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Formation of a Dithiophosphinate Ligand Ph_2PS_2 by Sulfur Insertion into the Metal−Phosphido Bond on Heterobimetallic Phosphido-Bridged Complex $Cp(CO)_2\overline{W(\mu\text{-}PPh_2)Mo}(CO)_5$: A Rare Example of a Neutral Six-Electron Mixed-Metal Cluster with a Mo_2WS_4 Core

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Reflux of a dichloromethane solution of elemental sulfur and phosphido-bridged heterodinuclear complex $Cp(CO)_2\overline{W(\mu\text{-}PPh_2)Mo}(CO)_5$ (**1**) afforded $Cp(S)\overline{W(\mu\text{-}S)_2Mo}(S)(S_2PPh_2)$ (**2**) and a neutral six-electron mixed-metal incomplete cubane-like cluster, $CpW(\mu_3\text{-}S)(\mu\text{-}S)_2Mo_2(\mu\text{-}S)(\mu\text{-}S_2PPh_2)(S_2PPh_2)_2$ (**3**), together with known compounds $Cp(CO)_3W(\mu\text{-}PPh_2)Mo(CO)_5$ and $(CpW(S)(\mu\text{-}S))_2$. The electron-deficient 28*e* heterodinuclear complex **2** is stabilized via $S(p_\pi) \rightarrow Mo(d)$ ligand-to-metal dative π-bonding interactions. Room-temperature stirring of a THF solution of **2** and DMAD (dimethyl acetylenedicarboxalate) yielded compounds $Cp(S_2C_2(COOMe_2))_2\overline{W(\mu\text{-}S)_2Mo}(O)(S_2PPh_2)$ (**4**) and $Cp(S_2C_2(COOMe_2)_2)\overline{W(\mu\text{-}S)_2W}(O)Cp$ (**5**). Compounds **2**−**5** were characterized by single-crystal X-ray diffraction analysis. Molecular structures of **2** and **3** reveal sulfur insertion into the metal−phosphido bond on **1**, resulting in a dithiophosphinate ligand Ph_2PS_2. Formation of the C−S bonds in **4** and **5** has resulted through the reaction of sulfide ligands on **2** and DMAD.

Introduction

Multimetallic sulfide clusters have attracted much attention in relevance to the active sites of metalloenzymes,[1] industrial hydrotreating catalysis,[2] and superconductive materials.[3] In particular, trinuclear triangular molybdenum clusters with the incomplete cubane-like cluster core Mo_3S_4 have attracted many chemists because these are used as the starting materials to form cubane-like cluster analogues of $Fe_4S_4(SR)_2^{2-4}$ and to form Mo_6S_8 clusters.[3] Although the homonuclear and heteronuclear incomplete cubane-like cluster cores Mo_3S_4,[5,6] W_3S_4,[7] MoW_2S_4,[8] and Mo_2MS_4 (M = W, Pd, Rh),[8] respectively, are known, the heteronuclear incomplete cubane-like ionic cluster cores with six cluster electrons such as Mo_2WS_4 or MoW_2S_4 are still limited [8a,b] and that of a neutral one is still unknown.

We have reported that the phosphido-bridged heterodinuclear complex $Cp(CO)_2\overline{W(\mu\text{-}PPh_2)Mo}(CO)_5$ (**1**), which has a reactive metal−metal bond and labile carbonyl ligands for further reaction,[9] is a suitable precursor for oxidative addition of both organic disulfides RSSR (R = alkyl or aryl group)[10] and inorganic disulfide $(Fe_2(\mu\text{-}S_2)(CO)_6)$[11] via the S−S bond cleavage. Formation of a hybrid ligand Ph_2PSR by interaction between phosphido-bridged PPh_2 on **1** and SR during RSSR activation and the $S(p_\pi) \rightarrow Mo(d)$ ligand-to-metal dative π-bonding interactions in the complexes where SR is a terminal ligand have also been reported.[10]

Elemental sulfur containing S−S bonding is reducing in nature. It acts as a source of the sulfide ligands. Among the

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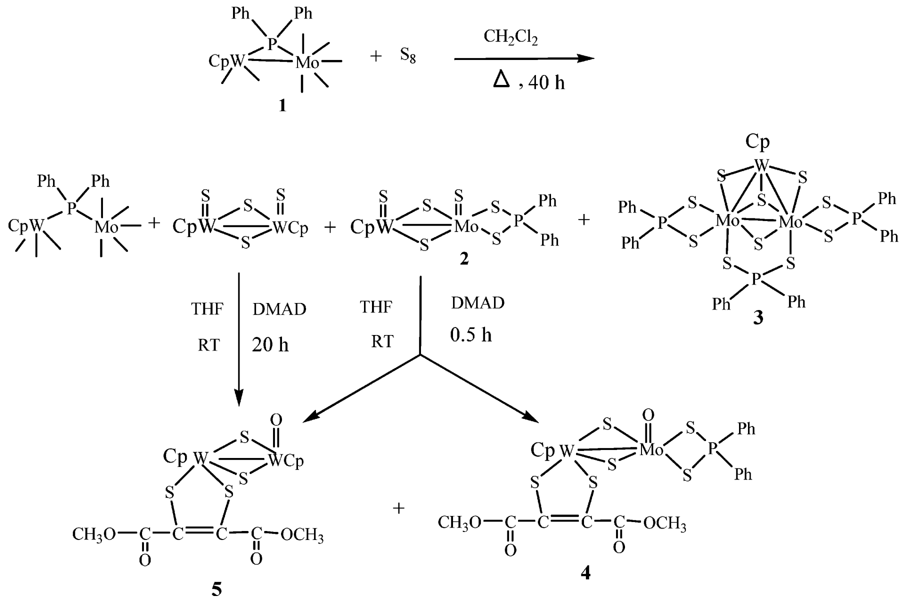
Scheme 1



