Preparation of Mononuclear Tungsten Tris(sulfido) and Molybdenum Sulfido−Tetrasulfido Complexes with Hydridotris(pyrazolyl)borate Coligand and Conversion of the Former into Sulfido-Bridged Bimetallic Complex Having Pt(μ-S)$_2$WS Core

Hidetake Seino,[†] Yasushi Arai,[†] Naohisa Iwata,[†] Shoken Nagao,[†] Yasushi Mizobe,*,[†] and Masanobu Hidai*,[‡]

Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106-8558, Japan, and Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Science University of Tokyo, Noda, Chiba 278-8510, Japan

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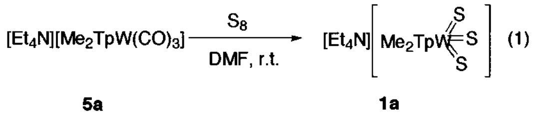
Treatment of [Et$_4$N][(Me$_2$Tp)W(CO)$_3$] (Me$_2$Tp = HB(3,5-dimethylpyrazol-1-yl)$_3$) with S$_8$ in DMF at room temperature afforded a tris(sulfido) complex [Et$_4$N][(Me$_2$Tp)WS$_3$] (**1a**), while that of [Et$_4$N][TpW(CO)$_3$] (Tp = HB(pyrazol-1-yl)$_3$) in MeCN resulted in the formation of [Et$_4$N][TpWS$_3$] (**1b**) along with [Et$_4$N]$_2$[{WO(S$_2$)$_2$}$_2$(μ-S)] (**6**) as a byproduct. Under similar conditions, [Et$_4$N][(Me$_2$Tp)Mo(CO)$_3$] gave a mixture of a sulfido−tetrasulfido complex [Et$_4$N][(Me$_2$Tp)MoS(S$_4$)] (**2a**) and its monooxo analogue [Et$_4$N][(Me$_2$Tp)MoO(S$_4$)], although a sulfido−tetrasulfido complex [Et$_4$N][TpMoS(S$_4$)] (**2b**) was exclusively obtained from [Et$_4$N][TpMo(CO)$_3$]. The reaction of **1a** with [PtCl$_2$(cod)] (cod = 1,5-cyclooctadiene) in MeCN at room temperature led to the formation of a sulfido-bridged mixed-metal complex [Et$_4$N][(Me$_2$Tp)WS(μ-S)$_2$PtCl$_2$] (**10**). The structures of new complexes have been determined in detail by the X-ray analyses for **1a**·MeCN, **1b**, **2a**, **2b**, **6**, and **10**.

Introduction

The chemistry of soluble transition metal sulfido complexes has been attracting significant attention owing to their unique structures and properties, especially in relevance to certain metalloenzymes and metal sulfide heterogeneous catalysts.[1] One of the most developed class of compounds in this area involves the sulfido complexes with cyclopentadienyl coligands, which serve also as the potential precursors to the mixed-metal sulfido clusters.[2] Tris(pyrazolyl)borate ligand as a tridentate nitrogen ligand has long been compared to cyclopentadienyls in their six-electron-donating monoanionic character and formally facial coordination mode, and the complexes containing a wide range of metals have also been synthesized numerously,[3] whereby the tris(pyrazolyl)borate complexes have often provided more sophisticated models for the bioinorganic systems. Among these, tris(pyrazolyl)borate complexes of Mo and W are the most extensively studied, which include a considerable number of compounds having a sulfur coligand. However, employment of these complexes as the building blocks of the sulfido complexes or clusters with higher nuclearity has rarely been attempted. In this paper, we report the synthesis and characterization of the new W and Mo tris(pyrazolyl)borate complexes containing sulfido ligands [Et$_4$N][LWS$_3$] (**1a**, L = Me$_2$Tp; **1b**, L = Tp, Me$_2$Tp = HB(3,5-dimethylpyrazol-1-yl)$_3$, Tp = HB(pyrazol-1-yl)$_3$) and [Et$_4$N][LMoS(S$_4$)] (**2a**, L = Me$_2$Tp; **2b**, L = Tp), as well as the reaction of **1a** with a platinum complex forming a novel sulfido-bridged mixed-metal complex having a Pt(μ-S)$_2$WS core. This finding might indicate that the W and Mo complexes obtained here are also capable of serving as good precursors to bimetallic sulfido clusters, as demonstrated extensively for [MS$_4$]$^{2-}$ (M = W, Mo)[4] and recently for [Cp*MS$_3$]$^-$ (M = W (**3**), Mo (**4**); Cp* = η^5-C$_5$Me$_5$).[5]

Results and Discussion

Preparation and Characterization of [Et$_4$N][LWS$_3$] (1). Treatment of a DMF solution of [Et$_4$N][(Me$_2$Tp)W(CO)$_3$] (**5a**) with 1 equiv of S$_8$ at room temperature for 18 h, followed by the crystallization of the product from MeCN−ether, afforded **1a**·MeCN as dark-red crystals in 68% yield (eq 1). The single-crystal X-ray analysis of **1a**·MeCN revealed the details of the



[†] The University of Tokyo.

[‡] Science University of Tokyo.

