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Alkylation Reactions of $[WS_4]^{2-}$ and $[(\eta^5\text{-}C_5Me_5)WS_3]^-$ with 2,6-Bis(bromomethyl)pyridine: The First Isolation of Bisalkylated Tetrathiometalate $WS_2\{2,6\text{-}(SCH_2)_2(C_5H_3N)\}$

Rong Cao and Kazuyuki Tatsumi*

Research Center for Materials Science and Department of Chemistry, Graduate School of Science,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

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The trithio and tetrathio complexes of tungsten $(PPh_4)[Cp^*WS_3]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) and $(PPh_4)_2[WS_4]$ undergo alkylation reactions with 2,6-bis(bromomethyl)pyridine to yield $[(Cp^*WS_2)_2\{2,6\text{-}(SCH_2)_2\text{-}(C_5H_3N)\}]\cdot CH_3CN$ (**1**·CH3CN) (73.1% yield) and $WS_2\{2,6\text{-}(SCH_2)_2\text{-}(C_5H_3N)\}$ (**2**) (76.0% yield), respectively. In the dinuclear complex **1**, two Cp^*WS_3 units are linked by a 2,6-dimethylenepyridine bridge, and the pyridine nitrogen is not coordinated at tungsten. Complex **2** is the first example of bisalkylated tetrathiometalates, the mononuclear structure of which is stabilized by coordination of the pyridine nitrogen.

Synthesis of the trithio/thiolato complex anions of group 6 transition metals, $[MS_3(SR)]^-$ (M = Mo, W), has recently been achieved by the reactions of tetrathiotungstate and tetrathiomolybdate with alkyl halides under carefully controlled conditions.[1,2] There are two important aspects of the isolation of the monoalkylated tetrathiometalates. One is that these species can be regarded as key intermediates in the reactions between alkyl halides and tetrathiometalates to form various organic disulfides.[3,4] The other is potential utility of the mononuclear trithio/thiolato complexes as precursors of cluster syntheses which may lead to synthetic models of the active metal/sulfide sites in a variety of enzymes.[5,6] Although the tetrathiometalates are robust, synthesis of trithio/thiolato complexes was particularly challenging due to the tendency of these species to degrade into various polythiometalates, in particular for the molybdenum complexes. Thus transformation of one M═S multiple bond to an M−SR single bond exerts a dramatic effect on the stability of the four-coordinate thiometalates, which is probably the consequence of an increase in coordinative unsaturation and/or electronic deficiency at the metal center. In this context, isolation of bisalkylated complexes of tetrathiometalates has been thought very difficult, if not impossible.

Our strategy to overcome this difficulty was 2-fold: introduction of a pentamethylcyclopentadienyl (Cp*) auxiliary to the tungsten center and use of a dihaloalkane which contains an N-donor site, i.e., 2,6-bis(bromomethyl)pyridine. We previously reported the synthesis of $(Ph_4P)[Cp^*MS_3]$ (M = Mo, W)[7,8] and $(Ph_4P)[Cp^*WOS_2]$[9] and their reactions with RBr (R = CH_3, ${}^tBu$, CH_2Ph) to give $Cp^*MS_2(SR)$ (R = ${}^tBu$, CH_2Ph) and $Cp^*WOS(SR)$ (R = CH_3, CH_2Ph). The Cp* auxiliary was found to stabilize these alkylated complexes substantially, compared with highly labile trithio/thiolato complexes $[MS_3(SR)]^-$. In this communication, we report the reactions of 2,6-bis(bromomethyl)pyridine with $(Ph_4P)[Cp^*WS_3]$ and $(Ph_4P)_2[WS_4]$, which resulted in successful isolation and characterization of $[(Cp^*WS_2)_2\{2,6\text{-}(SCH_2)_2\text{-}(C_5H_3N)\}]\cdot CH_3CN$ ($\mathbf{1}\cdot CH_3CN$) and $WS_2\{2,6\text{-}(SCH_2)_2(C_5H_3N)\}$ (**2**).

