Thiolate Ligand Transfer from Metallothiolates to Phosphido-Bridged Heterobimetallic Compounds: C–S Bond Cleavage in Benzenethiol and Formation of a Mixed-Metal Trinuclear Compound

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Thiolate ligand transfer occurred during the reaction between $CpMo(CO)_3SPh$ and $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_5$ (**1**) in dichloromethane at reflux, resulting in the new mixed-metal and mixed-ligand bridged compound $CpW(CO)(\mu\text{-}SPh)_2(\mu\text{-}PPh_2)Mo(CO)_3$ (**2**). However, when $CpW(CO)_3SPh$ reacted with **1** under similar conditions, **2** and the mixed-metal trinuclear compound $CpW(CO)(\mu\text{-}S)_2(\mu\text{-}PPh_2)Mo(CO)_2(\mu\text{-}PPh_2)W(CO)_2Cp$ (**4**) were formed. The presence of the $(\mu\text{-}S)_2$ bridges in **4** indicates C–S bond cleavage in the SPh ligand. Reflux of a dichloromethane solution of **1** and PhSH also produced **2** along with $CpW(CO)(\mu\text{-}SPh)_2(\mu\text{-}PPh_2)Mo(CO)(SPh)_2$ (**3**) and $CpW(CO)(\mu\text{-}SPh)_2(\mu\text{-}PPh_2)Mo(CO)_2(PPh_2H)$ (**5**). Moreover, the same reactants in benzene at reflux gave **2**, **3**, **5**, and the additional product $CpW(CO)(\mu\text{-}SPh)_2(\mu\text{-}PPh_2)Mo(CO)_2(PPh_3)$ (**6**). The reaction of **1** with Ph_2S_2 in dichloromethane at reflux produced compounds **2** and **3**. Similarly conducted reactions in benzene at reflux afforded **2**, **3**, and **6**. Compounds **2**–**6** were characterized by single-crystal X-ray diffraction analyses. Formation of the PPh_3 ligand, which coordinated to **6**, suggests C–S bond cleavage in PhSH and Ph_2S_2. Compounds **3**, **5**, and **6** were also synthesized in high yield by refluxing **2** with PhSH or Ph_2S_2, PPh_2H, and PPh_3, respectively, in benzene.

Introduction

Hydrodesulfurization (HDS) is a catalytic process, which is used to remove sulfur from organosulfur compounds in fossil fuel feedstocks. Although the exact mechanism of the catalytic process is still unresolved, coordination of the SR group to the metal surface is believed to be an essential step in the process.[1] The ligating behavior of organosulfur compounds to multi-metallic sites and then transformations are often expected to be similar to those on the surface of HDS catalysts. Thus, studies on coordination modes of the organosulfur compounds and then transformations on bimetallic complexes and clusters are informative in gaining insights into the HDS process. Organic sulfides, e.g. RSH and RSSR, are usually the source of the thiolate ligands SR in the synthesis of thiolato complexes with M–SR bonding.[2] In addition, metallothiolate itself can transfer thiolate ligand to other metal centers, and thus it has been proposed as a thiolate ligand source in the synthesis of thiolato complexes.[3] The effects of

polynuclear coordination to promote the cleavage of C–S bonds in organosulfur ligands in osmium and ruthenium carbonyl clusters have been also reported.[3h–p] It has also been reported that the μ_3 mode of coordination of SR on clusters activates the C–S bond by lowering its bond dissociation energy (BDE).[1a–c] Here metallothiolates are in a favorable position over the free thiols toward the