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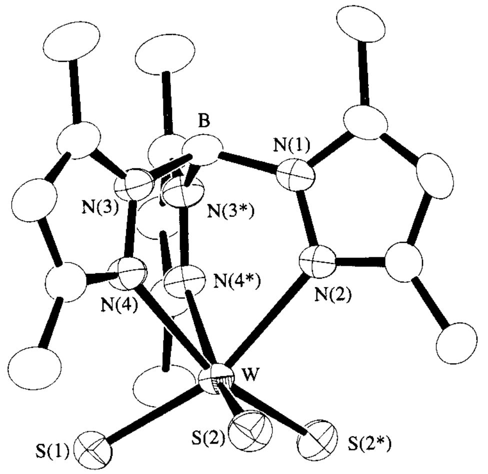


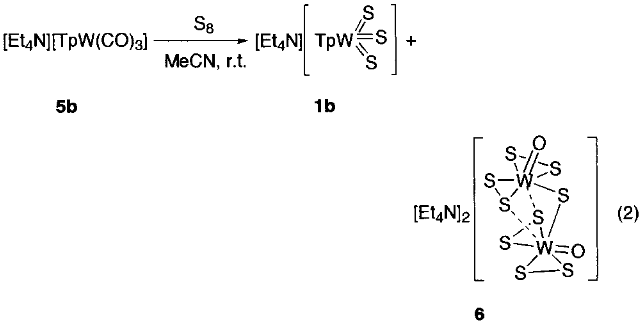
Figure 1. ORTEP drawing of the anion in **1a**. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) in **1a** and **1b**

	1a·MeCN		
W−S(1)	2.192(1)	W−S(2)	2.1942(9)
W−N(2)	2.370(4)	W−N(4)	2.335(3)
S(1)−W−S(2)	103.26(3)	S(2)−W−S(2*)	102.50(5)
N(2)−W−N(4)	77.14(9)	N(4)−W−N(4*)	77.4(1)
	1b		
W−S(1)	2.199(3)	W−S(2)	2.178(3)
W−S(3)	2.193(3)	W−N(2)	2.322(8)
W−N(4)	2.347(9)	W−N(6)	2.316(8)
S(1)−W−S(2)	103.7(1)	S(1)−W−S(3)	105.0(1)
S(2)−W−S(3)	104.6(1)	N(2)−W−N(4)	75.5(3)
N(2)−W−N(6)	73.7(3)	N(4)−W−N(6)	74.9(3)

structure; an ORTEP drawing of the anion is shown in Figure 1, while the important bonding parameters are listed in Table 1. The anion has a highly distorted octahedral W center, which is surrounded by the facial Me_2Tp and three terminal sulfido ligands. The W−S distances of 2.192(1)−2.1942(9) Å agree well with those in the Cp* analogue [Cat]**3** (Cat = Et_3NH, 2.178−2.207 Å;[6] Cat = Ph_4P, 2.188(2)−2.199(2) Å)[7] and are slightly longer than those in $[H_4N]_2[WS_4]$ (2.177 Å)[8] and $[Ph_4P][WS_3(SEt)]$ (2.142(3)−2.163(3) Å).[9] The W−S distances in **1a** suggest the presence of strong $d_\pi(W)-p_\pi(S)$ bonding interactions, which result in significantly wide S−W−S angles in the range 102.50(5)−103.26(3)° owing to the repulsion between these electron densities. On the other hand, the N−W−N angles associated with the Me_2Tp ligand are much smaller (77.14(9)° and 77.4(1)°). These structural features of **1a** are also similar to those in the oxo analogue $[Et_4N][(Me_2Tp)WO_3]\cdot 4H_2O$,[10] in which the O−W−O and N−W−N angles fall in the range 103.8(2)−104.8(2)° and 75.6(2)−78.2(2)°, respectively. The ^1H NMR spectrum demonstrated the equivalence of three 3,5-dimethylpyrazol-1-yl ligands in **1a**, while the IR spectrum showed the medium bands at 441 and 464 cm^{-1} assignable to ν(W═S), which are in good agreement with those reported for $[Ph_4P]$**3** (437 and 466 cm^{-1}).[7b]

Reaction of $[Et_4N][TpW(CO)_3]$ (5b) with Sulfur. In contrast to **5a**, which is sparingly soluble in common solvents, **5b** can easily be dissolved in MeCN and the reaction with S_8 was carried out in MeCN at room temperature. However, the reaction did not proceed cleanly. Thus, although the ^1H NMR spectrum of the reaction mixture in MeCN at room temperature indicated that the expected compound $[Et_4N][TpWS_3]$ (**1b**) was the major Tp-containing product, attempted purification from MeCN−ether only resulted in the deposition of **1b** as red crystals with the byproduct $[Et_4N]_2[\{WO(S_2)_2\}_2S]$ (**6**) as orange crystals (eq 2), both in low yields. For these complexes, single crystals were picked up and subjected to the X-ray diffraction study. Separation of the two products by chromatography failed, and the isolation of the analytically pure **1b** in satisfactory amounts is yet unsuccessful. The oxo ligand in **6** is likely to have its origin of the oxygen atom in the adventitious moisture, although details about the formation of **6** are uncertain. To our knowledge, **6** is not precedented. However, the sulfido analogue $[Ph_4P]_2[\{WS(S_2)_2\}_2S]$[11] and the Mo analogue $[Et_4N]_2[\{MoO(S_2)_2\}_2S]$ (**7**)[12] are known. It is to be noted that **7** was obtained from the oxidative coupling of $[Et_4N]_2[MoO(S_4)_2]$,[12] which is known to be available by the hydrolysis of $[Et_4N]_2[MoS(S_4)_2]$.[13]



5b **1b** **6**

As confirmed by the X-ray analysis, the anion in **1b** has a structure almost identical with that of **1a** except for the W−N distances (av 2.328 Å) that are slightly shorter than those in **1a** (av 2.347 Å) because of the absence of the methyl substituents at the 3-positions of the pyrazolyl groups. Selected bonding parameters in **1b** are listed in Table 1. The ^1H NMR spectrum of **1b** indicates that the three pyrazolyl goups are equivalent, while its IR spectrum exhibits the characteristic ν(W═S) bands at 439 and 448 cm^{-1}, which are almost comparable to those of **1a** described above.

