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A Series of Dinuclear Homo- and Heterometallic Complexes with Two or Three Bridging Sulfido Ligands Derived from the Tungsten Tris(sulfido) Complex $[Et_4N][(Me_2Tp)WS_3]$ (Me_2Tp = Hydridotris(3,5-dimethylpyrazol-1-yl)borate)

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The generation of heterobimetallic complexes with two or three bridging sulfido ligands from mononuclear tris(sulfido) complex of tungsten $[Et_4N][(Me_2Tp)WS_3]$ (**1**; Me_2Tp = hydridotris(3,5-dimethylpyrazol-1-yl)borate) and organometallic precursors is reported. Treatment of **1** with stoichiometric amounts of metal complexes such as $[M(PPh_3)_4]$ (M = Pt, Pd), $[(PtMe_3)_4(\mu_3\text{-}I)_4]$, $[M(cod)(PPh_3)_2][PF_6]$ (M = Ir, Rh; cod = 1,5-cyclooctadiene), $[Rh(cod)(dppe)][PF_6]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), $[Cp^*Ir(MeCN)_3][PF_6]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$), $[Cp^*Ru(MeCN)_3][PF_6]$, and $[M(CO)_3(MeCN)_3]$ (M = Mo, W) in MeCN or MeCN–THF at room temperature afforded either the doubly bridged complexes $[Et_4N][(Me_2Tp)W(=S)(\mu\text{-}S)_2M(PPh_3)]$ (M = Pt (**3**), Pd (**4**)), $[(Me_2Tp)W(=S)(\mu\text{-}S)_2M(cod)]$ (M = Ir, Rh (**7**)), $[(Me_2Tp)W(=S)(\mu\text{-}S)_2Rh(dppe)]$, $[(Me_2Tp)W(=S)(\mu\text{-}S)_2RuCp^*]$ (**10**), and $[Et_4N][(Me_2Tp)W(=S)(\mu\text{-}S)_2W(CO)_3]$ (**12**) or the triply bridged complexes including $[(Me_2Tp)W(\mu\text{-}S)_3PtMe_3]$ (**5**), $[(Me_2Tp)W(\mu\text{-}S)_3IrCp^*][PF_6]$ (**9**), and $[Et_4N][(Me_2Tp)W(\mu\text{-}S)_3Mo(CO)_3]$ (**11**), depending on the nature of the incorporated metal fragment. The X-ray analyses have been undertaken to clarify the detailed structures of **3**–**5**, **7**, and **9**–**12**.

Introduction

In a previous paper,[1] we reported the synthesis of mononuclear W or Mo sulfido complexes containing tris(pyrazolyl)borate ligands, $[Et_4N][Tp'WS_3]$ and $[Et_4N][Tp'MoS(S_4)]$ (Tp′ = Tp or Me_2Tp; Tp = hydridotris(pyrazol-1-yl)borate, Me_2Tp = hydridotris(3,5-dimethylpyrazol-1-yl)borate), from $[Et_4N][Tp'M(CO)_3]$ (M = W, Mo) and S_8. Although the chemistry of multinuclear transition metal–sulfur complexes attracts significant attention due to its relevance to biological and industrial catalysis,[2] complexes containing Tp′ coligands are still scarce because of, at least in part, the paucity of suitable precursors. This is in striking contrast to the presence of a number of well-defined multimetallic sulfido and thiolato complexes with cyclopentadienyl ligands that are isoelectronic with the Tp′ ligands.

In this context, the described Tp′ complexes of W and Mo are noteworthy as potential precursors to heterometallic species. The W complex $[Et_4N][(Me_2Tp)WS_3]$ (**1**) having three terminal sulfides is of particular interest, since **1** is available quite readily and it has been well demonstrated that the thiometalates $[MS_4]^{2-}$ (M = W, Mo) can serve as good starting compounds to synthesize numerous polymetallic complexes through sulfido ligands bridging to other metal centers.[3] Indeed, treatment of **1** with $[PtCl_2(cod)]$ (cod = 1,5-cyclooctadiene) resulted in the facile formation of a sulfido-bridged bimetallic complex $[Et_4N][(Me_2Tp)W(=S)(\mu\text{-}S)_2PtCl_2]$ (**2**) as reported already[1] (Scheme 1).

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(1) Seino, H.; Arai, Y.; Iwata, N.; Nagao, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **2001**, *40*, 1677.

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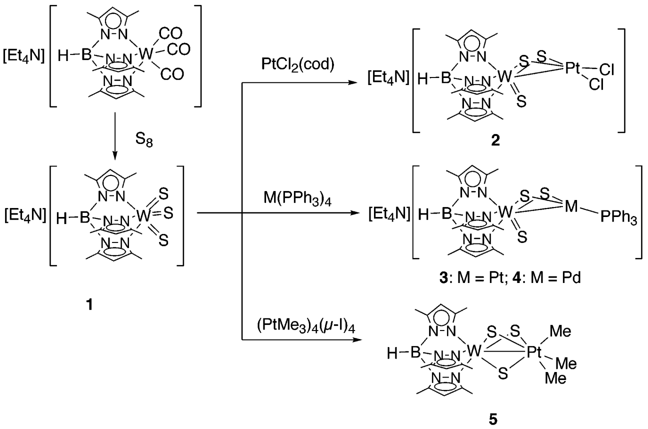
Scheme 1



Stimulated by this finding, further study has been done to clarify the reactivity of **1** toward a range of metal complexes, which has led to the isolation of a series of new dinuclear complexes with either two or three bridging sulfido ligands as summarized in the following text.

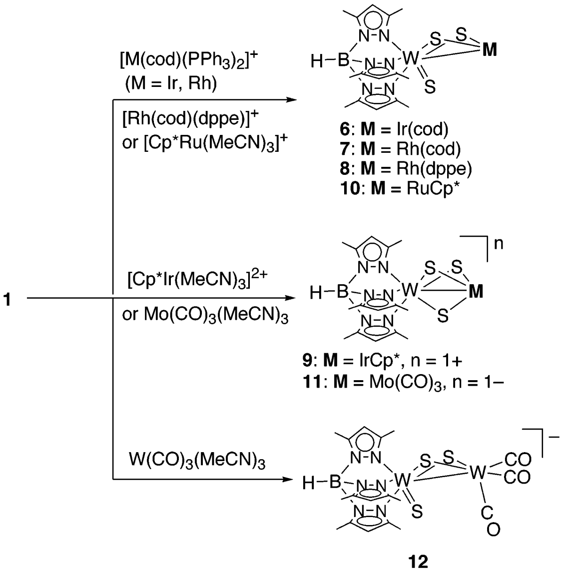
The Mo complex reported in the previous paper $[TpMoS(S_4)]^-$ has been shown to serve as a precursor to the cubane-type $MoFe_3S_4$ cluster by Holm et al.[4] It is also to be noted that the cyclopentadienyl complex $[Cp^*WS_3]^-$ ($Cp^* = \eta^5$-C_5Me_5) closely related to **1** has been prepared and its reactions with certain metal complexes of Cu, Ag, Au, Mn, Ni, Pd, and Ru forming mixed-metal sulfido cores have been reported by Tatsumi at al.[5]

Results and Discussion

Reactions of 1 with Pt and Pd Complexes. As reported already,[1] W^{VI} complex **1** reacts with an equimolar amount of a Pt^{II} complex $[PtCl_2(cod)]$ in MeCN at room temperature to give doubly bridged dinuclear complex **2** in moderate yield (Scheme 1). Complex **2**, which is assignable as a formal $W^{VI}-Pt^{II}$ compound, has a distorted square planar Pt center along with a W atom with a distorted octahedral geometry, if the Pt−W bond is ignored. Assuming these formal oxidation states, and therefore a d^0 W center, the metal−metal bond should be assigned to be a dative one from Pt to W.