several means for the synthesis of sulfido complexes, oxidative addition of elemental sulfur to a coordinatively unsaturated electron-rich metal is a convenient one.[12] Activation of the S−S bond in S_8 through its interaction with the phosphido bridge PPh_2 in **1** is promising to have different ligand combinations in a cluster with high nuclearity. It can also determine the ligating diversity through the π-donor ability of S when it is not bonded with organic moieties. Herein, we report the synthesis and single-crystal X-ray structures of a heterodinuclear electron-deficient 28*e* complex, $Cp(S)W(\mu\text{-}S)_2Mo(S)(S_2PPh_2)$ (**2**), and a neutral mixed-metal trinuclear triangular incomplete cubane-like cluster, $CpW(\mu_3\text{-}S)(\mu\text{-}S)_2Mo_2(\mu\text{-}S)(\mu\text{-}S_2PPh_2)(S_2PPh_2)_2$ (**3**), with a 6*e* Mo_2WS_4 core. The formation of the C−S bonds in $Cp(S_2C_2(COOMe_2)_2)W(\mu\text{-}S)_2Mo(O)(S_2PPh_2)$ (**4**) and $Cp(S_2C_2(COOMe_2)_2)W(\mu\text{-}S)_2W(O)Cp$ (**5**) when **2** is reacted with DMAD (dimethyl acetylenedicarboxalate) in THF solution is also reported.

Results and Discussion

Reaction of 1 with S_8. Reaction of **1** with 3 equiv of S_8 in refluxing dichloromethane gave compounds **2** and **3** and known compounds $Cp(CO)_3W(\mu\text{-}PPh_2)Mo(CO)_5$ and $(CpW(S)(\mu\text{-}S))_2$ reported earlier[9,13] (Scheme 1). Typical reaction of **1** with 1.5 equiv of S_8 produced compounds with comparatively low yields similar to those of the reaction products using 3 equiv of S_8. In addition, there was a new band in trace amounts which could not be characterized. Both **2** and **3** are air-stable, orange solids. Compound **2** is a thio-Mo−W mixed-metal complex with a Ph_2PS_2 ligand, as shown by its molecular structure (Figure 1).

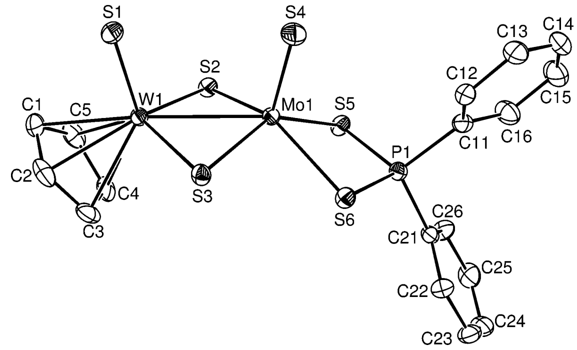


Figure 1. ORTEP drawing of **2**, with 30% thermal ellipsoids. Hydrogen atoms are omitted.

Molybdenum and tungsten complexes with oxo and/or thio ligands have been widely used as model compounds to mimic metalloenzymes whose active sites feature the said metals and ligands such as xanthine oxidase (LMoOS-possessing enzymes), sulfite oxidase ($LMoO_2$-possessing enzymes), and DMSO reductase (L_2MoX-possessing enzymes).[14] Moreover, when dithiophosphinate R_2PS_2 is a co-ligand in these complexes, its ambidentate nature facilitates reactions such as conversion of Me_2SO to Me_2S.[15] It is also realized that the generated $[MoOS]^{2+}$ center in the oxo-thio-M complex is stabilized via a weak S⋯S interaction[15] between the S of Mo═S and the noncoordinated S of the R_2PS_2 ligand. Thus, the oxo and/or thio compounds of molybdenum and tungsten with R_2PS_2 as a co-ligand are particularly relevant to mimic biological reactions.[15,16]

In compound **2**, sulfur is coordinated to Mo and W as a terminal as well as a bridging atom. Coordination of the ambidentate Ph_2PS_2 in **2** indicates sulfur insertion into the

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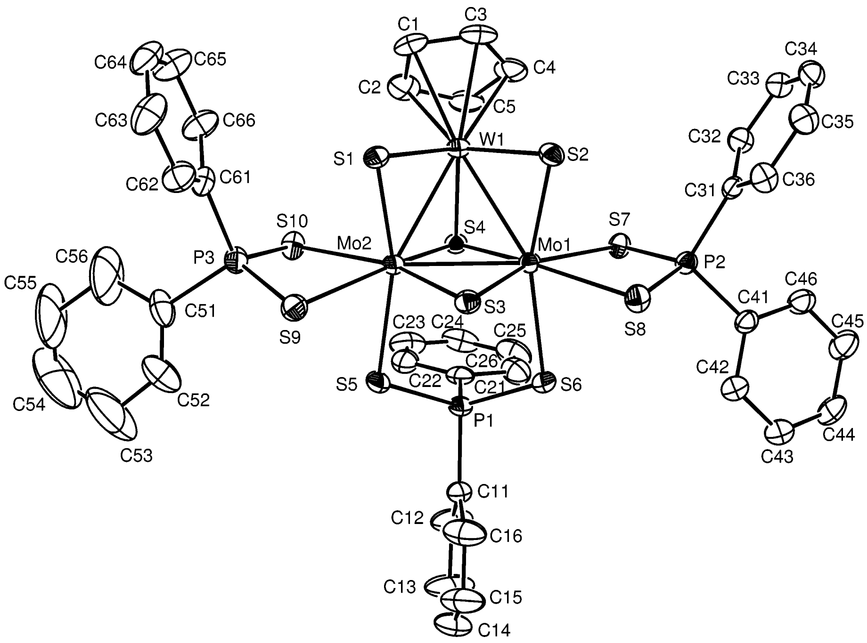