As shown in Figure 2, the anion in **6** consists of two analogous W units bridged by a sulfido ligand, where the distance between two W(VI) centers is 3.550(1) Å. Each W has a pentagonal bipyramidal structure with the oxo ligand at the apical position, whose trans site is occupied by a weakly interacting S atom of the disulfido ligand in the other W unit; the distances of W(1) from S(5) and of W(2) from S(1) are 2.830(4) and 2.819(4) Å, respectively. For comparison, the related Mo···Mo and Mo···S separations in the Mo analogue **7** were reported to be 3.606(1) and ca. 2.9 Å, respectively.[12] Pertinent bonding parameters in **6** are summarized in Table 2.

Reaction of $[Et_4N][(Me_2Tp)Mo(CO)_3]$ (8a) with Sulfur. Syntheses of the related Mo sulfido complexes have also been

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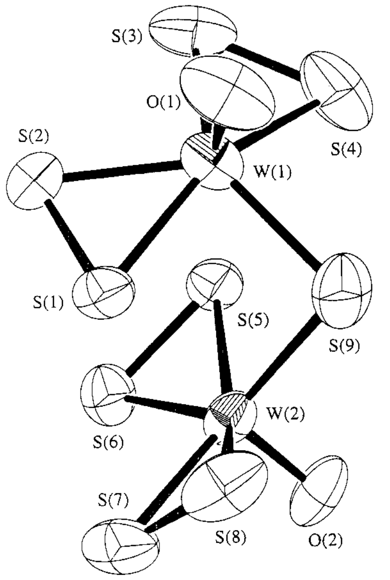
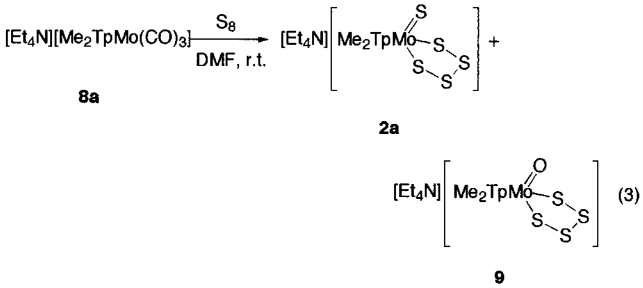


Figure 2. ORTEP drawing of the anion in **6**.

Table 2. Selected Bond Distances (Å) and Angles (deg) in **6**

W(1)−S(1)	2.420(4)	W(1)−S(2)	2.376(4)
W(1)−S(3)	2.392(5)	W(1)−S(4)	2.389(5)
W(1)−S(9)	2.486(5)	W(1)−O(1)	1.69(1)
W(2)−S(5)	2.428(4)	W(2)−S(6)	2.374(4)
W(2)−S(7)	2.404(5)	W(2)−S(8)	2.363(4)
W(2)−S(9)	2.495(5)	W(2)−O(2)	1.710(10)
S(1)−S(2)	2.051(6)	S(3)−S(4)	2.062(9)
S(5)−S(6)	2.057(6)	S(7)−S(8)	2.067(8)
W(1)···S(5)	2.830(4)	W(2)···S(1)	2.819(4)
S(1)−W(1)−S(2)	50.6(2)	S(3)−W(1)−S(4)	51.1(2)
S(9)−W(1)−O(1)	100.2(5)	S(5)−W(2)−S(6)	50.7(1)
S(7)−W(2)−S(8)	51.4(2)	S(9)−W(2)−O(2)	100.4(4)
W(1)−S(9)−W(2)	90.9(1)		



8a

2a

(3)

9

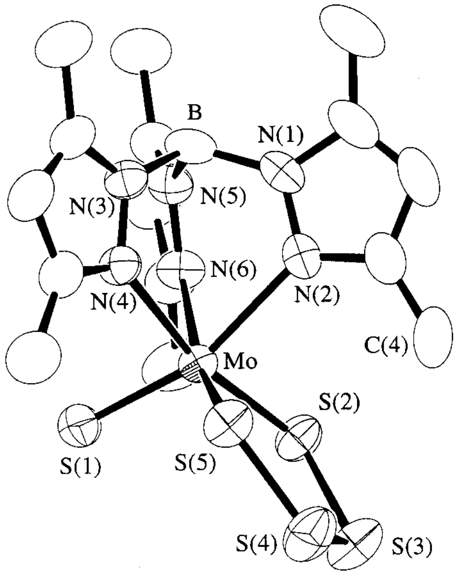


Figure 3. ORTEP drawing of the anion in **2a**. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) in **2a** and **2b**