First, the reaction of 2,6-bis(bromomethyl)pyridine with $(Ph_4P)[Cp^*WS_3]$ was examined in CH_3CN. When 2,6-bis(bromomethyl)pyridine was treated with 2 equiv of $(Ph_4P)[Cp^*WS_3]$, the two bromomethyl groups reacted with different $[Cp^*WS_3]^-$ anions, and the dinuclear complex $[(Cp^*WS_2)_2\{2,6\text{-}(SCH_2)_2(C_5H_3N)\}]\cdot CH_3CN$ ($\mathbf{1}\cdot CH_3CN$) was isolated as a reddish-brown solid in 73.1% yield (eq 1).[10] In

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[*] Author to whom correspondence should be addressed. E-mail: i45100a@nucc.cc.nagoya-u.ac.jp.

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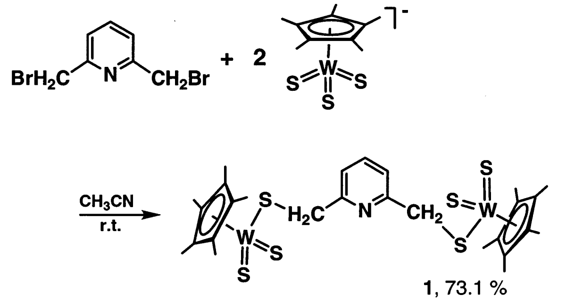


(1)

an attempt to synthesize a bisalkylated complex of $[Cp^*WS_3]^-$, a dilute CH_3CN solution of $(Ph_4P)[Cp^*WS_3]$ was added slowly into a CH_3CN solution of 1 equiv of 2,6-bis(bromomethyl)pyridine at 0 °C, to find that the dinuclear complex **1** was again the major product. The ^1H NMR spectra of the resulting solid in $CDCl_3$ indicated the presence of a monoalkylated species, $Cp^*WS_2\{2,6\text{-}(SCH_2)(CH_2Br)(C_5H_3N)\}$,[11] in addition to **1**. However, isolation of $Cp^*WS_2\{2,6\text{-}(SCH_2)(CH_2Br)(C_5H_3N)\}$ in a pure form has not been attained. Thus, even from the 1:1 reaction system, the remaining terminal sulfides do not react, and the doubly alkylated mononuclear tungsten complex $[Cp^*WS\{2,6\text{-}(SCH_2)_2(C_5H_3N)\}]Br$ was not formed.

Complex **1** was crystallized in the $P2_1/a$ space group, and an asymmetric unit contains two discrete molecules of **1** and two CH_3CN molecules as crystal solvent.[12] As the structures of two crystallographically independent molecules of **1** are very much alike, Figure 1 shows the ORTEP view of one molecule only and the selected geometric parameters are given in the caption. Two Cp^*WS_3 units are linked by a 2,6-dimethylenepyridine bridge, in such a way that the Cp^*WS_3 groups are situated above and below the pyridine plane. There is no interaction between the tungsten atoms and the pyridine nitorogen. Each of the two thiolate S−C bonds orients parallel to the Cp*(centroid)−W vector of the corresponding Cp^*WS_3 unit, the situation of which is similar to that of $Cp^*WS_2(SR)$ ($R = {}^tBu\ CH_2Ph$).[7,8] We rationalize this specific orientation of the S−C bonds in terms of the maximum $p_\pi - d_\pi$ overlap between an occupied S p orbital (p_y) and a vacant W(VI) d orbital (d_{xy}). The average W═S bond distance of 2.156 Å is notably shorter than that of $(PPh_4)[Cp^*WS_3]$ (2.192 Å), because $S(p_\pi)-W(d_\pi)$ interactions are streghtened as the number of terminal sulfides decreases. The IR bands arising from W═S stretching vibrations (492, 480 cm^{-1}) are shifted to higher energies as compared to those of $(PPh_4)[Cp^*WS_3]$ (466 and 437 cm^{-1}),[7] in agreement with the structural data. The S−C bond distances are normal.