Figure 2. ORTEP drawing of **3**, with 30% thermal ellipsoids. Hydrogen atoms are omitted.

phosphido-bridging PPh_2 ligand in **1**. The usual sources of Ph_2PS_2 ligand are the dithiophosphinic acid and its salts or disulfanes $R_2P(S)S_2(S)PR_2$.[17] The participation of bridging phosphido groups, with the insertion of small molecules into the M−P bonds, causes its transformation into unique bridging ligands such as μ-$R_2P{=}X$ (X = O^{18}, S^{18}, CH_2,[19] or CRR^{20}) and alkenyl- and butadienylphosphines[21] and -diphosphines.[22] The coupling of bridging phosphido ligands with CO and alkynes has also been reported.[23] Although insertion of sulfur into one of the Rh−P bonds of the Rh(μ-PPh_2)Rh system and formation of a bridging Rh(μ-$Ph_2P{=}S$)Rh is known,[18] insertion of sulfur into both the Mo−P and W−P bonds of the Mo(μ-PPh_2)W in **1** and formation of a dithiophosphinate Ph_2PS_2 on Mo in **2** is reported for the first time.

Table 1. List of a Few $M_2M'S_4$ Clusters with Six and Seven 3d Electrons

cluster	oxidation state	no. of 3d electrons	X-ray structure	ref
$[MoW_2(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]$-$(Pts)_4)\cdot 9H_2O$[a]	4 ($3d^2$)	6	yes	8a
$[Mo_2W(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]$ $(Pts)_4)\cdot 9H_2O$	4 ($3d^2$)	6	yes	8a
$Na_2[MoW_2(\mu_3\text{-}S)(\mu\text{-}S)_3(Hnta)_3]\cdot 5H_2O$[b]	4 ($3d^2$)	6	yes	8b
$Na_2[Mo_2W(\mu_3\text{-}S)(\mu\text{-}S)_3(Hnta)_3]$ $\cdot 5H_2O$	4 ($3d^2$)	6	yes	8b
$CpMo_2W(\mu_3\text{-}S)(\mu\text{-}S)_3(S_2PPh_2)_3$	4 ($3d^2$)	6	yes	this work
$Cp^*{}_3Mo_2W(\mu_3\text{-}S)(\mu\text{-}S)_3$	3 ($3d^3$), 4 ($3d^2$)	7	no	40
$Cp^*{}_3Mo_2Cr(\mu_3\text{-}S)(\mu\text{-}S)_3$	3 ($3d^3$), 4 ($3d^2$)	7	no	40

[a] Pts = *para*-toluenesulfonic acid. [b] Hnta = nitrilotriacetic.

The molecular structure of **3** (Figure 2) reveals a heterobimetallic trinuclear cluster containing the central Mo_2WS_4 unit that forms a trigonal pyramid with a Mo−Mo−W triangle capped by the μ_3-S atom, and the rest of the three sulfur atoms bridged each edge of the triangle. Moreover, each of the Mo sites is chelated by one Ph_2PS_2 ligand, and these Mo sites are also linked to each other by a third bridging Ph_2PS_2 ligand. Hence in **3**, sulfur shows four different bonding modes as μ-S, μ_3-S, η^2-S_2PPh_2, and μ-S_2PPh_2. It becomes a member of the class of classic clusters with a M_3S_4 core. These clusters are also classified on the basis of the total number of 3d electrons of the metals that they have (Table 1). In the case of a seven-electron Mo_3S_4-core cluster, the oxidation of the metal can be Mo^{III} and Mo^{IV}, while for a six-electron core it is Mo^{IV}. Compound **3** is a six-electron cluster since both the molybdenum and tungsten have +4 oxidation states. There are a few reports on six-electron and seven-electron clusters having a $M_2M'S_4$ central unit, which have been synthesized as ionic or neutral complexes (Table 1). A few mixed-metal complexes with MoW_2S_4 and Mo_2WS_4 cores have been reported that are also six-electron ionic complexes (Table 1). Compound **3** reported here is a neutral six-electron cluster heterobimetallic complex. To our knowledge, there are no other mixed-metal clusters with MoW_2S_4 or Mo_2WS_4 cores that are reported to be neutral (Table 1).

Reaction of 2 with DMAD. Room-temperature stirring of a THF solution of **2** and DMAD produced compounds **4** and **5** along with a few uncharacterized trace compounds. Compound **5** was also synthesized by the reaction of DMAD and the known compound $(CpW(S)(\mu\text{-}S))_2$ (Scheme 1). The molecular struc-

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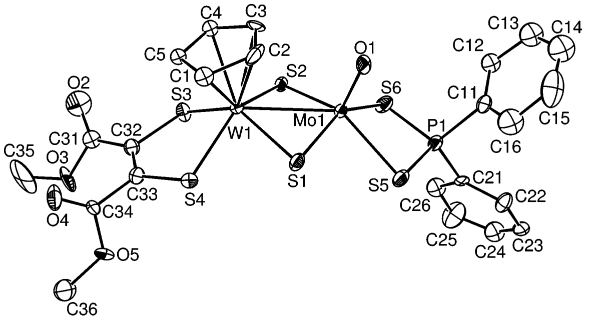

Figure 3. ORTEP drawing of **4**, with 30% thermal ellipsoids. Hydrogen atoms are omitted.