2a			
Mo−S(1)	2.172(1)	Mo−S(2)	2.240(1)
Mo−S(5)	2.254(1)	Mo−N(2)	2.382(3)
Mo−N(4)	2.288(3)	Mo−N(6)	2.300(3)
S(2)−S(3)	2.240(2)	S(3)−S(4)	1.982(2)
S(4)−S(5)	2.164(2)		
S(1)−Mo−S(2)	102.94(4)	S(1)−Mo−S(5)	103.70(4)
S(2)−Mo−S(5)	93.79(4)	N(2)−Mo−N(4)	77.4(1)
N(2)−Mo−N(6)	76.0(1)	N(4)−Mo−N(6)	83.4(1)
Mo−S(2)−S(3)	114.24(6)	S(2)−S(3)−S(4)	106.99(7)
S(3)−S(4)−S(5)	107.30(7)	Mo−S(5)−S(4)	116.11(6)
2b			
Mo−S(1)	2.144(2)	Mo−S(2)	2.282(2)
Mo−S(5)	2.307(2)	Mo−N(2)	2.368(4)
Mo−N(4)	2.254(5)	Mo−N(6)	2.222(5)
S(2)−S(3)	2.184(3)	S(3)−S(4)	2.000(3)
S(4)−S(5)	2.173(3)		
S(1)−Mo−S(2)	105.28(7)	S(1)−Mo−S(5)	103.02(7)
S(2)−Mo−S(5)	94.03(7)	N(2)−Mo−N(4)	75.2(2)
N(2)−Mo−N(6)	76.2(2)	N(4)−Mo−N(6)	82.9(2)
Mo−S(2)−S(3)	112.17(10)	S(2)−S(3)−S(4)	102.9(1)
S(3)−S(4)−S(5)	103.6(1)	Mo−S(5)−S(4)	108.03(10)

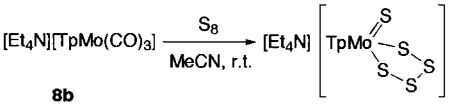
attempted. Thus, **8a** dissolved in DMF was treated with an equimolar amount of S_8 at room temperature. However, the reaction was quite slow and 7 days were required until the conversion of all **8a** was completed. Addition of ether to the filtered reaction mixture afforded a mixture of $[Et_4N][(Me_2Tp)MoS(S_4)]$ (**2a**) and its oxo analogue $[Et_4N][(Me_2Tp)MoO(S_4)]$ (**9**) in a combined yield of 81% (eq 3). The molar ratio of **2a** to **9** in this mixture was ca. 4:1 based on its ^1H NMR spectrum. It is to be noted that the reaction of the Mo(0) complex **8a** with sulfur has turned out to produce the Mo(IV) complexes, including the sulfido−tetrasulfido complex **2a** as the major product, whereas the W(VI) tris(sulfido) complex **1a** forms from the reaction of the corresponding W(0) complex **5a** conducted under similar conditions. This difference is ascribable to the more oxidizable nature of W compared with Mo. The oxygen source for **9** is presumed to be the adventitious moisture in the reaction mixture, although the mechanism for the formation of **9** is not clear. Although a mononuclear complex $[MoS(S_4)_2]^{2-}$ is known to be converted into $[MoO(S_4)_2]^{2-}$ to some extent upon hydrolysis as indicated above,[13] it is unlikely in this reaction that **2a** once formed is converted into **9** in an analogous manner because the ratio of **2a** to **9** was identical even after treatment of their mixture with H_2O (1 mol/(mol of **2a** + **9**)) at room temperature for 6 days.

The structure of **2a** was determined in detail by X-ray analysis (Figure 3 and Table 3), while **9** was characterized by elemental analysis and the spectral data. Complex **2a** has a distorted octahedral structure in which the N(4) and N(6) atoms of the Me_2Tp ligand and the S(2) and S(5) atoms of the tetrasulfido ligand are almost coplanar and comprise the basal plane. The Mo atom is displaced from this least-squares plane by 0.26 Å toward the S(1) atom. As for the three Mo−S bonds, the Mo−S(1) bond length at 2.172(1) Å for the terminal sulfido ligand is significantly elongated if compared with those of the common Mo−S double bonds (1.93−2.13 Å)[14] and almost comparable to the Mo−S bond distances in $[Et_4N]_2[MoS_4]$ (2.177(6) Å)[15] and [Ph_4P]**4** (2.183(3)−2.195(3) Å),[7b] while the Mo−S(2) and Mo−S(5) distances at 2.240(1) and 2.254(1) Å for the tetrasulfido ligand, respectively, are considerably shorter than those in most of the previously reported Mo(S_4) moieties (2.33−2.45 Å).[16] The S−Mo−S angles associated with S(1) (102.94(4)° and 103.70(4)°) are larger than the chelating angle of the S_4 ligand (S(2)−Mo−S(5): 93.79(4)°). The five-membered ring consisting of the tetrasulfido ligand and Mo is nearly planar with the maximum atom displacement, from the least-squares plane defined by these five atoms, being 0.14 Å (for S(5)). However, it is also possible to see this five-membered ring being puckered along the S(2)−S(5) vector toward S(1). Thus, the four S atoms in the S_4 ligand are almost perfectly coplanar with deviations less than 0.01 Å, and the dihedral angle between this plane and the Mo−S(2)−S(5) plane is 11.1°. In the S_4 ligand, the S(3)−S(4) bond at 1.982(2) Å is significantly shorter than the other two S−S bonds (S(2)−S(3), 2.240(2) Å; S(4)−S(5), 2.164(2) Å). These structural features of the Mo(S_4) unit are comparable to those in [(Me_2Tp)MoCl(S_4)].[16]

As for the Me_2Tp ligand, the Mo−N(2) distance of 2.382(3) Å is much longer than the other two Mo−N bonds at 2.288(3) and 2.300(3) Å, which is interpreted in terms of the stronger trans influence displayed by the sulfido S atom compared with the tetrasulfido S atoms. In the ^{1}H NMR spectrum of **2a**, two sets of resonances assignable to the 3,5-dimethylpyrazol-1-yl ligands appeared in a 2:1 intensity ratio, which is consistent with its solid structure. The appearance of one methyl resonance in the significantly higher field (δ 1.19) compared with the signals ascribable to the other five methyl groups (δ 2.03, 2.49, and 3.17) in the Me_2Tp ligand can be explained by the shielding effect exerted by the planar MoS_4 ring having dithiolene character on the methyl protons attached to C(4), which resides in this plane. The IR spectrum exhibited the characteristic ν(Mo═S) band at 473 cm^{-1}.