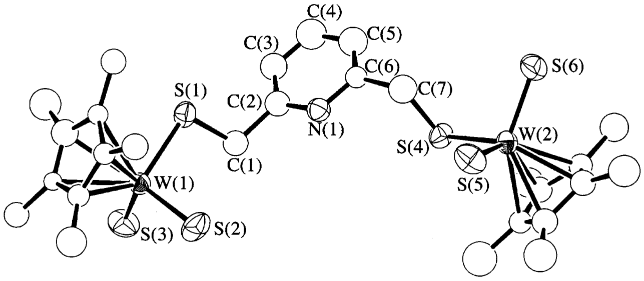
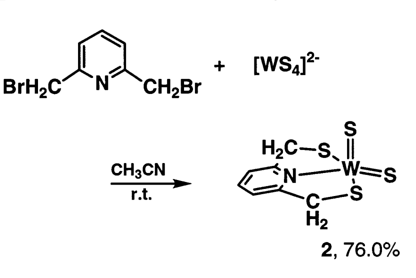


Figure 1. The molecular structure of $[(Cp^*WS_2)_2\{2,6\text{-}(SCH_2)_2(C_5H_3N)\}]\cdot CH_3CN$ (**1**·CH_3CN) showing 40% thermal ellipsoids. Selected bond distances (Å) and angles (deg), where the numbers in brackets are those of the other molecule in an asymmetric unit: W1−S1, 2.335(8) [2.347(8)]; W1−S2, 2.150(8) [2.127(9)]; W1−S3, 2.162(9) [2.15(1)]; W2−S4, 2.342(7) [2.342(9)]; W2−S5, 2.155(9) [2.16(1)]; W2−S6, 2.148(8) [2.161(9)]; W1−S1−C1, 102(1) [105(1)]; W2−S4−C7, 103(1) [104(1)].

Next, the reaction between 2,6-bis(bromomethyl)pyridine and 1 equiv of $(Ph_4P)_2[WS_4]$ was carried out by carefully layering an CH_3CN solution of the former onto the latter in the same solvent. After several days, purple-red crystals of $WS_2\{2,6\text{-}(SCH_2)_2(C_5H_3N)\}$ (**2**) were grown from the reaction system, and the neutral complex **2** was isolated in 76.0% yield (eq 2).[13] The elemental analysis and ^1H NMR spectra



(2)

were consistent with the formulation, and the monomeric structure was confirmed by X-ray analysis.[12] Complex **2** is the first example of bisalkylated thiometalates, and the successful synthesis of **2** opens new ground in transition metal sulfide chemistry. Our attempts to synthesize the Mo analogue of **2** by the reaction of $(Ph_4P)[MoS_4]$ with either 2,6-bis(bromomethyl)pyridine or 2,6-bis(chrolomethyl)pyridine did not give satisfactory results, even when the

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(10) All reactions and the manipulations were performed under argon using standard Schlenk techniques. For $[(Cp^*WS_2)_2\{2,6\text{-}(SCH_2)_2(C_5H_3N)\}]\cdot CH_3CN$ (**1**·CH_3CN): To an acetonitrile solution (30 mL) of $[Ph_4P](Cp^*WS_3)$ (190 mg, 0.25 mmol) was added 2,6-bis(bromomethyl)pyridine (33 mg, 0.125 mmol). A reddish-brown precipitate was formed and collected (89.25 mg, 73.1%). Purple-red needles suitable for X-ray analysis were obtained by standing the mother solution at 4 °C. ^1H NMR (ppm, CD_3Cl): 7.55 (t, 1H, β-H of C_5H_3N), 7.27 (d, 2H, α-H of C_5H_3N), 4.76 (s, 4H, $-CH_2-$), 2.29 (s, 30H, Cp*). IR (cm^{-1}, KBr): 3444 (b), 2914 (m), 2361 (m), 1568 (m), 1448 (s), 1376 (s), 1204 (m), 1111 (w), 1025 (m), 824 (w), 759 (w), 568 (w), 492 (s), 480 (s). Calcd for $C_{29}H_{40}N_2S_6W_2$: C, 35.66; H, 4.13; N, 2.87; S, 19.70. Found: C, 35.76; H, 4.14; N, 2.80; S, 19.82.

(11) The ^1H NMR data for $Cp^*WS_2(SCH_2C_5H_3NCH_2Br)$ (ppm, $CDCl_3$): 2.28 (Cp*, s, 15H), 4.52 ($BrCH_2-$, s, 2H), 4.74 ($-SCH_2-$, s, 2H), 7.30 (γ-H of C_5H_3N, d, 1H), 7.34 (α-H of C_5H_3N, d, 1H), 7.62 (β-H of C_5H_3N, t, 1H).