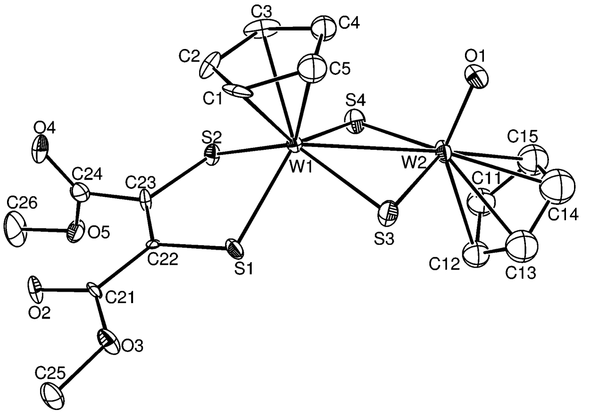

Figure 4. ORTEP drawing of **5**, with 30% thermal ellipsoids. Hydrogen atoms are omitted.

tures of **4** and **5** (Figures 3 and 4) reveal the formation of dithiolene ligands in these complexes. The thio ligand of **2** involved in the C−S bond formation with DMAD has resulted in the dithiolene linkages. There are two types of reactions of alkynes with S-ligand complexes. In one way they coordinate directly to the metal and produce either π-coordinated[24] or σ-cooridinated[25] complexes, which is classical type. In other way they react with sulfide, disulfide, or polysulfide ligands to form a 1,2-dithiolene ligand.[26] The latter one is interesting for the case of Mo and W complexes to mimic Mo−(W)-containing oxotransferase enzymes, which is featured by coordination of pterine-1,2-enedithiolate.[27] The activated alkynes such as $CH_3OC(O)CC(O)COCH_3$ and CF_3CCCF_3 are more reactive than nonactivated alkynes such as PhCCH and PhCCPh to form dithiolene ligands with S-ligand complexes.[28] On the other hand, reaction of alkynes with polysufides is occasionally observed,[28] and that with the bridging monothio ligands is rare[29] and even more rare with terminal thio ones.[30] Thus, the reaction of the terminal thio ligand of **2** with $CH_3OC(O)CC(O)COCH_3$ and formation of **4** and **5** is noteworthy. In both **4** and **5**, the Mo and W retained their same oxidation states as in the parent compound **2** by coordination of the oxo ligand on the Mo and W site.

NMR Spectra of 2−5. The ^{1}H NMR peaks at 6.43, 5.81, 5.50, and 6.12 ppm of the cyclopentadienyl group (Cp) for **2**−**5**, respectively, are shifted downfield compared to that of **1** (5.17 ppm) since the oxidation states of tungsten and molybdenum in **2**−**5** are increased compared to that of parent compound **1**. The ^{31}P{^{1}H} NMR spectrum of **3** exhibits two resonances at 92.09 and 68.83 ppm in the intensity ratio 2:1, respectively. This indicates that, out of the three phosphorus atoms, two are equivalent, and this corresponds to the downfield peak at 92.09 ppm. The upfield peak at 68.83 ppm corresponds to the third phosphorus atom. This is in agreement with the molecular structure of **3**, where the two terminal PPh_2S_2 ligands are equivalent and the third is in bridging mode. The signals for the phenyl proton of the PPh_2S_2 ligand in **2**−**4** and methyl protons of DMAD in **4** and **5** appear at normal positions.

X-ray Structure of 2−5. Compounds **2**−**5** were characterized by single-crystal X-ray diffraction analysis. Molecular structures of these compounds are shown in Figures 1−4, respectively. The experimental data are summarized in Table 2. Selected bond lengths and bond angles are listed in Tables 3 and 4, respectively. The Mo1−W1 bond distance in **2** is 2.8521(10) Å with average Mo−S−W acute angles of 76.31°. The Mo−W bond is a single bond and compares well with the reported Mo−W bond length of 34*e* dimers, such as Cp(CO)W(μ-SPh)$_2$(μ-PPh$_2$)Mo(CO)$_3$ (2.8427(14) Å) and Cp(CO)W(μ-SPh)$_2$(μ-PPh$_2$)Mo(CO)$_2$(PPh$_3$) (2.8382(13) Å).[10] This is quite unusual, as the heterobimetallic **2** is a 28*e* system (making it electron deficient according to the 18*e* rule). The average bond distances Mo1−S$_{br}$ (2.3233 Å), W1−S$_{br}$ (2.2929 Å), and W1═S$_{ter}$ (2.1505 Å) are within the range of reported bond distance values in the molybdenum and tungsten dimers tabulated in ref 31 (2.29−2.357 Å), ref 32 (2.29−2.39 Å), and ref 33 (2.09−2.144 Å), respectively. The bond length of Mo═S$_{ter}$ in molybdenum dimers has been reported as 2.10−2.12 Å.[33] In compound **2**, the Mo═S$_{ter}$ bond length is 2.0859(18) Å, which is even less than that in molybdenum dimers.[33] This suggests that the formal bond order between molybdenum and sulfur is greater than 2. The strong S(p$_\pi$)→Mo(d) ligand-to-metal dative π-bonding interaction involves the stabilization of the electron deficiency in **2**.[33] Furthermore, the average Mo1−S bond distance (2.489 Å) of the terminal Ph_2PS_2 in **2** is shorter than the reported average Mo−S bond distances for dimers such as [Mo(NC$_6$H$_4$CH$_3$)(S$_2$P(OC$_2$H$_5$)]$_2$(μ-S)(μ-SH)(μ-O$_2$CCF$_3$) (2.5242 Å),[34] [Mo(NC$_6$H$_4$CH$_3$)(S$_2$P(OC$_2$H$_5$)]$_2$(μ-S)(μ-SCH$_3$)(μ-O$_2$CCF$_3$) (2.5212