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Scheme 1
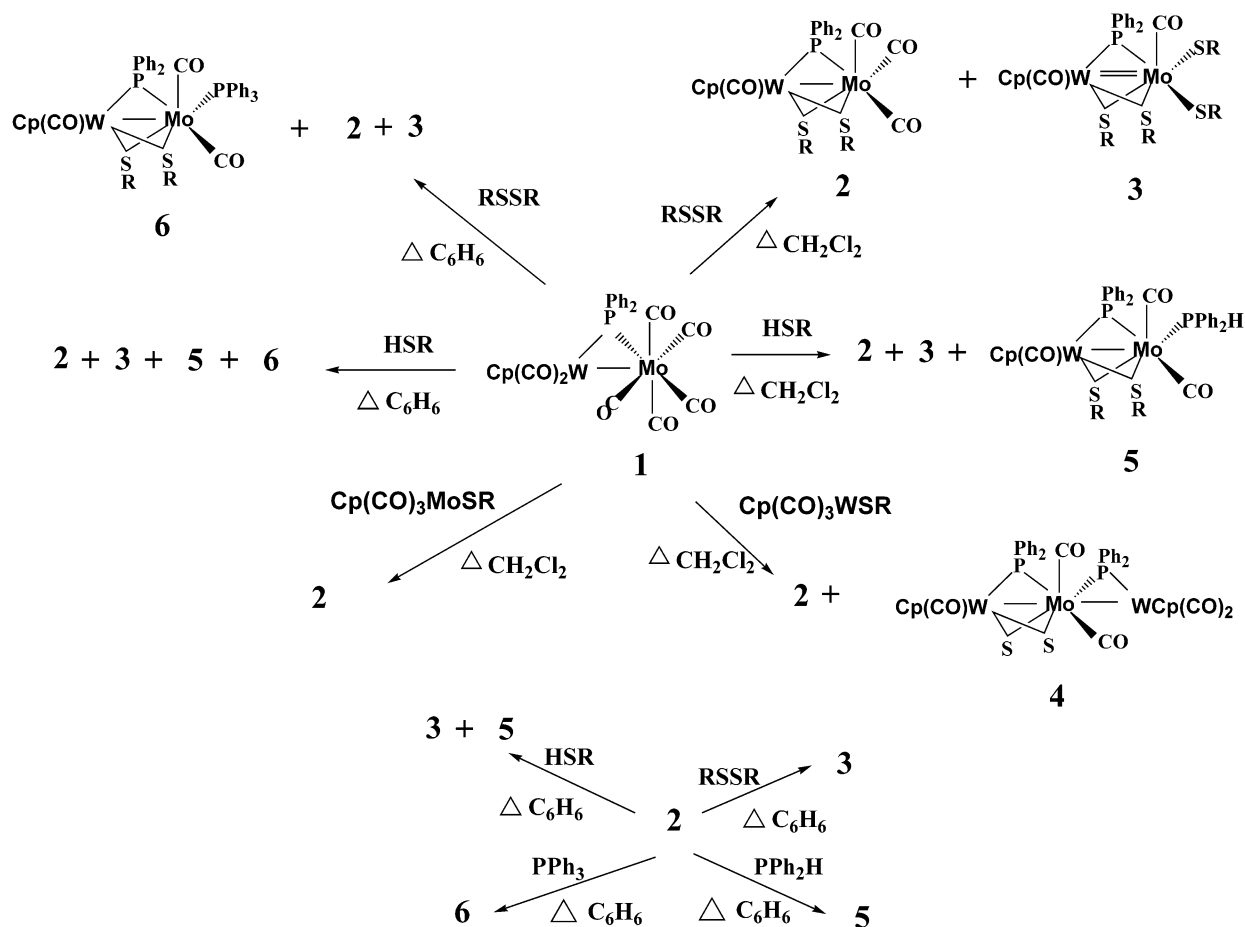
μ_3 mode of coordination of SR in the reaction with bimetallic compounds. It could be interesting to compare the reactivity of RSH, RSSR, and metallothiolates M−SR as sources of SR by reacting them with the same transition-metal substrate complex containing reactive sites. Such a comparative study may help in understanding the nature of SR bonding and its transformation, which may provide insight into the HDS process.