While a related Pt^{II} complex $[PtMe_2(cod)]$ was somehow unreactive toward **1** under the analogous conditions, it has been found that the reaction of **1** with 1 equiv of zerovalent Pt complex $[Pt(PPh_3)_4]$ in MeCN−THF at room temperature gives $[Et_4N][(Me_2Tp)W({=}S)(\mu\text{-}S)_2Pt(PPh_3)]$ (**3**), a doubly sulfido-bridged $W^{VI}-Pt^0$ complex with a trigonal planar Pt center (Scheme 1). The reaction with Pd^0 complex $[Pd(PPh_3)_4]$ proceeded in an analogous manner to afford $[Et_4N][(Me_2Tp)W({=}S)(\mu\text{-}S)_2Pd(PPh_3)]$ (**4**). In contrast, treatment of **1** with a Pt^{IV} complex $[(PtMe_3)_4(\mu\text{-}I)_4]$ results in the formation of a triply bridged bimetallic complex containing the formal W^{VI} and Pt^{IV} centers, $[(Me_2Tp)W(\mu\text{-}S)_3PtMe_3]$ (**5**), which is also shown in Scheme 1.

Scheme 2



Reactions of 1 with Other Transition Metal Complexes. It has turned out that **1** reacts readily with a series of transition metal complexes to give a variety of sulfido-bridged dinuclear complexes, which are summarized in Scheme 2. Thus, treatment of **1** with an Ir^I complex $[Ir(cod)(PPh_3)_2][PF_6]$ (cod = 1,5-cyclooctadiene) in MeCN at room temperature gives a doubly bridged product with a formal $W^{VI}-Ir^I$ core $[(Me_2Tp)W({=}S)(\mu\text{-}S)_2Ir(cod)]$ (**6**), although the isolated yield of 15% is not yet satisfactory. The Rh analogue $[Rh(cod)(PPh_3)_2][PF_6]$ reacts similarly with **1** to afford a corresponding $W^{VI}-Rh^I$ complex $[(Me_2Tp)W({=}S)(\mu\text{-}S)_2Rh(cod)]$ (**7**) in 27% yield. It has been reported that $[M(cod)(\mu\text{-}S)_2W(\mu\text{-}S)_2M(cod)]$ (M = Ir, Rh) prepared from $[WS_4]^{2-}$ and $[\{M(cod)\}_2(\mu\text{-}Cl)_2]$ are treated with PPh_3 to give the products $[M(PPh_3)_2(\mu\text{-}S)_2W(\mu\text{-}S)_2M(PPh_3)_2]$, resulting from the replacement of the cod ligands by PPh_3.[6] However, in the present reactions forming **6** and **7**, elimination of the PPh_3 ligands occurs, and the complexes are isolated as pure crystals containing only cod ligands at their Ir or Rh site. Interestingly, the reaction of equimolar **1** and $[Rh(cod)(dppe)][PF_6]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) gave the doubly bridged bimetallic complex $[(Me_2Tp)W({=}S)(\mu\text{-}S)_2Rh(dppe)]$ (**8**) in 42% yield, with concomitant loss of cod rather than the chelate-stabilized dppe ligand.

With respect to the Ir^{III} complexes, the reactions of **1** with $[(Cp^*IrX)_2(\mu\text{-}X)_2]$ (X = Cl, I) in MeCN did not proceed cleanly, and no tractable products were isolated, whereas treatment of **1** with $[Cp^*Ir(MeCN)_3][PF_6]_2$ in MeCN resulted in the formation of a triply bridged $W^{VI}-Ir^{III}$ complex $[(Me_2Tp)W(\mu\text{-}S)_3IrCp^*][PF_6]$ (**9**) in 62% isolated yield.

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In the reactions with Ru complexes, a zerovalent Ru complex [Ru(cod)(cot)] (cot = 1,3,5-cyclooctatriene) did not react with **1** in MeCN even at 55 °C. As for the Ru^{II} complexes, the reaction of **1** with [$(Cp^*Ru)_4(\mu_3\text{-}Cl)_4$] was elusive, while that with [$Cp^*Ru(MeCN)_3$][PF_6] proceeded cleanly at room temperature, affording a doubly bridged $W^{VI}-Ru^{II}$ complex [$(Me_2Tp)W(=S)(\mu\text{-}S)_2RuCp^*$] (**10**) in 26% isolated yield.

Reactions with early transition metal complexes were also undertaken. Thus, both the reactions of **1** with [$Mo(CO)_3(MeCN)_3$] and [$Mo(CO)_4(nbd)$] (nbd = norbornadiene) in MeCN gave a triply bridged $W^{VI}-Mo^0$ complex [Et_4N][$(Me_2Tp)W(\mu\text{-}S)_3Mo(CO)_3$] (**11**) in 37% and 16% yields, respectively. In contrast, the reaction of $[WS_4]^{2-}$ with [$Mo(CO)_4(nbd)$] gives the doubly bridged complexes $[WS_2(\mu\text{-}S)_2Mo(CO)_4]^{2-}$ [7] and $[Mo(CO)_4(\mu\text{-}S)_2W(\mu\text{-}S)_2Mo(CO)_4]^{2-}$.[7a,8] Interestingly, the $W^{VI}-W^0$ complex [Et_4N][$(Me_2Tp)W(=S)(\mu\text{-}S)_2W(CO)_3$] (**12**), prepared similarly from **1** and [$W(CO)_3(MeCN)_3$], has been shown by an X-ray analysis to comprise not a triply bridged but a doubly bridged dinuclear core as will be described.

In summary, we have found that a series of sulfido-bridged bimetallic complexes containing the $W(S)_3$**M** core can be prepared readily from the W tris(sulfide) complex **1** and certain transition metal complexes. The structure of this core is either $W(=S)(\mu\text{-}S)_2$**M** or $W(\mu\text{-}S)_3$**M**, depending on the nature and the oxidation state of the metal center M in the incorporated fragment **M**. Thus, the number of the valence electrons for the fragment **M** in an uncoordinated form is 12 for all complexes reported here. Nevertheless, the oxidation state and/or the number of d electrons of the metal center M involved in **M** differ from each other. When incorporated into the WS_3 site, the fragment **M** containing relatively electron-deficient or high-valent M is presumed to form the triply bridged core.

Among the complexes with the formal d^6 M center, for example, (1) the W^0 complex **12** has a doubly bridged core, whereas **11** containing Mo^0 in the same triad with less electrons is a triply bridged complex, and (2) the Ru^{II} complex **10** has only two bridging sulfides, whereas the higher valent Ir^{III} complex **9** has three bridging sulfides. With respect to the W−Pt complexes, for example, **3** and **2** containing Pt^0 and Pt^{II} are doubly bridged, while **5** with the Pt^{IV} center is triply bridged. It is also to be noted that the triply bridged structure is observed only for the complexes with the d^6 M center such as **5**, **9**, and **11**, whereas the complexes with the d^8 or d^{10} M center obtained in this study, viz. **2**, **3**, **4**, **6**, **7**, and **8**, comprise the doubly bridged cores exclusively.

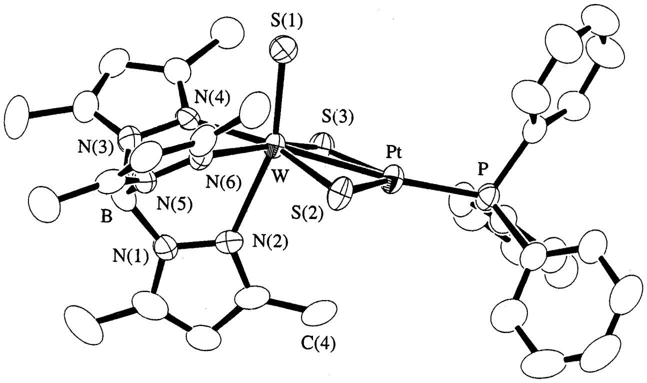

Figure 1. ORTEP drawing for the anion in **3**. Hydrogen atoms are omitted for clarity.