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Table 2. Summary of Crystal Data for 2−5

	2	**3**	**4**	**5**
formula	$C_{20}H_{18}PS_6MoW$	$C_{41}H_{35}S_{10}P_3Mo_2W$	$C_{23}H_{21}O_5S_6PMoW$	$C_{16}H_{16}O_5S_4W_2$
fw	761.46	1316.93	880.52	784.23
space group	$P\bar{1}$	$P\bar{1}$	$C2$	$Pcab$
a [Å]	6.1840(15)	11.4373(2)	28.204(6)	6.7919(14)
b [Å]	11.014(4)	11.4761(2)	6.7865(14)	23.052(5)
c [Å]	18.399(2)	20.4699(4)	18.204(4)	25.445(5)
α [deg]	73.172(19)	81.8180(10)		
β [deg]	81.516(17)	82.9540(10)	120.183(3)	
γ [deg]	87.50(3)	75.1590(10)		
V [Å^3]	1186.4(5)	2560.27(8)	3012.0(11)	3983(14)
ρ(calcd) [Mg m^{-3}]	2.132	1.708	1.942	2.615
Z	2	2	4	8
cryst dimens [mm]	0.23 × 0.20 × 0.11	0.08 × 0.06 × 0.02	0.27 × 0.25 × 0.20	0.25 × 0.20 × 0.18
temp [K]	298(2)	298(2)	298(2)	298(2)
λ(Mo Ka) [Å]	0.71073	0.71073	0.71073	0.71073
2θ range [deg]	50.0	50.0	50.0	50.0
scan type	ω	ω	ω	ω
no. of reflns	4206	41 385	3013	3479
no. of obsd reflns	4206 ($>2.0\sigma(I)$)	8948 ($>2.0\sigma(I)$)	2918 ($>2.0\sigma(I)$)	3479 ($>2.0\sigma(I)$)
no. of params refined	262	514	284	209
R	0.0275	0.0356	0.0558	0.0503
R_w	0.0577	0.1035	0.1320	0.0976
GoF	1.014	1.102	1.010	1.020
D_{map} min., max. [e/Å^3]	−0.951, 0.752	−2.414, 1.846	−2.166, 2.066	−3.106, 2.621

Table 3. Selected Bond Lengths (Å) for 2−5

		2	
W1−Mo1	2.8521(10)	Mo1−S2	2.3291(18)
W1−S1	2.1505(17)	Mo1−S3	2.3176(16)
W1−S2	2.2925(16)	Mo1−S4	2.0859(18)
W1−S3	2.2933(18)	Mo1−S5	2.4825(17)
W1−C1	2.381(6)	Mo1−S6	2.4955(19)
W1−C2	2.369(7)	P1−S5	2.026(2)
W1−C3	2.404(6)	P1−S6	2.018(2)
W1−C4	2.396(6)	P1−C11	1.824(6)
W1−C5	2.378(6)	P1−C21	1.807(6)
		3	
W1−Mo1	2.7757(7)	Mo1−S3	2.296(2)
W1−Mo2	2.7716(8)	Mo1−S4	2.351(2)
W1−S1	2.267(2)	Mo2−S1	2.337(2)
W1−S2	2.263(2)	Mo2−S3	2.299(2)
W1−S4	2.327(2)	Mo2−S4	2.347(2)
W1−C1	2.384(9)	Mo1−S6	2.576(2)
W1−C2	2.386(9)	Mo1−S7	2.606(2)
W1−C3	2.362(9)	Mo1−S8	2.578(2)
W1−C4	2.341(9)	Mo2−S5	2.566(2)
W1−C5	2.349(9)	Mo2−S9	2.587(2)
Mo1−Mo2	2.7403(10)	Mo2−S10	2.589(2)
Mo1−S2	2.332(2)		
		4	
W1−Mo1	2.893(2)	Mo1−S1	2.296(8)
W1−S1	2.371(7)	Mo1−S2	2.303(8)
W1−S2	2.355(7)	Mo1−S5	2.491(8)
W1−S3	2.397(8)	Mo1−S6	2.495(9)
W1−S4	2.434(7)	P1−S5	2.031(12)
W1−C1	2.34(3)	P1−S6	1.992(12)
W1−C2	2.41(3)	P1−C11	1.85(3)
W1−C3	2.41(3)	P1−C21	1.87(3)
W1−C4	2.27(2)	C32−S3	1.82(3)
W1−C5	2.28(3)	C33−S4	1.72(3)
Mo1−O1	1.684(19)		
		5	
W1−W2	2.9323(11)	W2−O1	1.688(13)
W1−S1	2.378(5)	W2−S3	2.280(5)
W1−S2	2.421(5)	W2−S4	2.282(5)
W1−S3	2.402(5)	W2−C11	2.40(3)
W1−S4	2.377(5)	W2−C12	2.42(2)
W1−C1	2.374(19)	W2−C13	2.38(3)
W1−C2	2.30(2)	W2−C14	2.35(3)
W1−C3	2.286(19)	W2−C15	2.38(3)
W1−C4	2.37(2)	S1−C22	1.755(19)
W1−C5	2.37(2)	S2−C23	1.721(18)

Å),[35] and $[Mo_2(NTo)_2(S_2P(OC_2H_5)_2)_2S(O_2CMe)(SSC_2H_5)]$ (2.534 Å).[36] This indicates delocalization of the Ph_2PS_2 π-electron density into the vacant metal dπ orbitals, leading to stabilization of electron-deficient **2**.