For **9**, the ^{1}H NMR spectrum showed a feature analogous to that of **2a**, whereas the band assignable to ν(Mo═O) appeared at 912 cm^{-1} in place of the ν(Mo═S) band observed for **2a**. The formula of **9** was further confirmed by the FAB mass spectrum.

Reaction of [Et_4N][TpMo(CO)$_3$] (8b) with Sulfur. If compared with the reaction of **8a**, that of the Tp analogue **8b** with S_8 proceeded more cleanly. Thus, **8b** dissolved in MeCN was allowed to react with S_8 at room temperature to give exclusively an Mo(IV) sulfido−tetrasulfido complex **2b** (eq 4), which was isolated in satisfactory yield as dark-green crystals.



(4)

8b **2b**

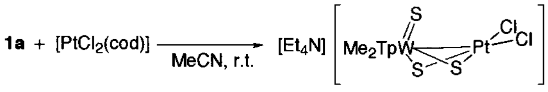
It is noteworthy that the reactions of S_8 with the related Me_2Tp- or Tp-carbonyl complexes of Mo were studied previously, and interestingly, the reaction of **8a** in $C_2H_4Cl_2$ at reflux[17] and that of a paramagnetic [(Me_2Tp)Mo(CO)$_3$] in THF at room temperature[18] both afforded [{(Me_2Tp)Mo(CO)$_2$}$_2$(μ-S)] in moderate or high yield, while treatment of [TpMoH(CO)$_3$] in toluene at 70 °C led to the formation of [{TpMo(CO)$_2$}$_2$(μ-S)] in moderate yield.[17] On the other hand, in the presence of S_8 in MeCN, [(Me_2Tp)Mo(NO)(CO)$_2$] was shown to give [(Me_2Tp)-Mo(NO)(S_5)] under photoirradiation.[19] Apparently, the nature of the products sharply depends on the choice of the solvents, and employment of the homogeneous system in the present work might somehow lead to the formation of the sulfur-rich products **2a** and **2b**.

The structure of **2b** was confirmed by X-ray analysis, whose ORTEP drawing is shown in Figure 4. Pertinent bonding parameters are summarized in Table 3. The most significant difference between the structures of **2b** and **2a** is the folded Mo(S_4) ring in the former in contrast to its essentially planar feature in the latter. Thus, this five-membered ring in **2b** is bent along the S(3)−S(5) vector toward S(1) with a dihedral angle of 42.3° between the least-squares plane defined by Mo, S(2), S(3), and S(5) atoms and the S(3)−S(4)−S(5) plane. The envelope structure of this type is well precedented for the Mo tetrasulfido anion complexes extensively explored previously, e.g., [MoE(S_4)$_2$]$^{2-}$ (E = S, O), [{MoS(S_4)}$_2$(μ-S)$_2$]$^{2-}$,[13] [MoS(S_4)(μ-S)$_2$MoS(E)]$^{2-}$ (E = S,[20] O[21]), and [MoS(S_4)(μ-S)$_2$MoS(S_2)]$^{2-}$.[22]

For the three Mo−S bonds in **2b**, the Mo−S(1) bond is shorter but the Mo−S(2) and Mo−S(5) bonds are longer than the corresponding Mo−S linkages in **2a**. With respect to the Mo−N distances, the Tp complex **2b** has shorter M−N bonds than the Me_2Tp analogue **2a**, as observed for the W complexes **1b** and **1a**. Other structural features in **2b** are essentially analogous to those in **2a**.

As expected from the difference in the Mo−S bond lengths, the ν(Mo═S) value of 491 cm^{-1} for **2b** is larger by 18 cm^{-1} than that of **2a**. In the ^{1}H NMR spectrum, the pyrazolyl signals appeared as two sets of resonances with an intensity ratio of 2:1, indicating that the Mo(S_4) ring with an envelope structure in the solid state is fluxional in solution.

Preparation of Sulfido-Bridged Dinuclear Complex Containing W and Pt. Reactions of **1** or **2** with noble metal complexes have been attempted to demonstrate their potential to serve as the precursors to mixed-metal sulfido complexes. It has been found that **1a** reacted with a slight excess [PtCl$_2$(cod)] (cod = 1,5-cyclooctadiene) in MeCN at room temperature to give a sulfido-bridged dinuclear complex [Et_4N][(Me_2Tp)WS(μ-S)$_2$PtCl$_2$] (**10**) as purple crystals in moderate yield (eq 5).