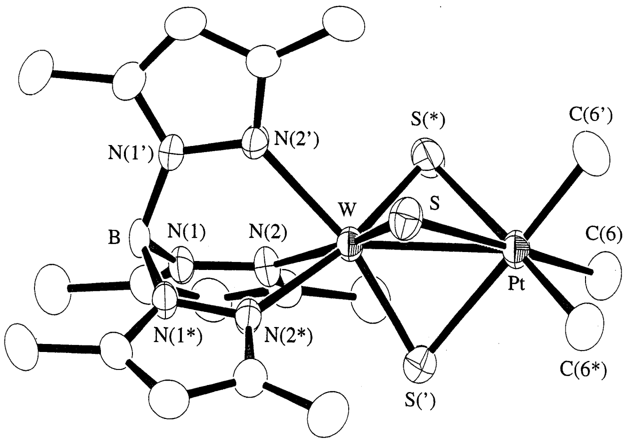

Figure 2. ORTEP drawing for **5**. Hydrogen atoms are omitted for clarity.

Although the doubly bridged bimetallic complexes containing the square planar 16-electron d^8 M centers as well as the trigonal planar d^{10} M centers have also been derived extensively from $[WS_4]^{2-}$, those consisting of the five-coordinate 16-electron d^6 M center such as **10** and **12** are unprecedented for $[WS_4]^{2-}$. In **10** and **12** with the $(Me_2Tp)WS_3$ unit, the 16-electron d^6 centers are stabilized by the significant π-donation from the two bridging sulfides as demonstrated by the X-ray analyses (*vide infra*), which is the feature unobserved for the complexes derived from $[WS_4]^{2-}$. The triply bridged structures found in **5**, **9**, and **11** are unknown with respect to the dinuclear complexes derived from $[WS_4]^{2-}$.

Related reactions forming sulfido-bridged bimetallic center from the Cp* analogue of **1**, $[Cp^*WS_3]^-$, and noble metal complexes have been reported: the reaction with [$PdCl_2(dppe)$] gives doubly bridged complex [$Cp^*W(=S)(\mu\text{-}S)_2Pd(dppe)$]Cl,[5c] while that with [$RuClX(PPh_3)_3$] (X = Cl, H) affords triply bridged complex [$Cp^*W(\mu\text{-}S)_3RuX(PPh_3)_2$].[5g]

Description of the X-ray Structures of the New Dinuclear Complexes. New complexes **3**−**12** have been characterized spectroscopically and by elemental analyses. The detailed structures have been determined by the X-ray analyses for **3**−**5**, **7**, and **9**−**12**. The ORTEP drawings for **3**, **5**, **7**, and **9**−**12** are shown in Figures 1−7, respectively. For **12**, only one of the two crystallographically independent molecules is shown, since their structures are analogous except for the slight difference in the torsion angles $S_{terminal}-W-W-C_{apical}$. The X-ray structure of **4** is essentially the same as that for the Pt analogue **3**, and the ORTEP plot is omitted. For **6**, preliminary X-ray results showed that it has the doubly bridged core identical to that observed in the Rh

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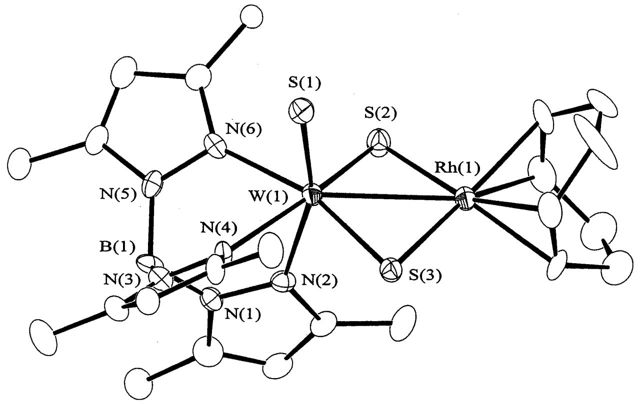

Figure 3. ORTEP drawing for **7**. Hydrogen atoms are omitted for clarity.

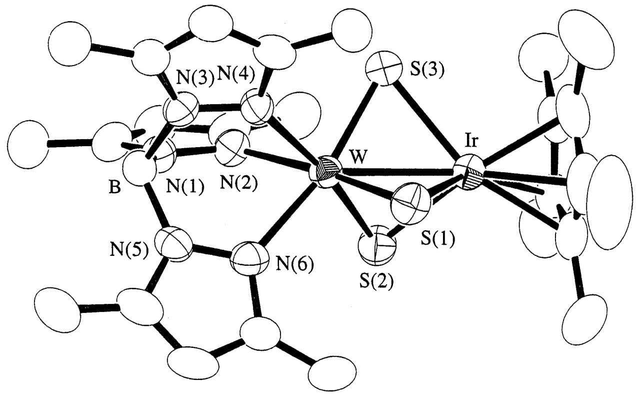

Figure 4. ORTEP drawing for the cation of **9**. Hydrogen atoms are omitted for clarity.

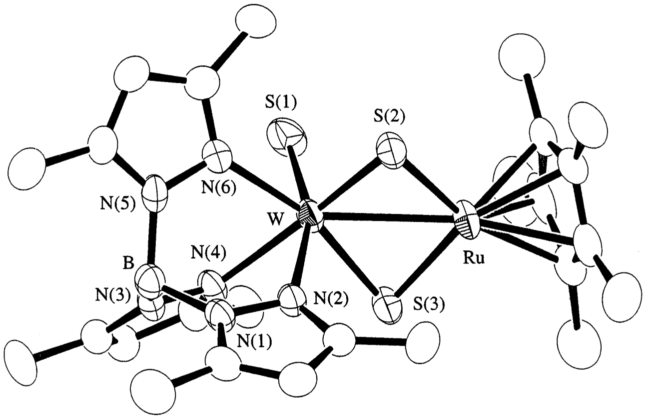

Figure 5. ORTEP drawing for **10**. Hydrogen atoms are omitted for clarity.

analogue **7**. Selected bond distances and angles in the doubly bridged complexes are summarized in Table 1, and those in the triply bridged complexes are listed in Table 2. The feature observed commonly for these clusters is that by coordination of the terminal sulfides and the formation of the dative bond from M to the high valent W in **1** the π-donation of the lone pair electron densities from the sulfide ligands to the W center decreases, which results in the elongation of the W−S bond lengths by 0.06−0.11 Å and, due to the weaker trans influence of the sulfide ligands, the shortening of the W−N bonds by 0.01−0.09 Å in the bimetallic complexes.

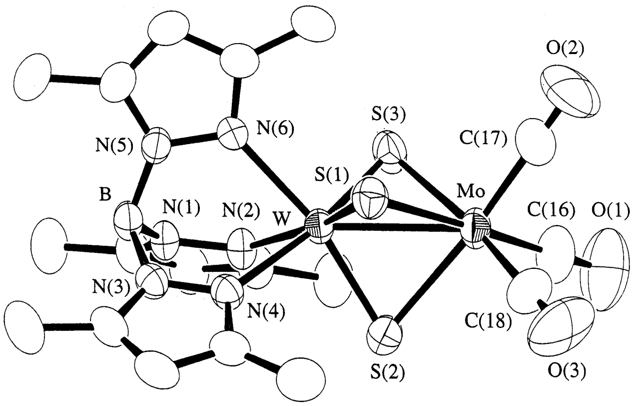

Figure 6. ORTEP drawing for the anion of **11**. Hydrogen atoms are omitted for clarity.

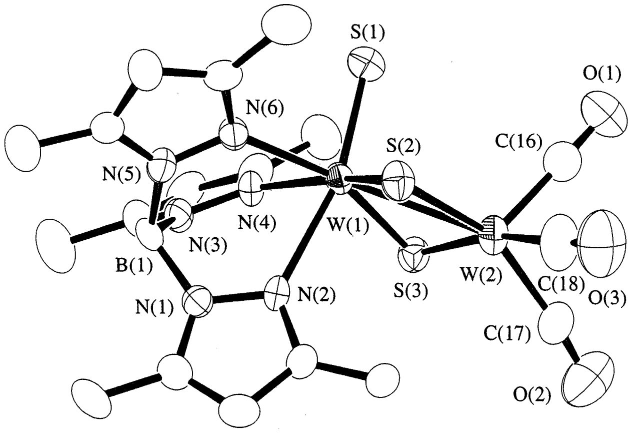

Figure 7. ORTEP drawing for the anion in one of the two independent molecules of **12**. Hydrogen atoms are omitted for clarity.