The bimetallic transition metal complex CpW(CO)$_2$-(μ-PPh$_2$)Mo(CO)$_5$ (**1**) was selected as a reactant for different thiolate ligand sources such as RSH, RSSR, and metallothiolates CpM(CO)$_3$SPh (M = Mo, W) on the basis of the following two reasons. First, **1** has a weak metal−metal bond, and the CO ligands on Mo are readily replaced by other ligands to produce CpW(CO)$_3$-(μ-PPh$_2$)Mo(CO)$_4$L (L = CO, PR$_3$),[4] which does not possess a metal−metal bond. Thus, the complex can provide a coordination site to a SR group on Mo under mild conditions. Second, group 6 transition-metal complexes and clusters have been used as models to mimic the hydrodesulfurization catalyst.[1,5] Here we report the reaction between CpM(CO)$_3$SPh (M = Mo, W) and **1**. Thiolate ligand transfer from the metallothiolates CpM-(CO)$_3$SPh (M = Mo, W) to the heterobimetallic phosphido-bridged compound **1** to form the mixed-metal and

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mixed-ligand bridged compound CpW(CO)(μ-SPh)$_2$(μ-PPh$_2$)Mo(CO)$_3$ (**2**) was observed under mild reaction conditions. Cleavage of the C−S bond to form the mixed-metal trinuclear compound CpW(CO)(μ-S)$_2$(μ-PPh$_2$)Mo-(CO)$_2$(μ-PPh$_2$)W(CO)$_2$Cp (**4**) occurred when CpW(CO)$_3$SPh was the source of the SPh ligand. Cleavage of the C−S bonds in RSH and RSSR at higher temperature is also described.

Results and Discussion

Thiolate Ligand Transfer and C−S Bond Scission. When a dichloromethane solution of CpMo-(CO)$_3$SPh and **1** was refluxed for 60 h, the greenish brown compound **2** was obtained in moderate yield. In addition to **2**, the green mixed-metal trinuclear compound **4** was obtained in low yield when CpW(CO)$_3$SPh was reacted with **1** under similar conditions (Scheme 1). The destination of the fragments of CpM(CO)$_3$ (M = W, Mo) after SPh ligand transfer from CpM(CO)$_3$SPh (M = W, Mo) is unclear. The possible formation of [CpM-(CO)$_3$]$_2$ (M = W, Mo) from the fragments was not observed. Isolated **2** did not react with **1** or CpW-(CO)$_3$SPh under comparable conditions; therefore, **4** is a direct product of CpW(CO)$_3$SPh and **1**.

Compounds **2** and **4** were each characterized by a single-crystal X-ray diffraction analysis. The molecular structures of **2** (Figure 1) and **4** (Figure 2) show that **2**
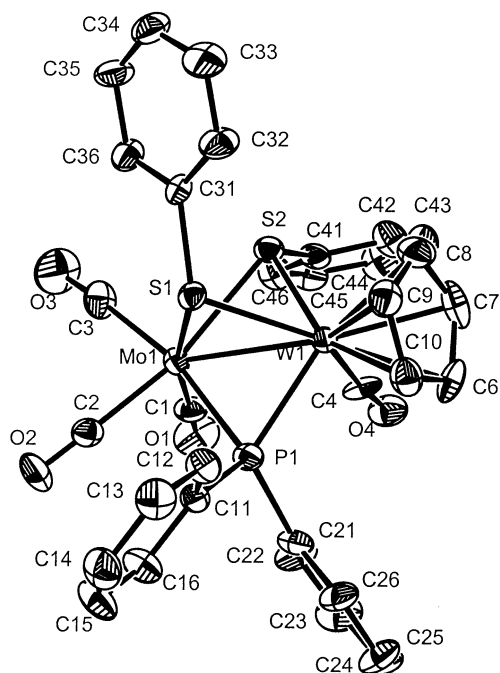
Figure 1. ORTEP drawing of **2**, with 30% thermal ellipsoids. Hydrogen atoms are omitted.

is a mixed thiolato- and phosphido-bridged heterobimetallic complex, whereas **4** is a sulfido- and phosphido-bridged mixed-metal trinuclear complex. These structures indicate that when CpMo(CO)₃SPh reacted with **1**, only thiolate ligand transfer occurred. However, during reaction between CpW(CO)₃SPh and **1**, not only thiolate ligand transfer but also scission of its C−S bond was observed. There are a few reports on thiolate ligand transfer, and those concern early to late transition metals: for example, from titanium to cobalt,[3a] rhodium,[3b] or platinum.[3c] This behavior is rationalized as being due to hard and soft mismatch in coordination between titanium and the thiolato ligand.[3c] Reports on thiolate

ligand transfer between transition metals in a group are rare.[3g] Thus, thiolate ligand transfer from molybdenum to molybdenum or from tungsten to tungsten under mild conditions in the above reaction is notable.