(5)

10

The structure of **10** was determined by X-ray crystallography. For the Cp* analogue **3**, in addition to the reactions with the compounds containing coinage metals such as Cu and Ag leading to the mixed-metal sulfido clusters with a nuclearity of 4 or more,[5] formation of the WS(μ-S)$_2$Pd core related to **10** was observed from the reaction with [Pd(dppe)Cl$_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$), where the binding of two sulfido ligands to Pd occurred with concurrent dissociation of the Cl ligands to give the cationic complex [Cp*WS(μ-S)$_2$Pd(dppe)]Cl.[5c]

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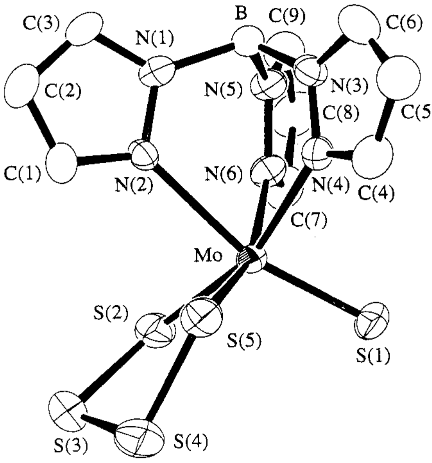

Figure 4. ORTEP drawing of the anion in **2b**. Hydrogen atoms are omitted for clarity.

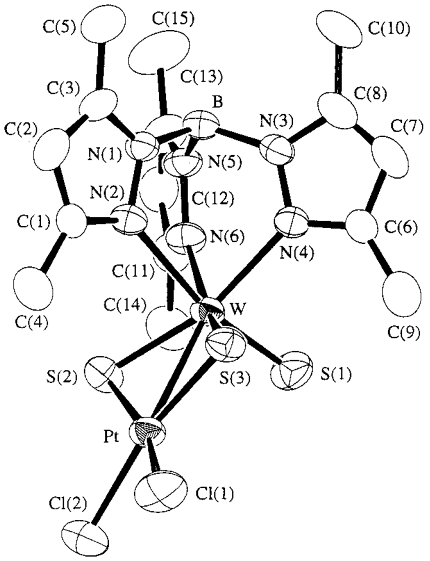

Figure 5. ORTEP drawing of the anion in **10**. Hydrogen atoms are omitted for clarity.

Treatment of $[WS_4]^{2-}$ with $[PtCl_2(cod)]$ in MeCN was reported to afford the sulfido-bridged bimetallic complex $[WS_2(\mu\text{-}S)_2Pt(cod)]$.[23] Also in this reaction, the elimination of the Cl anions from the Pt center occurred rather than the dissociation of cod observed in the present work. It is well-known that the reaction of $[WS_4]^{2-}$ with $[PtCl_4]^{2-}$ also proceeds via the loss of the Cl anions, forming $[S_2W(\mu\text{-}S)_2Pt(\mu\text{-}S)_2WS_2]^{2-}$.[24]

An ORTEP drawing and selected bond distances and angles in **10** are shown in Figure 5 and Table 4, respectively. In **10**, there exists a formal dative bond from a Pt(II) atom to a W(VI) center, as implicated by the Pt−W distance of 2.7792(6) Å. If this single bond is ignored, the Pt and W atoms have a distorted square planar and octahedral configuration, respectively. The $W(\mu\text{-}S)_2Pt$ core is folded, where the dihedral angle between two WSPt planes is 22.8°. The W−S bond for the terminal sulfido ligand (W−S(1): 2.148(3) Å) is slightly shorter than those in **1a** (2.192(1) and 2.1942(9) Å), whereas the remaining W−S(2) and W−S(3) bonds are elongated significantly to 2.259(3) and 2.262(3) Å, respectively, by further coordination to Pt. The Pt−S bond distances of 2.290(3) and 2.287(3) Å are slightly longer than the $W-S_{bridging}$ bond lengths. This trend was more distinctively observed in the related $Pt^{II}(\mu\text{-}S)_2W^{VI}$ core in $[WS_2(\mu\text{-}S)_2Pt(PEt_3)_2]$ with the Pt−S bond lengths at 2.362(2) and 2.388(3) Å and with $W-S_{bridging}$ bond distances of 2.225(2) and 2.225(3) Å.[25] In **10**, the three S−W−S angles are not different from one another (101.8(1)−103.4(1)°). The ^1H NMR data are consistent with this structure, while the IR spectrum showed two bands at 473 and 435 cm^{-1} in the ν(WS) region.

Table 4. Selected Bond Distances (Å) and Angles (deg) in **10**

Pt−W	2.7792(6)	Pt−Cl(1)	2.330(3)
Pt−Cl(2)	2.342(3)	Pt−S(2)	2.290(3)
Pt−S(3)	2.287(3)	W−S(1)	2.148(3)
W−S(2)	2.259(3)	W−S(3)	2.262(3)
W−N(2)	2.392(8)	W−N(4)	2.262(9)
W−N(6)	2.243(9)		
Cl(1)−Pt−Cl(2)	87.3(1)	Cl(1)−Pt−S(2)	165.9(1)
Cl(1)−Pt−S(3)	85.9(1)	Cl(2)−Pt−S(2)	87.7(1)
Cl(2)−Pt−S(3)	168.8(1)	S(2)−Pt−S(3)	100.9(1)
S(1)−W−S(2)	101.8(1)	S(1)−W−S(3)	103.4(1)
S(2)−W−S(3)	102.7(1)	N(2)−W−N(4)	79.6(3)
N(2)−W−N(6)	77.3(3)	N(4)−W−N(6)	80.4(3)
Pt−S(2)−W	75.30(10)	Pt−S(3)−W	75.32(9)

Experimental Section

General. All manipulations were done under an atmosphere of N_2 using standard Schlenk techniques. IR and NMR spectra were recorded on a JASCO FT/IR 420 spectrometer at room temperature and on a JEOL LA-400 spectrometer at 20 °C, respectively. The mass spectra were obtained by a JEOL JMS600H spectrometer. Elemental analyses were carried out with a Perkin-Elmer 2400 series II CHN analyzer. Complexes **5a** and **5b** were prepared by using essentially the same method reported previously,[26] although we did not use $[W(CO)_6]$ but $[W(CO)_3(MeCN)_3]$ as a precursor. Other complexes **8a**, **8b**,[27] and $[PtCl_2(cod)]$[28] were obtained by using literature methods.