As shown in Figure 1 and Table 1, the complex anion of **3** has a core consisting of the $Me_2TpW{=}S$ and $Pt(PPh_3)$ fragments connected by two μ-S bridges as well as a formal dative bond from the d^{10} Pt atom to the d^0 W atom (2.7216(4) Å). The W center has a distorted octahedral configuration with three pyrazolyl N atoms and three sulfido ligands. In **3**, the $W{-}S_{terminal}$ bond length (W−S(1)) is 2.172(2) Å, which is comparable to that in parent **1** (2.192(1), 2.1942(9) Å)[1] and the mean $W{-}S_{terminal}$ bond length of 2.15 Å reported recently on the basis of the X-ray results of some 80 complexes.[9] These values are significantly shorter than those of the formal bond order 2 observed in the 18-electron complexes $[W({=}S)_2(PMe_3)_4]$ (2.253 Å) and $[W({=}S)_2(PMe_3)_2(CNBu^t)_2]$ (2.248(2) Å),[10] which are interpreted in terms of the presence of the resonance structure with formal triple bond $W^-{\equiv}S^+$ in addition to W=S owing to the presence of the electron-deficient W center. The W−μ-S bond distances (W−S(2), 2.302(2) Å; W−S(3), 2.289(2) Å) are also considerably shorter than the typical W−S single bond length (2.39 Å)[9] due to the contribution of the π-bonding of the lone-pair electrons on the bridging S atom. As for the W−N bonds, that trans to the terminal sulfide S(1) (W−N(2), 2.386(6) Å) is much elongated from the remaining two (W−N(4), 2.302(6) Å; W−N(6), 2.319(6) Å), indicating that the trans influence exerted by the terminal sulfide is much stronger than that by the bridging sulfide.

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Table 1. Pertinent Bonding Parameters (Å or deg) in Doubly Bridged Complexes $[(\mathrm{Me_2Tp})\mathrm{W}({=}\mathrm{S})(\mu\text{-}\mathrm{S})_2\mathbf{M}]^n$

	3	**4**	**7**	**10**	**12**	**2**[a]
M	$Pt(PPh_3)$	$Pd(PPh_3)$	Rh(cod)	RuCp*	$W(CO)_3$	$PtCl_2$
n	1−	1−	0	0	1−	1−
W−M	2.7216(4)	2.7234(5)	2.852(1)	2.7716(5)	2.8988(6), 2.8993(7)	2.7792(6)
W−S(1)	2.172(2)	2.180(2)	2.157(4)	2.167(2)	2.165(3), 2.152(3)	2.148(3)
W−S(2)	2.302(2)	2.284(2)	2.253(3)	2.286(2)	2.304(3), 2.300(3)	2.259(3)
W−S(3)	2.289(2)	2.275(2)	2.262(4)	2.290(2)	2.291(3), 2.294(3)	2.262(3)
M−S(2)	2.307(2)	2.327(2)	2.298(4)	2.269(2)	2.395(3), 2.409(3)	2.290(3)
M−S(3)	2.284(2)	2.306(2)	2.314(4)	2.273(2)	2.421(3), 2.393(3)	2.287(3)
W−N(2)	2.386(6)	2.380(5)	2.33(1)	2.356(5)	2.396(8), 2.428(8)	2.392(8)
W−N(4)	2.302(6)	2.319(4)	2.29(1)	2.268(4)	2.274(9), 2.277(9)	2.262(9)
W−N(6)	2.319(6)	2.324(5)	2.27(1)	2.265(5)	2.263(8), 2.262(9)	2.243(9)
S(1)−W−S(2)	102.31(8)	102.57(6)	103.3(1)	103.14(7)	101.1(1), 102.6(1)	101.8(1)
S(1)−W−S(3)	101.84(8)	101.83(6)	103.0(1)	102.99(7)	102.8(1), 102.4(1)	103.4(1)
S(2)−W−S(3)	106.49(7)	107.59(5)	102.7(1)	102.86(6)	105.9(1), 105.5(1)	102.7(1)
S(2)−M−S(3)	106.49(7)	105.09(5)	99.7(1)	103.97(6)	99.22(10), 99.2(1)	100.9(1)
W−S(2)−M	72.37(6)	72.41(5)	77.6(1)	74.96(5)	76.15(9), 75.96(10	75.30(10)
W−S(3)−M	73.03(6)	72.95(4)	77.1(1)	74.81(5)	75.88(9), 76.40(10)	75.32(9)
S(2)−W−M−S(3)[b]	168.30(9)	167.11(7)	163.4(5)	162.61(8)	164.1(1), 163.6(1)	157.2(1)

[a] Reference 1. [b] Torsion angle.

Table 2. Pertinent Bonding Parameters (Å or deg) in Triply Bridged Complexes $[(\mathrm{Me_2Tp})\mathrm{W}(\mu\text{-}\mathrm{S})_3\mathbf{M}]^n$

	5	**9**	**11**
M	$PtMe_3$	IrCp*	$Mo(CO)_3$
n	0	1+	1−
W−M	2.6865(5)	2.6415(6)	2.7783(4)
W−S(1)	2.238(2)	2.264(3)	2.247(1)
W−S(2)		2.262(2)	2.250(1)
W−S(3)		2.244(3)	2.240(1)
M−S(1)	2.513(2)	2.414(3)	2.549(1)
M−S(2)		2.395(3)	2.577(1)
M−S(3)		2.402(2)	2.567(1)
W−N(2)	2.248(4)	2.207(8)	2.246(3)
W−N(4)		2.188(7)	2.270(3)
W−N(6)		2.213(8)	2.270(3)
S(1)−W−S(2)	97.89(5)	93.50(10)	97.57(4)
S(1)−W−S(3)		94.9(1)	97.99(4)
S(2)−W−S(3)		95.7(1)	97.06(4)
S(1)−M−S(2)	84.40(5)	86.56(9)	82.60(4)
S(1)−M−S(3)		87.20(9)	82.88(4)
S(2)−M−S(3)		88.29(9)	81.69(4)
W−S(1)−M	68.60(4)	68.68(7)	70.48(3)
W−S(2)−M		69.05(7)	69.91(3)
W−S(3)−M		69.21(7)	70.25(3)

The geometry around the Pt atom is trigonal planar, with the sum of one S−Pt−S angle (106.49(7)°) and two S−Pt−P angles (131.94(7), 121.41(7)°) around Pt being 360°. The Pt−μ-S bond distances (Pt−S(2), 2.307(2) Å; Pt−S(3), 2.284(2) Å) are almost identical with the W−μ-S bond lengths already described. Due to the presence of the metal−metal single bond, the W−S−Pt angles (72.37(6)°, 73.03(6)°) are significantly acute. The $WPtS_2$ ring is puckered slightly with the dihedral angle of 168° around the W−Pt vector.

As listed in Table 1, the bonding parameters in the Pd analogue **4** (W−Pd, 2.7234(5) Å; W=S, 2.180(2) Å; W−μ-S, 2.284(2) and 2.275(2) Å; Pd−μ-S 2.327(2) and 2.306(2) Å; W−S−Pd, 72.41(5)° and 72.95(4)°) are all in good agreement with those in **3**. The structural features demonstrated previously for the $W(=S)(\mu\text{-}S)_2Pt$ core in **2**[1] containing a square planar Pt^{II} center are also essentially similar to those of **3**, although in **2** the W−Pt single bond of 2.7792(6) Å is slightly longer, whereas the W−S bonds with the lengths of 2.148(3), 2.259(3), and 2.262(3) Å are all slightly shorter than the corresponding bonds in **3**. The dihedral angle between two WPtS planes is 157° for **2**. It is noteworthy that the reactions of $[WS_4]^{2-}$ with Pt^{II} and Pd^{II} species forming bimetallic W^{VI}−Pt^{II} and W^{VI}−Pd^{II} complexes, e.g., $[S_2W(\mu\text{-}S)_2Pt(PEt_3)_2]$,[11] $[S_2W(\mu\text{-}S)_2Pd(dppe)]$,[12] etc., have been reported extensively, whereas those with Pt^0 and Pt^0 compounds are unprecedented.