The trinuclear cluster **3** has 42 electrons assuming that the μ_3-S sulfur serves as a four-electron donor. It is electron-deficient because a trinuclear cluster is expected to have an electron count of 48. Formally, one can consider the metal−metal bond order is 2 according to the 18-electron rule. However, the number of metal d electrons is 6. The metal−metal bond order should be 1. Therefore, it is expected that the π electrons of the μ_2-bridging sulfido ligands participate in the bonding of the WMo_2S_4 core. In other words, π-bonding must exist between the three metal atoms and the three μ_2-bridging sulfido ligands, making the Mo−W and Mo−Mo bond distances shorter than expected. The Mo1−W1, Mo2−W1, and Mo1−Mo2 bond distances are 2.7757(7), 2.7716(8), and 2.7403(10) Å, respectively, and these are longer than the reported Mo═W (2.702−2.718 Å)[37] and Mo═Mo (2.705(2) Å)[32] bond distances. However, they are shorter than the Mo1−W1 single bond distance in **2** (2.8521(10) Å). This indicates the bond order between the metals in cluster **3** is between 1 and 2 and is smaller than expected. The average Mo−S_{br} (2.3270 Å) and W−S_{br} (2.2857 Å) bond distances match well with the reported values.[31,32] The average Mo−S bond distance (2.590 Å) of the terminal Ph_2PS_2 is normal.[34−36]

Compound **4** is a 28*e* dimer like **2**. The Mo1−W1 bond distance (2.893(2) Å) is a little longer than in **2** but quite similar to the doubly bridged molybdenum and tungsten dimers.[10] It is also quite unusual like **2** (according to the 18*e* rule). The shortening of the Mo1−S (2.493 Å (av)) bond distance of the terminal S_2PPh_2 ligand from the reported molybdenum dimers with S_2PR_2[34−36] and also from that of **3** again suggest that

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Table 4. Selected Bond Angles (deg) for 2−5

	2		
W1−S2−Mo1	76.21(5)	S2−Mo1−W1	51.32(4)
W1−S3−Mo1	76.42(5)	S3−Mo1−S4	107.26(7)
S1−W1−S2	106.54(6)	S3−Mo1−S5	142.25(6)
S1−W1−S3	105.08(7)	S3−Mo1−S6	80.56(6)
S1−W1−Mo1	102.26(5)	S3−Mo1−W1	51.41(4)
S2−W1−S3	102.14(6)	S4−Mo1−S5	108.48(7)
S2−W1−Mo1	52.48(4)	S4−Mo1−S6	104.92(7)
S3−W1−Mo1	52.17(4)	S4−Mo1−W1	103.84(6)
S2−Mo1−S3	100.30(6)	S5−Mo1−S6	78.94(6)
S2−Mo1−S4	106.36(7)	S5−Mo1−W1	128.21(5)
S2−Mo1−S5	80.95(6)	S6−Mo1−W1	129.44(4)
S2−Mo1−S6	146.83(6)	S6−P1−S5	102.98(9)
	3		
W1−S1−Mo2	74.01(7)	S4−Mo1−S7	86.39(7)
W1−S2−Mo1	74.31(7)	S4−Mo1−S8	161.84(8)
W1−S4−Mo2	72.74(6)	S4−Mo1−W1	53.21(5)
W1−S4−Mo1	72.79(6)	S4−Mo1−Mo2	54.25(5)
Mo1−S3−Mo2	73.22(7)	S6−Mo1−S7	80.92(8)
Mo1−S4−Mo2	71.38(6)	S6−Mo1−S8	78.05(8)
S1−W1−S2	100.23(8)	S7−Mo1−S8	77.79(7)
S1−W1−S4	106.44(8)	W1−Mo1−Mo2	60.32(2)
S1−W1−Mo1	99.13(6)	S1−Mo2−S3	95.47(8)
S1−W1−Mo2	54.16(6)	S1−Mo2−S4	103.55(8)
S2−W1−S4	105.65(8)	S1−Mo2−S5	164.19(8)
S2−W1−Mo1	53.97(6)	S1−Mo2−S9	88.70(8)
S2−W1−Mo2	100.58(6)	S1−Mo2−S10	87.64(8)
S4−W1−Mo1	53.99(5)	S1−Mo2−Mo1	98.38(6)
S4−W1−Mo2	53.96(5)	S1−Mo2−W1	51.83(6)
Mo1−W1−Mo2	59.21(2)	S3−Mo2−S4	106.94(8)
S2−Mo1−S3	97.81(8)	S3−Mo2−S5	91.03(8)
S2−Mo1−S4	102.74(8)	S3−Mo2−S9	87.46(6)
S2−Mo1−S6	162.48(8)	S3−Mo2−S10	87.47 (8)
S2−Mo1−S7	88.79(8)	S3−Mo2−W1	97.41(6)
S2−Mo1−S8	85.96(8)	S3−Mo2−Mo1	53.33(6)
S2−Mo1−W1	51.72(6)	S4−Mo2−S5	88.23(8)
S2−Mo1−Mo2	99.73(6)	S4−Mo2−S9	86.73(8)
S3−Mo1−S4	106.94(8)	S4−Mo2−S10	160.50(8)
S3−Mo1−S6	88.64(8)	S4−Mo2−W1	53.30(5)
S3−Mo1−S7	163.25(8)	S4−Mo2−Mo1	54.38(5)
S3−Mo1−S8	87.30(8)	S5−Mo2−S9	81.38(8)
S3−Mo1−W1	97.38(6)	S5−Mo2−S10	78.24(8)
S3−MoI−Mo2	53.45(6)	S9−Mo2−S10	77.49(8)
S4−Mo1−S6	90.80(8)	W1−Mo2−Mo1	60.471(2)
	4		
W1−S1−Mo1	76.6(3)	O1−Mo1−S5	105.7(7)
W1−S2−Mo1	76.8(3)	O1−Mo1−S6	104.3(7)
S1−W1−S2	97.3(3)	O1−Mo1−W1	103.1(6)
S1−W1−S3	134.8(3)	S1−Mo1−S2	101.0(3)
S1−W1−S4	75.9(3)	S1−Mo1−S5	81.3(3)
S1−W1−Mo1	50.53(19)	S1−Mo1−S6	146.3(3)
S2−W1−S3	74.8(3)	S1−Mo1−W1	52.85(18)
S2−W1−S4	136.1(3)	S2−Mo1−S5	140.5(3)
S2−W1−Mo1	50.79(18)	S2−Mo1−S6	79.9(3)
S3−W1−S4	80.1(3)	S2−Mo1−W1	52.41(18)
S3−W1−Mo1	121.1(2)	S5−Mo1−S6	77.7(3)
S4−W1−Mo1	122.33(19)	S5−Mo1−W1	131.2(2)
O1−Mo1−S1	106.6(8)	S6−Mo1−W1	131.0(2)
O1−Mo1−S2	111.1(7)	S5−P1−S6	102.0(4)
	5		
W1−S3−W2	77.49(15)	S3−W1−S4	95.96(18)
W1−S4−W2	77.98(15)	S3−W1−W2	49.40(13)
S1−W1−S2	79.85(18)	S4−W1−W2	49.57(14)
S1−W1−S3	76.31(18)	O1−W2−S3	107.3(5)
S1−W1−S4	130.8(2)	O1−W2−S4	106.6(5)
S1−W1−W2	118.63(12)	O1−W2−W1	102.1(4)
S2−W1−S3	139.9(2)	S3−W2−S4	102.19(18)
S2−W1−S4	76.06(18)	S3−W2−W1	53.11(14)
S2−W1−W2	122.06(12)	S4−W2W1	52.45(13)

