − 0.05 (trans SR)).

Scheme 3. Reaction Mechanism of **10** with DMAD To Give **11** via Intermediates **12**, **13**, **13a**, **13b**, and **13c**



as follows (see Scheme 3). The reaction of **10** with DMAD gave **12**, and protonation at one of the ethylenic carbon atoms caused the C−S bond scission to give **13**. The second protonation gave **13a**, the second DMAD addition yielded **13b**, and loss of the proton gave **13c**. Hydrolysis of one of the ester groups and coordination of the resultant carboxylic group to the tungsten atom resulted in the formation of **11**, where the carboxylate and ester groups in the moiety μ-SC-(CO_2-)═CHR were trans to each other, and no species with a cis configuration was detected in the final product by ^{1}H NMR spectroscopy. This is probably due to the steric reason that the trans species **13c** has less steric hindrance than the imaginary cis species that could form on the loss of proton from **13b**, which is in contrast to the case of **6**, where no steric problem occurs in the acetylene moiety.

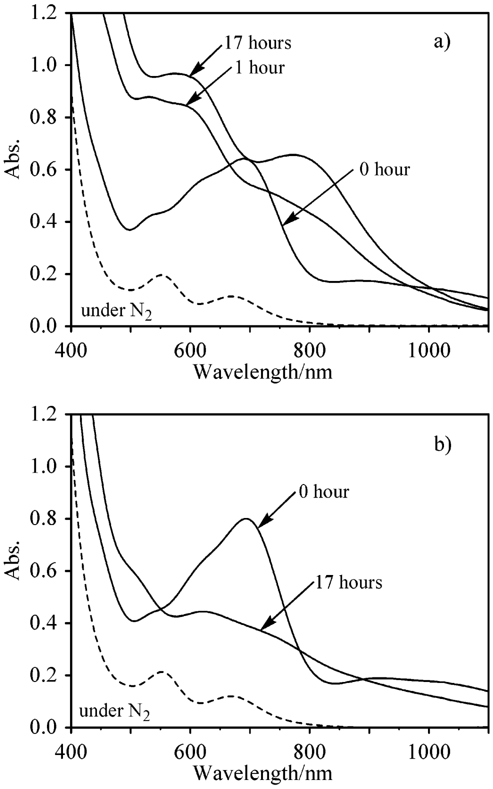


Figure 9. Electronic spectral changes in the reaction of **10**·CH_3CN with DMAD: (a) in CH_3CN containing HOAc; (b) in CH_3CN without HOAc.

The formation and scission of the C−S bond in dinuclear molybdenum complexes has been investigated by Rakowski DuBois and co-workers in detail.[1a,2i] The characteristic of the reactivity of the trinuclear clusters having $W_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cores toward acetylene or its derivative DMAD is that, after the scission of one C−S bond, the resultant complexes have the ability to combine with another acetylene or DMAD. Further C−S bond scission was not observed for **6** or **11**.

Conclusion

We have presented here a novel reaction for sulfur-bridged incomplete cubane-type tungsten clusters having $W_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cores with acetylene and its derivative dimethylacetylenedicarboxylate (DMAD). The reaction of the isothiocyanate tungsten cluster $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(NCS)_9]^{5-}$ (**5**) with acetylene in dilute HCl afforded $[W_3(\mu_3\text{-}S)(\mu_3\text{-}SCH{=}CHS)$-

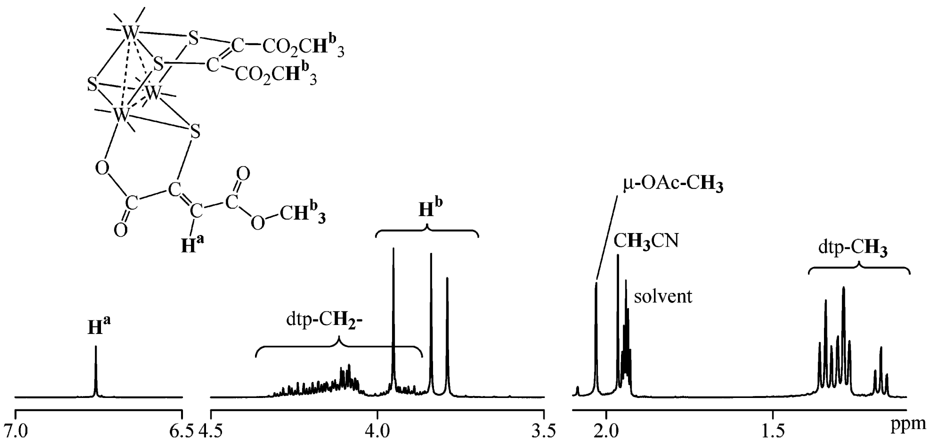


Figure 10. ^{1}H NMR spectrum of **11**·CH_3CN (20 °C, 400 MHz, CD_3CN).

(μ-SCH=CH$_2$)(NCS)$_9$]$^{4-}$ (**6**). The reaction of the diethyldithiophosphate (dtp) tungsten cluster [W_3(μ_3-S)(μ-S)$_3$(μ-OAc)(dtp)$_3$(CH_3CN)] (**10**) with DMAD in acetonitrile containing acetic acid gave [W_3(μ_3-S)(μ-SC(CO_2)=CH(CO_2CH_3))(μ_3-SC(CO_2CH_3)=C(CO_2CH_3)S)(μ-OAc)(dtp)$_3$] (**11**). The clusters were characterized by UV−vis spectroscopy, ^{1}H NMR spectroscopy, and X-ray crystallography, and the formation of **6** and **11** was examined in detail from a mechanistic point of view. First, the trinuclear cluster **5** reacts with one molecule of acetylene to give [W_3(μ_3-S)(μ-S)(μ_3-SCH=CHS)(NCS)$_9$]$^{5-}$ (**7**) having two C−S bonds, and after the scission of one C−S bond by the attack of H$^+$, the resultant complex still has the ability to combine with another acetylene molecule to give **6** having two acetylene molecules in different adduct formation modes. A similar reaction mechanism is suggested as to the formation of **11**.

As to oxygen- and sulfur-bridged cluster [W_3(μ_3-S)(μ-O)(μ-S)$_2$(NCS)$_9$]$^{5-}$ (**3**), the reaction product [W_3(μ_3-S)(μ-O)(μ-S)(μ-SCH=CH$_2$)(NCS)$_9$]$^{4-}$ (**4**) obtained from **3** and one molecule of acetylene (see Scheme 1c) did not receive a second acetylene molecule: at least two free μ-S species are necessary for the adduct formation.

No reaction was observed between **10** and acetylene with and without acetic acid, while addition of DMAD into **5** in 0.1 M HCl containing 1.5 M KSCN caused immediate color change (from green to brown) and formation of precipitate.[26] Therefore, the reactivity of DMAD toward **10** is much higher than that of acetylene. In addition, neither of the aqua clusters [W_3(μ_3-S)(μ-O)(μ-S)$_2$(H_2O)$_9$]$^{4+}$ (**1**) and [W_3(μ_3-S)(μ-S)$_3$(H_2O)$_9$]$^{4+}$ (**2**) in diluted HCl react with acetylene,[9] and it is clear that the coordination of NCS$^-$ to the clusters seems to give a large influence on the electronic structure of the bridging sulfurs.

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds **6″** and **11**·CH_3CN. Additional figures and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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[26] No detailed characterization has been made.