The presence of the μ-S ligands in **4** indicates C−S bond cleavage in the SPh ligand. Recently there have been several interesting reports on the C−S bond cleavage of organosulfur compounds, particularly for the case of thiophene, as thiophenic compounds are more difficult to desulfurize than thiols or alkyl sulfides.[1d,6] There have been a few reports on desulfurization of benzenethiols on clusters at higher temperature.[1a−d] It is realized that the SR ligands in a cluster can easily utilize the lone pairs of sulfur to form μ_3-SR ligands, since sulfur has a strong bridging ability. This μ_3-SR bridging mode of SR can decrease the BDE of the C−S bond, which facilitates its activation.[1a−d] The metallothiolate CpW(CO)₃SPh has a terminal thiolate ligand with two lone pairs on sulfur, which possibly coordinated to bimetallic **1** in a μ_3-SPh bridging mode and thus facilitated cleavage of the C−S bond in the SPh ligand under mild conditions. A GC-MS spectra of the volatiles from the reaction of **1** and CpW(CO)₃SPh in CH₂Cl₂ indicated formation of benzene after C−S bond cleavage in the SPh ligand.

Although cleavage of the C−S bond in SR (R = alkyl) is common,[7,8] such a cleavage in the SPh ligand at low temperature is rare.[1a−d,9] This is understandable because the BDE of the C−S bond in an S−Ph ligand is higher than that in an S−alkyl ligand.[1] Cleavage of the C−S bond by using a metal alkanethiolate as a sulfurization reagent has been reported, however, generally for alkali-metal thiolate and alkaline-earth-metal thiolates.[7,8] Similar methods in the case of arenethiolate are rare.[10] Thus, cleavage of the C−S bond in the reaction between CpW(CO)₃SPh and **1** under mild conditions is interesting and noteworthy.

C−S bond cleavage has been reported in CpW(SR)₃, and the CpW moiety was proposed to activate it.
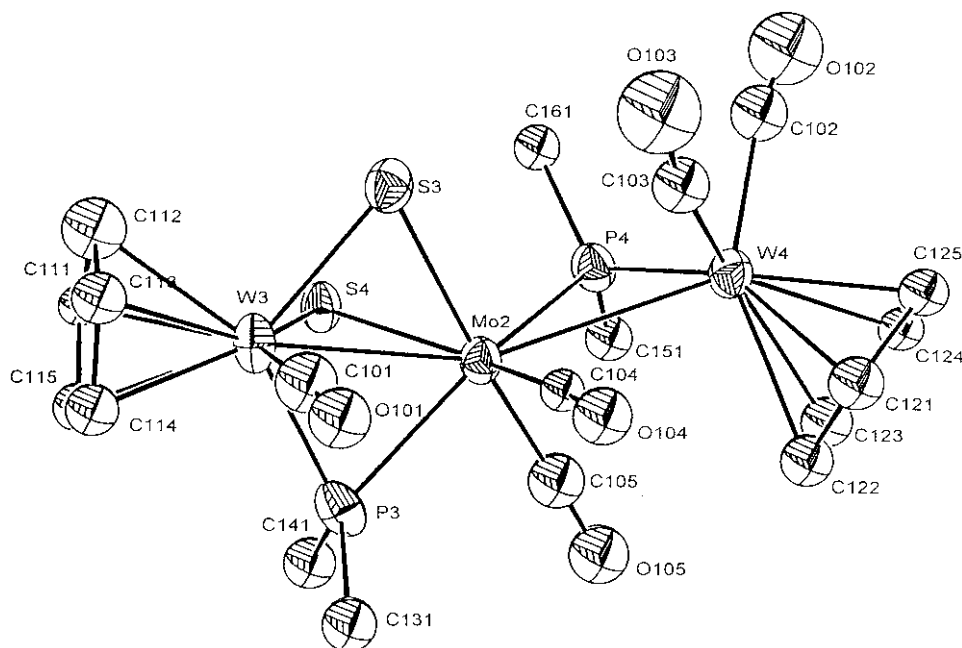