The other new complexes having doubly bridged cores **7**, **10**, and **12** show the structural features analogous to **2**−**4** with respect to the $(Me_2Tp)W(=S)(\mu\text{-}S)_2M$ chromophore as shown in Table 1. In particular, the bonding parameters associated with the W^{VI}−S and W^{VI}−N linkages in these complexes are in good agreement with those in **3** and **4**.

If the metal−metal bonds are ignored, the geometries around M in **7** and **10** are square planar and two-legged piano stool, respectively. For **12**, that around W^0 is square pyramidal in one crystallographically independent molecule and distorted square pyramidal for the other. In **10**, the Ru−C distances vary considerably from 2.119(6) Å for C(16) to 2.204(6) Å for C(18), which may be explained by the presence of the steric repulsion between the methyl groups of the Me_2Tp and Cp* ligands. In **12**, the W(2)−CO bond length for the apical CO ligand (W(2)−C(16), 1.89(1) Å) is much shorter than those for the CO ligands in the basal plane (W(2)−C(17), 1.98(1) Å, W(2)−C(18), 1.96(2) Å). This feature is also observed in the other crystallographically independent molecule of **12** with the $W-C_{apical}$ and $W-C_{basal}$ bond lengths at 1.91(1) vs 1.99(1) and 1.98(2) Å. The WMS_2 rings in **7**, **10**, and **12** are not planar with the dihedral angles between two WMS planes of 163°, 163°, and 164°, respectively.

The Rh^I−W^{VI} complexes related to **7** such as $[Rh(cod)(\mu\text{-}S)_2W(\mu\text{-}S)_2Rh(cod)]$[6,13] and $[(cod)Rh(\mu\text{-}S)_2W(\mu\text{-}S)_2WCl(NN{=}CMePh)(dppe)]$[14] have been structurally characterized,

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whose bonding parameters associated with the W(μ-S)$_2$Rh fragments are similar to those in **7** listed in Table 1 except for the W−S distances which are slightly shorter by av 0.060−0.065 Å than those in **7**.

A considerable number of the W^{VI}−Ru^{II} complexes have been isolated from the reactions of [WS$_4$]$^{2-}$ with Ru^{II} complexes, which include, for example, [(η^6-cymene)Ru(PPh$_3$)(μ-S)$_2$WS$_2$][15] and [CpRu(CNMe)(μ-S)$_2$W(μ-S)$_2$RuCp(CNMe)].[16] As compared to these complexes containing six-coordinate, electronically saturated Ru centers, **10** with the two-legged piano stool Ru atom has the significantly short Ru−S bonds; these differences amounting to ca. 0.1 Å indicate clearly the presence of the π-electron donation from the μ-S ligands to Ru in **10**.

Complex **12** incorporating a d^6 W center with three electron-withdrawing CO ligands has a relatively long metal−metal bond (2.8988(6), 2.8993(7) Å) among the new complexes reported here. This complex has two types of W−μ-S bonds, where the W^0−μ-S bonds (2.393(3)−2.421(3) Å) are significantly longer than the W^{VI}−μ-S bonds in the range 2.291(3)−2.304(3) Å, indicating clearly the stronger π-donation of the lone-pair electron densities of the bridging S atoms toward the higher valent W. It is noteworthy that the mononuclear *fac*-W^0 tricarbonyl complexes with three thioether ligands [{RE(CH$_2$SMe)$_3$}W(CO)$_3$] (RE = Bu^{n}Sn,[17] MeSi[18]) have more elongated W^0−S bonds (2.55−2.61 Å) compared to those in **12**.

Table 2 shows the bonding parameters in the triply bridged complexes. In these complexes, the W−μ-S bonds are 0.04−0.07 Å longer and the W−N bonds are 0.06−0.14 Å shorter than those in the parent **1**. The former W−μ-S bond lengths are intermediate between the W−S$_{terminal}$ and W−S$_{bridging}$ bond distances in the doubly bridged complexes shown here. The S−W−S and W−S−M angles are all smaller in these triply bridged complexes than those in the doubly bridged ones.

Complex **5** containing high valent, octahedral W^{VI} and Pt^{IV} centers has a considerably shorter metal−metal bond (2.6865(5) Å) as compared to the doubly bridged complexes. This W−Pt bond coincides with the C_{3v} axis of the molecule. The Pt−S bond distance at 2.513(2) Å is almost comparable to those in [(PtMe$_3$)$_4$(μ_3-SR)$_4$] (R = Ph,[19] Me,[20] 2.46−2.54 Å) and is much longer than those in **3** and **2** (2.284(2)−2.307(2) Å) owing to the strong trans influence by the methyl ligands.

Both **9** with a three-legged piano stool Ir center and **11** with an octahedral Mo center have the (Me$_2$Tp)W(μ-S)$_3$M cores with a pseudo C_{3v} symmetry; the deviations observed for the W−S, W−N, and M−S bonding parameters in each complex are small and might be insignificant. The W−Ir distance at 2.6415(6) Å is much shorter than those (2.85−2.87 Å) and the Ir−S bond lengths in the range 2.395(3)−2.414(3) Å are analogous to those (2.37−2.41 Å) in the doubly bridged Cp*Ir^{III} complex [Cp*IrCl(μ-S)$_2$W(μ-S)$_2$-IrCp*Cl].[21]

For **11**, the W−Mo separation of 2.7783(4) Å is much shorter than those in the related doubly bridged complexes [NEt$_4$]$_2$[Mo(CO)$_4$(μ-S)$_2$W(μ-S)$_2$Mo(CO)$_4$] (3.03 Å)[8] and [NEt$_4$]$_2$[S$_2$W(μ-S)$_2$Mo(CO)$_4$] (3.03 Å),[7b] whereas the W−μ-S and Mo−μ-S bond lengths in the range 2.240(1)−2.250(1) and 2.549(1)−2.577(1) Å, respectively, in **11** are almost comparable to those of 2.20−2.23 and 2.53−2.56 Å in the latter. It is to be noted that the Mo−S bond distances in **11** are much longer than the M−S bond lengths of the other complexes reported here. The Mo−C bond distances from 1.952(5) to 1.967(5) Å are comparable to the W−C bond lengths of the basal CO ligands in **12**.

Spectroscopic Data for the New Dinuclear Complexes. The ^{1}H NMR spectrum of the doubly bridged **3** recorded at room temperature shows two singlets at δ 1.31 and 2.15 each integrating for three protons and the two singlets at δ 2.50 and 3.58 each integrating for six protons due to the methyl protons in the Me$_2$Tp ligand. This as well as the appearance of the pyrazolyl methine protons at δ 5.13 and 6.12 in an intensity ratio of 1:2 is consistent with the octahedral structure of W occupying one terminal sulfide and two bridging sulfides trans to the pyrazolyl N atoms. This feature was also observed previously for **2**. However, in the spectra of all other doubly bridged complexes, the pyrazolyl methyl protons are recorded at room temperature as only two signals with the same intensities each corresponding to nine protons. This finding indicates that the structures of these complexes with two bridging sulfides are fluxional at room temperature, where rapid interconversion between the terminal and bridging sulfides is taking place by the facile dissociation and formation of the M′−S bonds with respect to all three sulfides. As expected, the spectra of **4** in acetone-d_6 and **6**−**8** in THF-d_8 recorded at −80 °C are consistent with the rigid doubly bridged structure clarified by the X-ray analysis. Line shape analyses of the pyrazolyl methyl signals for **4** in the range −60 to +40 °C and for **6**−**8** in the range −40 to +40 °C have given the activation energies for this interconversion ($\Delta G^\ddagger$) to be 47, 53, 47, and 53 kJ·mol^{-1}, respectively. Meanwhile, in the spectra for **10** and **12** the resonances due to the Me$_2$Tp protons are still quite broad even at −80 °C and were unresolvable. For the triply bridged complexes, the 3-methyl and 5-methyl groups are each equivalent, and the ^{1}H NMR spectra showed two singlets with the same intensities assignable to the pyrazolyl methyl protons.