delocalization of S_2PPh_2 π-electron density into vacant metal dπ orbitals occurred in order to stabilize electron-deficient **4**. The average Mo1−S_{br} (2.2995 Å) and W1−S_{br} (2.363 Å) bond distances are within the ranges tabulated in refs 31 and 32. The W1−S (2.4155 Å (av)) of dithiolene and Mo═O1 (1.684(19) Å) bond distances are normal.[33,38]

Compound **5** contains 30 valence electrons, which is 6 electrons less to satisfy the 18*e* rule. Thus, it is an electronically poor compound, and the expected formal W−W bond order between tungsten atoms is 3. The disulfide-bridged W1−W2 bond distance is 2.9323(11) Å, which is comparable to the reported doubly bridged single-bonded tungsten dimers.[13] This deficiency of electrons in **5** may be compensated by the π electrons of oxo and thio donors around it. Although, the average distance W1−S_{br} (2.3895 Å) is within the range of the reported values listed in ref 32, the average W2−S_{br} (2.281 Å) distance is less than that of the reported values,[32] indicating that strong S(p_π)→Mo(d) ligand-to-metal dative π-bonding interactions between bridged sulfur and tungsten may exist. The average W1−S (2.3995 Å) of dithiolene and W2═O1 (1.688 Å) bond distances are normal.[38]

Conclusion

Generation of the ligands S^{2-} and Ph_2PS_2 and their participation in the formation of the electron-deficient 28*e* dimer **2** and the neutral Mo_2WS_4 core cluster **3** in a single flask during the reaction of elemental sulfur and **1** is really a unique observation. Thus conversion of **1** into **2** and **3**, in which sulfur is the key element in both the ambidentate ligand Ph_2PS_2 and the thio ligand S^{2-}, illustrated the formation of Mo═S, W═S, Mo−S−W, and Mo−S−P bonds in the same reaction. Formation of the thiophosphinate ligand PPh_2S_2 ligand by sulfur insertion into the M−P bond of the phosphido-bridged PPh_2 ligand on **1** is reported for the first time. The 28*e* dimer **2**, where both metals have a $3d^1$ configuration shortage of 3d electrons for further bonding between them other than a single bond, is stabilized via S(p_π)→Mo(d) ligand-to-metal dative π-bonding interactions, keeping almost a single Mo−W bond order.[10] Participation of π electrons of the μ_2-bridging sulfido ligands in the electron-deficient WMo_2S_4 core of **3** makes the metal−metal bond order higher than 1, and thus Mo−W and Mo−Mo bond distances shorter than expected are observed. The involvement of the terminal thio ligand of **2** in the C−S bond formation to form **4** and **5** is also a rare occurrence.