(12) Diffraction data of **1**·CH_3CN and **2** were collected at room temperature on a Rigaku AFC7R four-cycle diffractometer employing graphite-monochromated Mo Kα radiation (0.71069 Å) and using the $\omega-2\theta$ scan technique. The raw intensities were corrected for Lorentz and polarization effects, and empirical absorption corrections based on φ scans were applied. The structures were solved by direct methods along with expanded Fourier techniques and were refined by full-matrix least squares. Anisotropic refinements were applied to the W and S atoms in **1**·CH_3CN and all non-hydrogen atoms in **2**. The hydrogen atoms were put at calculated positions. Calculations were carried out on a Silicon Graphics work station with the TEXSAN crystallographic software package. The crystal data for **1**·CH_3CN: $C_{29}H_{40}N_2W_2S_6$, $M_r = 976.71$, monoclinic, space group $P2_1/a$, $a = 15.112(3)$ Å, $b = 21.515(6)$ Å, $c = 21.445(2)$ Å, $\beta = 94.76(1)°$, $V = 6948(2)$, $Z = 8$, $D_{calcd} = 1.867$ Mg/m^3, $\mu = 70.06$ cm^{-1}, 11231 reflections collected, 10722 independent reflections, GOF = 1.22, $R = 0.056$, $R_w = 0.056$ ($I > 3.00\sigma(I)$). For **2**: $C_7H_7NWS_4$, $M_r = 417.23$, triclinic, space group $P\bar{1}$, $a = 8.620(2)$ Å, $b = 9.455(2)$ Å, $c = 7.636(2)$ Å, $\alpha = 104.44(2)°$, $\beta = 115.75(2)°$, $\gamma = 73.60(2)°$, $V = 531.9(2)$, $Z = 2$, $D_{calcd} = 2.605$ Mg/m^3, $\mu = 116.05$ cm^{-1}, 2600 reflections collected, 2440 independent reflections, GOF = 1.83, $R = 0.025$, $R_w = 0.031$ ($I > 3.00\sigma(I)$).

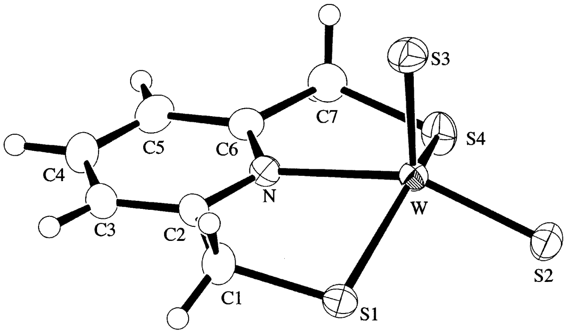

Figure 2. The structure of $WS_2\{2,6\text{-}(SCH_2)_2(C_5H_3N)\}$ (**2**) showing 40% thermal ellipsoids. Selected bond distances (Å) and angles (deg): W−S1, 2.332(2); W−S2, 2.138(2), W−S3, 2.139(2); W−S4, 2.338(2); W−N, 2.264(4); S1−W−S2, 91.29(6); S1−W−S3, 109.24(6); S1−W−S4, 135.56(6), S2−W−S3, 109.60(6): S2−W−S4, 93.52(6); S3−W−S4, 110.51(7); N−W−S1, 77.4(1); N−W−S2, 151.8(1); N−W−S3, 98.5(1); N−W−S4, 77.8(1).

reactions were carried out in a dilute solution at low temperature.

As the ORTEP drawing in Figure 2 shows, the W(VI) center of **2** is coordinated by two terminal sulfides, two thiolate sulfur atoms, and one pyridine nitrogen. The five-coordination geometry is highly distorted. One way to describe the structure is a square pyramid with S3 at the apical position, and this view is emphasized in the ORTEP drawing of Figure 2. The N atom is 0.41 Å off from the least-squares plane defined by the four basal atoms, and the W atom sits 0.75 Å above this basal plane. Alternatively, the molecule may be viewed as trigonal prismatic, where the W−N and W−S2 bonds are at axial positions, although the axial N−W−S2 spine is substantially bent and W moves 0.28 Å from the equatorial S1−S3−S4 plane. The average W═S bond distance of 2.139 Å is shorter than those of $[WS_4]^{2-}$ (2.195 Å) and $[WS_3(SR)]^-$ (R = Et, ^{i}Pr, ^{i}Bu) (2.152 Å)[1] and **1** (2.156 Å). In the IR spectra of **2**, a band assignable to W═S stretching vibration arises at 501 cm^{-1}, which is in fact shifted to higher energy as compared to that of $[WS_4]^{2-}$ (458 cm^{-1}).[14]