Figure 2. ORTEP drawing of **4**, with 30% thermal ellipsoids. Hydrogen atoms and all but the attached carbon atoms of the phenyl groups of the bridging phosphido ligands are omitted.

However, CpMo(SR)$_3$ did not undergo cleavage of its C−S bond under similar conditions.[10] We have made a similar observation that CpMo(CO)$_3$SPh reacts with **1** to produce **2** only. An analogue of **4** was not formed, and thus C−S bond scission did not occur in the reaction. The CpW(CO)$_2$PPh$_2$ unit in **4** likely originates from the fragmentation of **1** after cleavage of its W−Mo bond. However, the combination of PPh$_2$ and CpW(CO)$_3$, from the fragmentation of **1** and CpW(CO)$_3$SPh, respectively, after thiolate ligand transfer and further C−S bond cleavage cannot be totally excluded.

Reactions of 1 with PhSH and Ph$_2$S$_2$. Refluxing a dichloromethane solution of **1** and PhSH afforded **2** (41%), **3** (8%), and CpW(CO)(μ-SPh)$_2$(μ-PPh$_2$)Mo(CO)$_2$-(PPh$_2$H) (**5**) (2%), and a similar treatment in benzene gave CpW(CO)(μ-SPh)$_2$(μ-PPh$_2$)Mo(CO)$_2$(PPh$_3$) (**6**) (trace) in addition of **2** (36%), **3** (15%), and **5** (7%) (Scheme 1). When the reaction was carried out at room temperature in dichloromethane, only **2** was formed after long stirring, according to both TLC and ^{31}P NMR. Compounds **3** and **5** were also synthesized by reaction of **2** with PhSH and PPh$_2$H, respectively, in benzene (Scheme 1) at reflux. Thus, **2** could be a possible intermediate for **3** and **5**. The formation of **2** showed that PhSH can coordinate to metal to form a metal−SPh bond, but how the proton is removed remains unclear. Oxidative addition of two molecules of PhSH to the Mo of **1** followed by reductive elimination of hydrogen may be the reaction pathway. The preparation of **3** by reacting isolated pure **2** with PhSH under similar reaction conditions (Scheme 1) further supports the above possibility. The molecular structure of **3** (Figure 3) shows that it is a substitution product of **2**, where two carbonyl ligands on molybdenum are replaced by thiolate ligands; however, since the thiolate ligand in **3** is a one-electron donor, then **3** is a 32-electron dinuclear complex with an additional metal−metal bond compared to the bonds of 34-electron **2** to fulfill the 18-electron rule. Compound **5** was characterized by single-crystal X-ray diffraction studies (Figure 4). It is also a substitution product of **2**, where one of the carbonyl ligands on **2** is replaced by a PPh$_2$H ligand. The PPh$_2$H ligand is probably formed by protonation of the bridging PPh$_2$ on **1** in the reaction medium. The proton source is PhSH instead of solvent, since **5** is not formed in the case of Ph$_2$S$_2$ under similar reaction conditions (Scheme 1). In addition, we did not observe any CpW(CO)(μ-SPh)$_2$(μ-PPh$_2$)Mo(CO)$_2$(PPh$_2$D), as indicated by ^{31}P{^{1}H} NMR in the reaction of **1** with PhSH in C$_6$D$_6$, further supporting the above statement. Reaction of **2** with PPh$_2$H produced **5** in high yield (Scheme 1). The structure of **6** (Figure 5) shows that this complex is simply a substitution product of **2** with a carbonyl ligand on the Mo center replaced by PPh$_3$. The presence of PPh$_3$ indicates cleavage of the C−S bond in PhSH at higher temperature. Compound **6** was
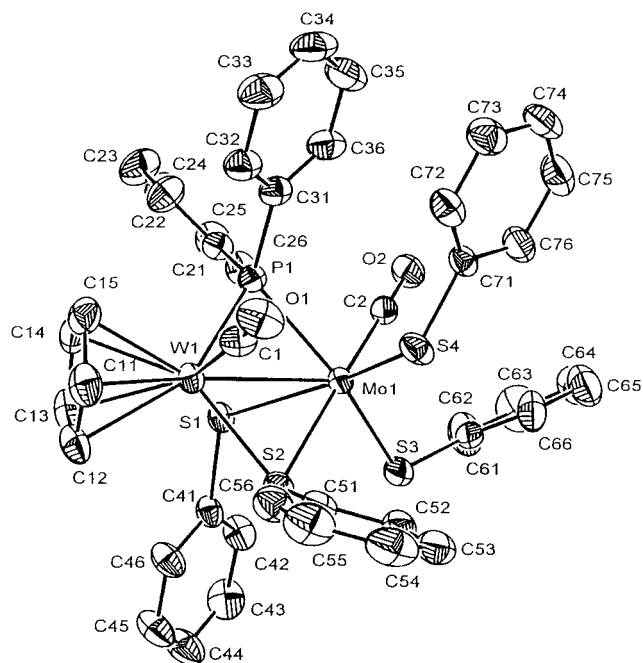