The IR spectra of the doubly bridged complexes are featured by the appearance of the characteristic ν(W=S$_{terminal}$) and ν(W−S$_{bridging}$) bands in the range 459−478 and 405−440 cm^{-1}, respectively, along with the ν(B−H) bands

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varying from 2540 to 2552 cm^{-1}. Among these, assignments of the $\nu(W{-}S_{bridging})$ bands are somewhat tentative, since these are generally so weak. For the triply bridged complexes, the bands at 420 cm^{-1} for **5**, 409 cm^{-1} for **9**, and 405 cm^{-1} for **11** might be assignable to the $\nu(W{-}S)$ bands.

The spectra of **11** and **12** showed the $\nu(C{\equiv}O)$ bands at 1923 (s), 1852 (m), and 1814 (s) cm^{-1}, and at 1932 (s), 1867 (s), and 1794 (s) cm^{-1}, respectively, as the additional characteristic bands. For comparison, the $\nu(C{\equiv}O)$ values for the $M(CO)_3$ fragments with three thioether coligands, *fac*-$[\{MeSi(CH_2SMe)_3\}M(CO)_3]$,[18] are 1918 and 1785 cm^{-1} for M = Mo and 1910 and 1770 cm^{-1} for M = W, while those for the parent complexes are 1913 and 1776 cm^{-1} for *fac*-$[Mo(CO)_3(MeCN)_3]$ and 1904 and 1786 cm^{-1} for *fac*-$[W(CO)_3(MeCN)_3]$, respectively.

Experimental Section

General. All manipulations were carried out under an atmosphere of N_2. IR and NMR spectra were recorded on a JASCO FT/IR 420 spectrometer at room temperature and a JEOL alpha-400 spectrometer at 20 °C except for those stated otherwise. Elemental analyses were done with a Perkin-Elmer 2400 series II CHN analyzer. Complexes **1**,[1] $[M(PPh_3)_4]$ (M = Pt,[22] Pd[23]), $[PtMe_3I]_4$,[24] $[M(cod)(PPh_3)_2][BF_4]$ (M = Ir, Rh),[25] $[Rh(cod)(dppe)][PF_6]$,[26] $[Cp^*Ir(MeCN)_3][PF_6]_2$,[27] $[Cp^*Ru(MeCN)_3][PF_6]$,[28] $[M(CO)_3(MeCN)_3]$ (M = Mo, W),[29] and $[Mo(CO)_4(nbd)]$[30] were prepared according to the literature methods.

$[Et_4N][(Me_2Tp)W({=}S)(\mu\text{-}S)_2Pt(PPh_3)]$ (3). A mixture of **1**·MeCN (75 mg, 0.10 mmol) and $[Pt(PPh_3)_4]$ (125 mg, 0.100 mmol) in MeCN−THF (5 mL/3 mL) was stirred overnight at room temperature. The resulting dark red mixture was filtered, and the filtrate was concentrated to ca. half its volume. Addition of ether gave **3**·MeCN as black crystals (82 mg, 68% yield). ^1H NMR (CD_3CN) δ 1.20 (t, J_{H-H} = 7.2 Hz, 12H, NCH_2CH_3), 1.31, 2.15 (s, 3H each, Me in Me_2Tp), 1.95 (s, 3H, MeCN), 2.50, 3.58 (s, 6H each, Me in Me_2Tp), 3.15 (q, J_{H-H} = 7.2 Hz, 8H, NCH_2), 5.13 (s, 1H, CH in Me_2Tp), 6.12 (s, 2H, CH in Me_2Tp), 7.3−7.5 (m, 9H, *m*- and *p*-H of Ph), 7.89 (dd, *J* = 10.8 and 6.8 Hz, 6H, *o*-H of Ph). $^{31}P\{^1H\}$ NMR (CD_3CN) δ 70.5 (s with ^{195}Pt satellites, *J* = 6268 Hz). IR (KBr): 2540 (B−H), 460 (W=S) cm^{-1}. Anal. Calcd for $C_{43}H_{60}N_8BPS_3WPt$: C, 42.83; H, 5.01; N, 9.29. Found: C, 42.39; H, 5.02; N, 9.07.

$[Et_4N][(Me_2Tp)W({=}S)(\mu\text{-}S)_2Pd(PPh_3)]$ (4). This complex was obtained as black crystals of **4**·MeCN from equimolar amounts of **1**·MeCN (75 mg, 0.10 mmol) and $[Pd(PPh_3)_4]$ (117 mg, 0.101 mmol) in 77% yield (86 mg) by the same procedure as that for **3**. ^1H NMR (CD_3CN) δ 1.20 (t, J_{H-H} = 7.2 Hz, 12H, NCH_2CH_3), 1.95 (s, 3H, MeCN), 2.38 (s, 9H, Me in Me_2Tp), 2.88 (br, 9H, Me in Me_2Tp), 3.15 (q, J_{H-H} = 7.2 Hz, 8H, NCH_2), 5.78 (s, 3H, CH in Me_2Tp), 7.3−7.5 (m, 9H, *m*- and *p*-H of Ph), 7.85 (dd, *J* = 10.8 and 6.8 Hz, 6H, *o*-H of Ph). ^1H NMR ($(CD_3)_2CO$, −90 °C) δ 1.58, 2.12 (s, 3H each, Me in Me_2Tp), 2.41, 3.54 (s, 6H each, Me in Me_2Tp), 5.20 (s, 1H, CH in Me_2Tp), 6.05 (s, 2H, CH in Me_2Tp). $^{31}P\{^1H\}$ NMR (CD_3CN) δ 68.3 (s). IR (KBr): 2541 (B−H), 459 (W=S) cm^{-1}. Anal. Calcd for $C_{43}H_{60}N_8BPS_3WPd$: C, 46.23; H, 5.41; N, 10.03. Found: C, 45.44; H, 5.15; N, 10.03.

$[(Me_2Tp)W(\mu\text{-}S)_3PtMe_3]$ (5). A mixture of **1**·MeCN (83 mg, 0.11 mmol) and $[PtMe_3I]_4$ (41 mg, 0.028 mmol) in MeCN (5 mL) was stirred overnight at room temperature. A black solid precipitated, which was filtered off and crystallized from THF−hexane, yielding **5** as dark purple crystals (30 mg, 33% yield). ^1H NMR (C_6D_6) δ 1.90, 2.86 (s, 9H each, Me in Me_2Tp), 2.43 (s with ^{195}Pt satellites, *J* = 73.0 Hz, 9H, PtMe), 5.37 (s, 3H, CH in Me_2Tp). IR (KBr): 2552 (B−H), 420 (W=S) cm^{-1}. Anal. Calcd for $C_{18}H_{31}N_6BS_3WPt$: C, 26.45; H, 3.82; N, 10.28. Found: C, 26.40; H, 3.79; N, 10.18.

$[(Me_2Tp)W({=}S)(\mu\text{-}S)_2Ir(cod)]$ (6). A mixture of **1**·MeCN (78 mg, 0.10 mmol) and $[Ir(cod)(PPh_3)_2][PF_6]$ (98 mg, 0.10 mmol) in MeCN (5 mL) was stirred overnight at room temperature. The resultant red-brown mixture was filtered off, and the remained solid was washed with MeCN and ether. The residue was crystallized from benzene−hexane. The yield of **6** as black microcrystals was 14 mg (15%). ^1H NMR (THF-d_8): δ 2.3−2.5 (m, 17H, 3Me in Me_2Tp and CH_2 in cod), 2.5−3.3 (v br, 9H, 3Me in Me_2Tp), 5.19 (br s, 4H, CH in cod), 5.8−6.0 (br, 3H, CH in Me_2Tp). ^1H NMR (THF-d_8, −80 °C): δ 1.86, 2.22 (s, 3H each, Me in Me_2Tp), 2.2−2.3 (m, 2H, CH_2 in cod), 2.35−2.45 (m, 6H, CH_2 in cod), 2.50, 3.26 (s, 6H each, Me in Me_2Tp), 4.95−5.05, 5.35−5.45 (m, 2H each, CH in cod), 5.44 (s, 1H, CH in Me_2Tp), 6.24 (s, 2H, CH in Me_2Tp). IR (KBr): 2551 (B−H), 478 (W=S), 426 (W−S) cm^{-1}. Anal. Calcd for $C_{23}H_{34}N_6BS_3WIr$: C, 31.48; H, 3.90; N, 9.58. Found: C, 31.93; H, 3.92; N, 9.39.