Experimental Section

General Procedures. All reactions and other manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques unless otherwise stated. Commercially available chemicals were purchased and used without further purification. All solvents were dried with Na and benzophenone under N_2 and distilled immediately prior to use. Compound **1** was prepared following the reported procedure.[9] The ^{1}H and ^{31}P NMR spectra were run using a Bruker Ac-300 spectrometer. The ^{31}P shifts are referenced to 85% H_3PO_4. Microanalyses were performed by use of a Perkin-Elmer 2400 CHN analyzer

Reaction of 1 with Sulfur (S_8). To a solid mixture of **1** (500 mg, 0.68 mmol) and 3 equiv of sulfur (500 mg, 1.95 mmol) was added dichloromethane (50 mL) and the mixture heated at reflux for 40 h. The reaction mixture was filtered through Celite to remove insoluble materials and evaporated to dryness. The residue was then dissolved in dichloromethane (10 mL), and the solution was subjected to silica gel chromatographic workup. Elution with CH_2Cl_2/hexane (1:1) afforded three fractions. Compounds $Cp(CO)_3W(\mu\text{-}PPh_2)Mo(CO)_5$ and $(CpWS(\mu\text{-}S))_2$ were separated as the first,

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yellow and the second, dirty-green band, respectively. Compound **2** was obtained from the third, orange-red band. Elution with neat dichloromethane afforded compound **3** as the fourth, brown band. $Cp(CO)_3W(\mu\text{-}PPh_2)Mo(CO)_5$: Yield: 109 mg, 23%. $(CpWS(\mu\text{-}S))_2$: Yield: 33 mg, 15%. **2**: Yield: 105 mg, 21%. Anal. Calcd for $C_{17}H_{15}PS_6MoW$: C, 28.25; H, 2.08. Found: C, 28.48; H, 2.09. ^1H NMR (CD_3COCD_3): δ 7.85−7.52 (m, 10H, C_6H_5), 6.43 (s, 5H, C_5H_5). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 110.68 (s). **3**: Yield: 60 mg, 13%. Anal. Calcd for $C_{41}H_{35}P_3S_{10}Mo_2W$: C, 37.36; H, 2.66. Found: C, 37.51; H, 2.73. ^1H NMR ($CDCl_3$): δ 7.99−7.81 (m, 10H, C_6H_5), 7.58−7.31 (m, 20H, C_6H_5), 5.81 (s, 5H, C_5H_5). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 92.09 (s, 2P, $\eta\text{-}S_2PPh_2$), 68.83 (s, 1P, $\mu\text{-}S_2\text{-}PPh_2$). When 1.5 equiv of S_8 (256 mg, 1 mmol) was used in this reaction, compounds $Cp(CO)_3W(\mu\text{-}PPh_2)Mo(CO)_5$, $(CpWS(\mu\text{-}S))_2$, **2**, and **3** were isolated in 10% (51 mg), 9% (22 mg), 14% (72 mg), and 9% (42 mg) yield, respectively. An additional small orange band was eluted as the fifth band, and the residue was not characterized.

Reaction of 2 with DMAD. To a THF solution (50 mL) of **2** (100 mg, 0.14 mmol) was added DMAD (29 μL, 34 mg, 0.28 mmol), and the mixture was stirred for 0.5 h in air. The reaction mixture was evaporated to dryness. The residue was then dissolved in dichloromethane (10 mL), and the solution was subjected to preparative TLC workup. Two bands were collected after elution with dichloromethane. The first, orange-red band contained compound **4**. The second, orange-red band was compound **5**. **4**: Yield: 22 mg, 18%. Anal. Calcd for $C_{23}H_{21}O_5PS_6MoW$: C, 31.36; H, 2.38. Found: C, 31.69; H, 2.53. ^1H NMR ($CDCl_3$): δ 7.71−7.39 (m, 10H, C_6H_5), 5.50 (s, 5H, C_5H_5), 3.89 (s, 6H, CH_3). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 105.83 (s). **5**: Yield: 8 mg, 14%. Anal. Calcd for $C_{16}H_{16}O_5P_2S_4W_2$: C, 24.49; H, 2.04. Found: C, 24.58; H, 2.06. ^1H NMR ($CDCl_3$): δ 6.12 (s, 10H, C_5H_5), 3.85 (s, 6H, CH_3). Typical reaction with the same molar ratio of **2** (100 mg, 0.14 mmol) and DAMD (29 μL, 34 mg, 0.28 mmol) under nitrogen produced compounds **4** and **5** in 21% (26 mg) and 9% (5 mg) yields, respectively.

Reaction of $(CpWS(\mu\text{-}S))_2$ with DMAD. To a dichloromethane solution (50 mL) of $(CpWS(\mu\text{-}S))_2$ (100 mg, 0.16 mmol) was added DMAD (45 mg, 0.32 mmol), and the mixture was stirred for 20 h in air and then evaporated to dryness. The residue was then dissolved in dichloromethane, and the solution was subjected to preparative TLC workup using dichloromethane. Compound **5** was collected as an orange-red band in 27% yield (33 mg).

Crystal Structure Determination of 2−5. The single crystals of **2** for X-ray diffraction analyses were grown by slow evaporation of dichloromethane solution layered by benzene, and those of **3**−**5** from the evaporation of their respective dichloromethane solution layered by hexane at 0 °C. Crystals of **2**−**5** were mounted on a glass fiber for data collection, and the data of **2**, **4**, and **5** were collected by using Mo Kα radiation on an Enraf Nonius CAD4 diffractometer, whereas those of **3** were collected on a Nonius Kappa CCD diffractometer at room temperature. Detailed data collection parameters are given in Table 2. Cell parameters were refined from 25 reflections with the 2θ range 20−37°. Three standard reflections were monitored every 1 h throughout the data collection. The variation was within 6%. Lorentz and polarization corrections were applied. A semiempirical absorption correction was applied based on azimuthal scans of three reflections. The structures were solved by the direct method. The atomic and isotropic thermal parameters for all hydrogen atoms were fixed. Structure refinement was performed using the NRCSDP[39] program on a VAX workstation machine.

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Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and all bond distances and angles and experimental details of the X-ray studies for **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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