The crystals of **2** are not soluble in common organic solvents except for DMF and DMSO. Surprisingly, complex **2** is very stable and does not show a tendency to degrade in these solvents. For instance, even if its DMSO solution was kept standing in air for several weeks, no visible changes were noticed, and **2** was recovered as crystals by diffusion of Et_2O into the solution. On the other hand, when **2** was treated with KBH_4 in DMF, S−C bond cleavage occurred to give $[WS_4]^{2-}$. The unusual stability of **2** must arise from coordination of the pyridine portion of $2,6\text{-}(SCH_2)_2(C_5H_3N)$ (2−), which could sterically protect the W(VI) center and could reduce electron deficiency at the metal center. By our earlier study, a similar stabilization of $(PPh_4)[WS_3(SEt)]$ was attained by replacement of EtS^- with the S−P hybrid ligands, $R_2PCH_2CH_2S^-$ (R = CH_3, Ph), while the resulting five-coordinate complexes, $(PPh_4)[WS_3(SCH_2CH_2PR_2)]$ (**3**), were not as stable as **2**.[15] On the other hand, the O-donor sites of thiolates in $(PPh_4)[WS_3(\text{S-mthp})]$ (**4**) and $(PPh_4)[WS_3(\text{S-edo})]$ (**5**) were found not to coordinate at W in their crystal structures, which were synthesized by alkylation reactions of $(PPh_4)_2[WS_4]$ with 2-(bromomethyl)tetrahydro-2*H*-pyran (Br-mthp) and 2-(bromoethyl)-1,3-dioxane (Br-edo).[2] The reactions of alkyl dihalides with $[MS_4]^{2-}$ (M = Mo, W) and $Mo_2S_{12}{}^{2-}$ were reported to yield organic cyclic disulfides[3] and cyclic sulfide,[16] where the metal sulfides decomposed into polythiometalates. These degradation processes via dissociation of thiolates/dithiolates appear to be hindered by the tridentate coordination mode of $2,6\text{-}(SCH_2)_2(C_5H_3N)$ (2−).

It should be noted that the 1:2 reaction system of 2,6-bis(bromomethyl)pyridine and $(Ph_4P)[WS_4]$ did not produce the dinuclear complex $(Ph_4P)_2[(WS_4)_2\{2,6\text{-}(SCH_2)_2(C_5H_3N)\}]$, and the mononuclear bisalkylated complex **2** was generated, instead. This observation implies that the N-coordination plays a key role also in the process of formation of **2**. We presume that the first step of the reaction would give a monoalkylated intermediate, $[(WS_3)\{2,6\text{-}(SCH_2)(BrCH_2)\text{-}(C_5H_3N)\}]^-$. And coordination of the pyridine portion in the intermediate would facilitate an intramolecular second alkylation step, by bringing the bromomethyl group in the vicinity of one of the remaining terminal sulfides.

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Supporting Information Available: X-ray crystallographic files that include the structural data for $\mathbf{1}\cdot CH_3CN$ and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) For $WS_2\{2,6\text{-}(SCH_2)_2(C_5H_3N)\}$ (**2**): $(Ph_4P)_2[WS_4]$ (250 mg, 0.25 mmol) was dissolved in acetonitrile (30 mL), on which an acetonitrile solution (15 mL) of 2,6-bis(bromomethyl)pyridine (66 mg, 0.25 mmol) was carefully layered. Several days later, purple-red block crystals were formed (79.28 mg, 76.0%). ^1H NMR (ppm, DMSO-d_6): 8.20 (t, 1H, β-H of C_5H_3N), 7.80 (d, 2H, α-H of C_5H_3N), 5.28 (s, 4H, $-CH_2-$). IR (cm^{-1}, KBr): 3438 (b), 2964 (w), 2931 (w), 1599 (m), 1460 (s), 1398 (m), 1388 (m), 1261 (m), 1205 (m), 1169 (m), 1095 (m), 1016 (s), 804 (m), 777 (s), 692 (m), 501 (vs), 449 (w). Anal. Calcd for $C_7H_7NS_4W$: C, 20.15; H, 1.69; N, 3.36; S, 30.74. Found: C, 20.46; H, 1.79; N, 3.36; S, 30.76.

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