$[(Me_2Tp)W({=}S)(\mu\text{-}S)_2Rh(cod)]$ (7). This complex was prepared by the same procedure as that for **6** using **1**·MeCN (75 mg, 0.10 mmol) and $[Rh(cod)(PPh_3)_2][PF_6]$ (89 mg, 0.10 mmol) except that the product was finally crystallized from THF−hexane as pale brown microcrystals. Yield: 21 mg (27%). ^1H NMR (THF-d_8): δ 2.38 (s, 9H, Me in Me_2Tp), 2.4−2.5, 2.5−2.6 (m, 4H each, CH_2 in cod), 2.86 (br s, 9H, Me in Me_2Tp), 5.52 (br, 4H, CH in cod), 5.86 (s, 3H, CH in Me_2Tp). ^1H NMR (THF-d_8, −80 °C): δ 2.01, 2.24 (s, 3H each, Me in Me_2Tp), 2.3−2.4 (m, 2H, CH_2 in cod), 2.47 (s, 6H, Me in Me_2Tp), 2.4−2.6 (m, 4H, CH_2 in cod), 2.6−2.7 (m, 2H, CH_2 in cod), 3.24 (s, 6H, Me in Me_2Tp), 5.35−5.45 (m, 2H, CH in cod), 5.48 (s, 1H, CH in Me_2Tp), 5.6−5.7 (m, 2H, CH in cod), 6.19 (s, 2H, CH in Me_2Tp). IR (KBr): 2551 (B−H), 477 (W=S), 424 (W−S) cm^{-1}. Anal. Calcd for $C_{23}H_{34}N_6BS_3RhW$: C, 35.04; H, 4.35; N, 10.66. Found: C, 34.99; H, 4.48; N, 10.20.

$[(Me_2Tp)W({=}S)(\mu\text{-}S)_2Rh(dppe)]$ (8). A mixture of **1**·MeCN (43 mg, 0.057 mmol) and $[Rh(cod)(dppe)][PF_6]$ (42 mg, 0.055 mmol) was stirred in MeCN at room temperature for 16 h. The resulting deep purple solution was dried up, and the residue was extracted with benzene. Addition of hexane to the concentrated extract gave purple crystals of **8**·C_6H_6 (25 mg, 40% yield). ^1H NMR (THF-d_8): δ 2.34 (br s, 9H, Me in Me_2Tp), 2.5−2.9 (v br, 13H, PCH_2 and 3Me in Me_2Tp), 5.5−6.0 (br, 3H, CH in Me_2Tp), 7.3−7.4 (m, 18H, *m*- and *p*-H of Ph and C_6H_6), 7.8−7.9 (m, 8H, *o*-H of Ph). ^1H NMR (THF-d_8, −80 °C): δ 1.17, 2.15 (s, 3H each, Me in Me_2Tp), 2.25−2.4 (m, 2H, CH_2 in dppe), 2.46 (s, 6H, Me in Me_2Tp), 3.05−3.2 (m, 2H, CH_2 in dppe), 3.36 (s, 6H, Me in Me_2Tp), 5.15 (s, 1H, CH in Me_2Tp), 6.14 (s, 2H, CH in Me_2Tp), 7.3−7.4 (m, 18H, *m*- and *p*-H of Ph and C_6H_6), 7.75−7.85, 7.95−8.05 (m, 4H each, *o*-H of Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 79.8 (d, J_{Rh-P} = 163 Hz). IR (KBr): 2546 (B−H), 466 (W=S), 419 (W−S) cm^{-1}. Anal. Calcd for $C_{41}H_{46}N_6BP_2S_3RhW$: C, 48.80; H, 4.53; N, 7.27. Found: C, 48.38; H, 4.49; N, 7.34.

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Table 3. Crystallographic Data for **3**·MeCN, **4**·MeCN, **5**, **7**, **9**, **10**, **11**·MeCN, and **12**

	3·MeCN	**4**·MeCN	**5**	**7**	**9**	**10**	**11**·MeCN	**12**
formula	$C_{43}H_{60}N_8BPS_3WPt$	$C_{43}H_{60}N_8BPS_3PdW$	$C_{18}H_{31}N_6BS_3WPt$	$C_{23}H_{34}N_6BS_3RhW$	$C_{25}H_{37}N_6BF_6PS_3WIr$	$C_{25}H_{37}N_6BS_3RuW$	$C_{28}H_{45}N_8O_3BS_3MoW$	$C_{26}H_{42}N_7O_3BS_3W_2$
fw	1205.90	1117.21	817.41	788.31	1049.63	813.52	928.50	975.35
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$R\bar{3}$ (No. 148)	$Pna2_1$ (No. 33)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	10.940(1)	10.938(2)	13.057(2)	17.508(2)	8.461(2)	11.927(3)	10.756(2)	11.625(3)
b (Å)	17.208(3)	17.197(2)	13.057(2)	10.773(3)	13.966(1)	19.502(4)	11.684(2)	48.571(6)
c (Å)	25.248(1)	25.315(1)	24.950(4)	14.569(2)	29.489(2)	13.047(2)	15.757(4)	12.644(2)
α (deg)	90.00	90.00	90.00	90.00	90.00	90.00	81.06(1)	90.00
β (deg)	97.449(8)	97.181(8)	90.00	90.00	92.27(1)	92.18(1)	77.86(1)	105.03(2)
γ (deg)	90.00	90.00	120.00	90.00	90.00	90.00	78.12(1)	90.00
V (Å^3)	4713.0(10)	4724.5(8)	3683(1)	2747.9(9)	3481.7(8)	3032.6(9)	1881.5(6)	6894(2)
Z	4	4	6	4	4	4	2	8
ρ_{calcd} (g cm^{-3})	1.699	1.571	2.211	1.905	2.002	1.782	1.639	1.879
μ_{calcd} (cm^{-1})	56.01	30.22	106.26	50.40	74.19	45.25	35.97	68.96
cryst size (mm^3)	0.35 × 0.35 × 0.15	0.50 × 0.30 × 0.20	0.25 × 0.20 × 0.15	0.15 × 0.10 × 0.10	0.45 × 0.10 × 0.10	0.15 × 0.15 × 0.15	0.40 × 0.40 × 0.30	0.40 × 0.20 × 0.15
no. data	6106 ($I > 3.00\sigma(I)$)	7479 ($I > 3.00\sigma(I)$)	1504 ($I > 3.00\sigma(I)$)	3701 ($I > 3.00\sigma(I)$)	5185 ($I > 3.00\sigma(I)$)	4631 ($I > 3.00\sigma(I)$)	7069 ($I > 3.00\sigma(I)$)	8277 ($I > 3.00\sigma(I)$)
no. variables	528	524	92	354	452	335	445	758
transm factor	0.49−1.00	0.54−1.00	0.61−1.00	0.77−1.00	0.19−1.00	0.92−1.00	0.73−1.00	0.59−1.00
R^a	0.037	0.038	0.026	0.036	0.043	0.032	0.026	0.042
$R_w{}^b$ or wR2^c	0.037^b	0.043^b	0.026^b	0.098^c	0.044^b	0.033^b	0.028^b	0.043^b
GOF^d	1.30	1.61	1.39	1.00	1.70	1.20	1.59	1.24
residual peaks (e Å^{-3})	1.23,−1.29	2.39, −0.75	0.81, −0.82	1.44, −1.14	2.34, −1.79	0.56, −0.62	0.79, −0.59	1.78, −1.21

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$ ($w = [\{\sigma(F_o)\}^2 + (p^2/4)F_o{}^2]^{-1}$). [c] $wR2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$. [d] $GOF = [\sum w(|F_o| - |F_c|)^2/\{(\text{no. observed}) - (\text{no. variables})\}]^{1/2}$.