$[Et_4N][(Me_2Tp)WS_3]$ (1a). Into a DMF solution (20 mL) of **5a** (500 mg, 0719 mmol) was added S_8 (186 mg, 0.725 mmol), and the mixture was stirred at room temperature for 18 h. The resultant solution was concentrated and filtered, and ether was added slowly to the filtrate. Dark-red crystals were deposited, which were filtered off, washed with ether, and recrystallized from MeCN−ether to give **1a**·MeCN (342 mg, 68% yield). Anal. Calcd for $C_{23}H_{42}BN_7S_3W\cdot MeCN$: C, 40.11; H, 6.06; N, 14.97. Found: C, 40.04; H, 5.93; N, 14.84. ^1H NMR (DMSO-d_6): δ 1.14 (m, 12H, NCH_2CH_3), 2.06 (s, 3H, MeCN), 2.30 and 3.01 (s, 9H each, Me in Me_2Tp), 3.19 (q, 8H, NCH_2CH_3), 4.5 (vbr, 1H, BH), 5.83 (s, 3H, CH in Me_2Tp). IR (KBr disk): ν(W=S), 441 and 464; ν(B−H), 2448 cm^{-1}.

$[Et_4N][TpWS_3]$ (1b) and $[Et_4N]_2[\{WO(S_2)_2\}_2S]$ (6). A solution containing **5b** (123 mg, 0.200 mmol) and S_8 (53 mg, 0.20 mmol) was stirred overnight at room temperature. The resultant mixture was filtered, and ether was added to the filtrate, affording a mixture of **1b** as red crystals and **6** as orange crystals. Data for **1b**. ^1H NMR (DMSO-d_6): δ 1.14 (m, NCH_2CH_3), 3.20 (q, NCH_2CH_3), 4.4 (vbr, 1H, BH), 6.21 (br t, 3H, J = 2 Hz, 4-CH in Tp), 7.75 (br d, 3H, J = 2 Hz, 3- or 5-CH in Tp), 8.31 (br d, 3H, J = 2 Hz, 3- or 5-CH in Tp). IR (KBr disk): ν(W=S), 439 and 448; ν(B−H), 2469 cm^{-1}. Data for **6**: IR (KBr disk): ν(W=O), 940 cm^{-1}.

$[Et_4N][(Me_2Tp)MoS(S_4)]$ (2a) and $[Et_4N][(Me_2Tp)MoO(S_4)]$ (9). Into a DMF solution (15 mL) of **8a** (608 mg, 1.00 mmol) was added S_8 (258 mg, 1.00 mmol), and the mixture was stirred at room temperature for 7 days. The resultant mixture was filtered, and the filtrate was concentrated. Addition of ether afforded a mixture of dark-

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Table 5. Crystallographic Data for **1a**·MeCN, **1b**, **2a**, **2b**, **6**, and **10**

	1a·MeCN	**1b**	**2a**	**2b**	**6**	**10**
formula	$C_{25}H_{45}N_8BS_3W$	$C_{17}H_{30}N_7BS_3W$	$C_{23}H_{42}N_7BS_5Mo$	$C_{17}H_{30}N_7BS_5Mo$	$C_{16}H_{40}N_2O_2S_9W_2$	$C_{23}H_{42}N_7BS_3Cl_2WPt$
fw	748.52	623.31	683.68	599.52	948.74	973.47
space group	*Pnma* (No. 62)	*Pbca* (No. 61)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	*Pbca* (No. 61)
a (Å)	16.056(1)	17.132(2)	10.285(2)	10.255(3)	16.805(4)	17.271(4)
b (Å)	10.974(1)	16.258(2)	16.470(2)	14.873(3)	10.384(2)	18.961(2)
c (Å)	18.250(2)	17.542(2)	19.405(1)	16.959(5)	17.550(2)	20.337(5)
β (deg)	90	90	103.320(9)	95.13(3)	97.69(1)	90
V (Å^3)	3215.5(8)	4886(1)	3198.7(7)	2576(1)	3035.2(8)	6659(1)
Z	4	8	4	4	4	8
ρ_{calc} (g cm^{-3})	1.546	1.695	1.420	1.545	2.076	1.942
μ_{calcd} (cm^{-1})	38.20	50.08	7.61	9.33	82.19	80.10
R [a]	0.023	0.043	0.037	0.040	0.049	0.043
R_w [b]	0.025	0.050	0.038	0.040	0.052	0.043

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$ ($w = [\{(F_o)\}^2 + (p^2/4)F_o^2]^{-1}$).