[(Me$_2$Tp)W(μ-S)$_3$IrCp*][PF$_6$] (9). A mixture of **1**·MeCN (75 mg, 0.10 mmol) and [Cp*Ir(MeCN)$_3$][PF$_6$]$_2$ (75 mg, 0.10 mmol) in MeCN (5 mL) was stirred overnight at room temperature. The resultant red mixture was dried up and washed successively with ethanol and ether. The residue was extracted with MeCN, and the extract was concentrated to ca. 1 mL. Addition of ether gave **9** as red crystals in 62% yield (65 mg). ^{1}H NMR (CD$_3$CN): δ 2.17 (s, 15H, Cp*), 2.39, 2.55 (s, 9H each, Me in Me$_2$Tp), 6.08 (s, 3H, CH in Me$_2$Tp). IR (KBr): 2575 (B−H), 841 (P−F), 409 (W−S) cm^{-1}. Anal. Calcd for $C_{25}H_{37}N_6BF_6PS_3WIr$: C, 28.61; H, 3.55; N, 8.01. Found: C, 28.46; H, 3.59; N, 7.78.

[(Me$_2$Tp)W(=S)(μ-S)$_2$RuCp*] (10). A mixture of **1**·MeCN (67 mg, 0.090 mmol) and [Cp*Ru(MeCN)$_3$][PF$_6$] (45 mg, 0.089 mmol) in MeCN (5 mL) was stirred overnight at room temperature. A green solid precipitated, which was filtered off and washed with MeCN and then with ether. The residue was crystallized from benzene−hexane. The title compound was obtained as dark green crystals in 26% yield (19 mg). ^{1}H NMR (C$_6$D$_6$): δ 1.78 (s, 15H, Cp*), 2.06, 2.91 (s, 9H each, Me in Me$_2$Tp), 5.55 (s, 3H, CH in Me$_2$Tp). In the spectrum recorded at −80 °C in THF-d_8, broadening of the Me$_2$Tp signals was observed, but these were not resolved. IR (KBr): 2553 (B−H), 465 (W=S), 440 (W−S) cm^{-1}. Anal. Calcd for $C_{25}H_{37}N_6BS_3RuW$: C, 36.91; H, 4.58; N, 10.33. Found: C, 36.78; H, 4.62; N, 10.38.

[Et$_4$N][(Me$_2$Tp)W(μ-S)$_3$Mo(CO)$_3$] (11). A mixture of **1**·MeCN (79 mg, 0.11 mmol) and [Mo(CO)$_3$(MeCN)$_3$] (32 mg, 0.11 mmol) in MeCN (5 mL) was stirred overnight at room temperature. The resultant mixture was filtered, and ether was added to the filtrate, affording red-brown crystals of **11**·MeCN (38 mg, 39%).

As for the mixture of **1**·MeCN (75 mg, 0.10 mmol) with [Mo(CO)$_4$(nbd)] (30 mg, 0.10 mmol) in MeCN (5 mL) after overnight stirring at room temperature, the NMR spectrum showed that all [Mo(CO)$_4$(nbd)] was consumed, whereas ca. 25% of charged **1** remained unreacted in the resultant mixture. Hence, 12 mg (0.040 mmol) of [Mo(CO)$_4$(nbd)] was added, and the mixture was stirred further at room temperature overnight. The analogous workup gave **11**·MeCN in 16% yield (15 mg). ^{1}H NMR (CD$_3$CN): δ 1.20 (t, J_{H-H} = 7.2 Hz, 12H, NCH$_2$CH_3), 1.95 (s, 3H, MeCN), 2.34, 2.58 (s, 9H each, Me in Me$_2$Tp), 3.15 (q, J_{H-H} = 7.2 Hz, 8H, NCH$_2$), 5.91 (s, 3H, CH in Me$_2$Tp). IR (KBr): 2549 (B−H), 1923(s), 1852(m), 1814(s) (C≡O), 405 (W−S) cm^{-1}. Anal. Calcd for $C_{28}H_{45}N_8O_3BS_3MoW$: C, 36.22; H, 4.88; N, 12.07. Found: C, 35.66; H, 4.83; N, 11.92.

[Et$_4$N][(Me$_2$Tp)W(=S)(μ-S)$_2$W(CO)$_3$] (12). This complex was obtained from **1**·MeCN (90 mg, 0.12 mmol) and [W(CO)$_3$(MeCN)$_3$] (49 mg, 0.12 mmol) in 76% yield (90 mg) as dark green crystals by the procedure analogous to that for **1**·MeCN and [Mo(CO)$_3$(MeCN)$_3$]. ^{1}H NMR (CD$_3$CN): δ 1.20 (t, J_{H-H} = 7.2 Hz, 12H, NCH$_2$CH_3), 2.36, 2.47 (s, 9H each, Me in Me$_2$Tp), 3.15 (q, J_{H-H} = 7.2 Hz, 8H, NCH$_2$), 5.91 (s, 3H, CH in Me$_2$Tp). The spectrum recorded at −90 °C in (CD$_3$)$_2$CO showed the broadened but still unresolvable Me$_2$Tp resonances. IR (KBr): 2550 (B−H), 1932(s), 1867(s), 1794(s) (C≡O), 472 (W=S), 405 (W−S) cm^{-1}. Anal. Calcd for $C_{26}H_{42}N_7O_3BS_3W_2$: C, 32.02; H, 4.34; N, 10.05. Found: C, 31.91; H, 4.30; N, 10.01.

X-ray Crystallography. Single crystals of **3**·MeCN, **4**·MeCN, **5**, **7**, **9**, **10**, **11**·MeCN, and **12** were sealed in glass capillaries under argon and mounted on a Rigaku AFC7R diffractometer equipped with a graphite monochromatized Mo Kα source. All diffraction studies were done at room temperature. Intensity data were corrected for Lorentz-polarization effect and for absorption. Decay correction was also applied to **3**·MeCN (linear decay by 16%). Details are listed in Table 3.

Structure solution and refinements were carried out by using the program packages of teXsan[31] for **3**, **4**, **5**, **9**, **10**, **11**, and **12** and CrystalStructure[32] for **7**. The positions of non-hydrogen atoms were determined by Patterson methods (PATTY)[33] and subsequent Fourier synthesis (DIRDIF 94 or 99),[34] which were refined with

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

(32) *CrystalStructure 3.00: Crystal Structure Analysis Package*; Rigaku and Rigaku/MSC, 2000−2002. Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS* Issue 10; Chemical Crystallography Laboratory: Oxford, U.K.

anisotropic thermal parameters by full-matrix least-squares techniques. The BH hydrogens were also located in the Fourier maps but were not refined except for that for **3** which was isotropically refined. All other hydrogen atoms were placed at the calculated positions and included in the final stages of the refinements with fixed parameters. Disordered models were applied for the refinements of the PF_6 anion in **9** and the NEt_4 cation in **11**. The absolute structure of **7** was determined by the refinement of Flack parameter ($\chi = 0.22(1)$).

Because of the poor quality of the crystal, refinements of the structure for **6** were not successful to a satisfactory level, although the atom connecting scheme has been demonstrated unambiguously. Crystal data for **6**: $C_{23}H_{34}N_6BS_3WIr$, $M = 877.62$, $Pna2_1$ (No. 33), $a = 17.520(2)$ Å, $b = 10.745(2)$ Å, $c = 14.549(3)$ Å, $V = 2738.9(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.128$ g cm^{-3}, $\mu_{calcd} = 93.22$ cm^{-1}.

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Supporting Information Available: Tables of crystallgraphic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) PATTY: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykall, C. *The DIRDIF program system*; Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.

(34) DIRDIF94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. *The DIRDIF-94 program system*; Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1994. DIRDIF99: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. *The DIRDIF-99 program system*; Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1999.