green crystals of **2a** and reddish-brown crystals of **9** (552 mg) whose ^{1}H NMR spectrum showed the presence of these two products in a ratio of 4:1. Hence, the combined yield is calculated to be 81%. Data for **2a**. Anal. Calcd for $C_{23}H_{42}BN_7S_5Mo$: C, 40.40; H, 6.19; N, 14.34. Found: C, 40.34; H, 6.26; N, 14.24. ^{1}H NMR (DMSO-d_6): δ 1.15 (m, 12H, NCH_2CH_3), 1.19 and 2.03 (s, 3H each, Me in Me_2Tp), 2.49 and 3.17 (s, 6H each, Me in Me_2Tp), 3.18 (m, 8H, NCH_2CH_3), 4.6 (vbr, 1H, BH), 5.12 (s, 1H, CH in Me_2Tp), 6.17 (s, 2H, CH in Me_2Tp). IR (KBr disk): ν(Mo═S), 473; ν(B−H), 2546 cm^{-1}. Data for **9**. Anal. Calcd for $C_{23}H_{42}BN_7OS_4Mo$: C, 41.38; H, 6.34; N, 14.69. Found: C, 41.73; H, 6.26; N, 14.58. ^{1}H NMR (DMSO-d_6): δ 1.14 (m, 12H, NCH_2CH_3), 1.70 and 2.11 (s, 3H each, Me in Me_2Tp), 2.41 and 2.73 (s, 6H each, Me in Me_2Tp), 3.18 (m, 8H, NCH_2CH_3), 4.5 (vbr, 1H, BH), 5.31 (s, 1H, CH in Me_2Tp), 6.06 (s, 2H, CH in Me_2Tp). IR (KBr disk): ν(Mo═O), 912; ν(B−H), 2548 cm^{-1}. FAB-MS (negative, *m*/*z*): 538.9. Calcd: 539.0 (anion).

[Et$_4$N][TpMoS(S$_4$)] (2b). Into an MeCN solution (3 mL) of **8b** (103 mg, 0.200 mmol) was added S_8 (52 mg, 0.20 mmol), and the mixture was stirred overnight at room temperature. The resultant dark-green suspension was concentrated to one-third its volume, and the solid obtained was filtered off. After being washed with ether and then hexane, the residue was extracted with DMF (3 mL) and a mixture of ether and hexane was layered on the extract. Complex **2b** precipitated as green crystals in 75% yield. Anal. Calcd for $C_{17}H_{30}BN_7S_5Mo$: C, 34.06; H, 5.04; N, 16.35. Found: C, 34.10; H, 5.08; N, 16.13. ^{1}H NMR (DMSO-d_6): δ 1.14 (m, 12H, NCH_2CH_3), 3.19 (m, 8H, NCH_2CH_3), 4.4 (vbr, 1H, BH), 5.54 (br t, 1H, J = 2 Hz, 4-H in Tp), 6.36 (d, 1H, J = 1.5 Hz, 5-H in Tp), 6.54 (br t, 2H, J = 2 Hz, 4-H in Tp), 7.26 (d, 1H, J = 1.7 Hz, 3-H in Tp), 8.00 (d, 2H, J = 2.4 Hz, 5-H in Tp), 8.76 (d, 2H, J = 1.7 Hz, 3-H in Tp). IR (KBr disk): ν(Mo═S), 491; ν(B−H), 2477 cm^{-1}. The single crystals for X-ray diffraction were grown by recrystallization of the product from DMSO-benzene.

[Et$_4$N][Tp*WS(μ-S)$_2$PtCl$_2$] (10). A mixture of **1a** (67 mg, 0.089 mmol) and [PtCl$_2$(cod)] (37 mg, 0.10 mmol) in MeCN (5 mL) was stirred overnight at room temperature. The resulting solution was filtered to remove a small amount of solid, and then ether was added to the concentrated filtrate. The title compound was obtained as purple crystals (61 mg, 70% yield based on W). Anal. Calcd for $C_{23}H_{42}BN_7S_3Cl_2WPt$: C, 28.38; H, 4.35; N, 10.07. Found: C, 28.47; H, 4.38; N, 10.22. ^{1}H NMR (CD_3CN): δ 1.20 (t, 12H, NCH_2CH_3), 2.25 and 2.30 (s, 3H each, Me in Me_2Tp), 2.48 and 3.17 (s, 6H each, Me in Me_2Tp), 3.15 (q, 8H, NCH_2CH_3), 4.6 (vbr, 1H, BH), 5.57 (s, 1H, 4-H in Me_2Tp), 6.18 (s, 2H, 4-H in Me_2Tp). IR (KBr disk): ν(WS), 473 and 435; ν(B−H), 2547 cm^{-1}.

X-ray Crystallography. All diffraction studies were carried out at room temperature by using a Rigaku AFC7R diffractometer equipped with a graphite-monochromated Mo Kα source (λ = 0.710 69 Å). Structure solution and refinements were carried out by using the teXsan program package,[29] whereby the positions of the non-hydrogen atoms were determined by Patterson methods (PATTY)[30] and subsequent Fourier synthesis (DIRDIF 94).[31] Details for **1a**·MeCN, **1b**, **2a**, **2b**, **6**, and **10** are listed in Table 5. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at the calculated positions and included at the final stages of refinements with fixed parameters except for those of the Me_2Tp ligand in **1a**·MeCN, which were refined isotropically. Significant disorders were observed for the positions of the C atoms in the Et_4N cations in **1a**·MeCN, **2a**, **2b**, and **6**.

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Supporting Information Available: ORTEP drawing for complex **1b** and X-ray crystallographic files in CIF format for complexes **1a**, **1b**, **2a**, **2b**, **6**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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