Figure 3. ORTEP drawing of **3**, with 30% thermal ellipsoids. Hydrogen atoms are omitted.

not observed when the same reactions were carried out in dichloromethane at 40 °C (Scheme 1).

It has been reported that during C−S bond scission in alkanethiols, the resulting alkyl radical is trapped by nucleophiles such as iodide and SCN.[11] The probability of trapping the benzene radical by dissociated PPh$_2$ seems unlikely. The generated benzene radical, after C−S bond scission of PhSH in our case, is more likely coupled with PPh$_2$ within the coordination spheres of **1** to form PPh$_3$, which then substitutes for a carbonyl ligand on **2** to afford **6**. Compound **6** was also synthesized directly in high yield by the reaction of **2** with PPh$_3$ under similar reaction conditions (Scheme 1).

Refluxing a dichloromethane solution of **1** and Ph$_2$S$_2$ produced **2** and **3**, and reaction in benzene at reflux temperature afforded **6** in the addition of **2** and **3** (Scheme 1). Reaction between **2** and Ph$_2$S$_2$ produced **3** (Scheme 1). Thus, **2** may be the intermediate in the formation of **3** in the reaction between **1** and Ph$_2$S$_2$. Oxidative addition of Ph$_2$S$_2$ to the Mo in **1** and replacement of the CO ligands on Mo to form the bridging SR may be the reaction path. Similarly, two carbonyl ligands on **2** are replaced by two SPh ligands to produce the 32-electron dinuclear complex **3** from the 34-electron **2**. To investigate the source of the phenyl group on the PPh$_3$ in **6**, a similar reaction between (CH$_3$C$_6$H$_4$)$_2$S$_2$ and **1** was carried out in benzene at reflux. Isolated products of the reaction were CpW(CO)(μ-SC$_6$H$_4$CH$_3$)$_2$(μ-PPh$_2$)-Mo(CO)$_3$ (**7**), CpW(CO)(μ-SC$_6$H$_4$CH$_3$)$_2$(μ-PPh$_2$)Mo(CO)$_2$-(PPh$_2$C$_6$H$_4$CH$_3$) (**8**), and CpW(CO)(μ-SC$_6$H$_4$CH$_3$)$_2$(μ-PPh$_2$)Mo(CO)(SC$_6$H$_4$CH$_3$)$_2$ (**9**). They are characterized on the basis of elemental analyses and spectroscopic

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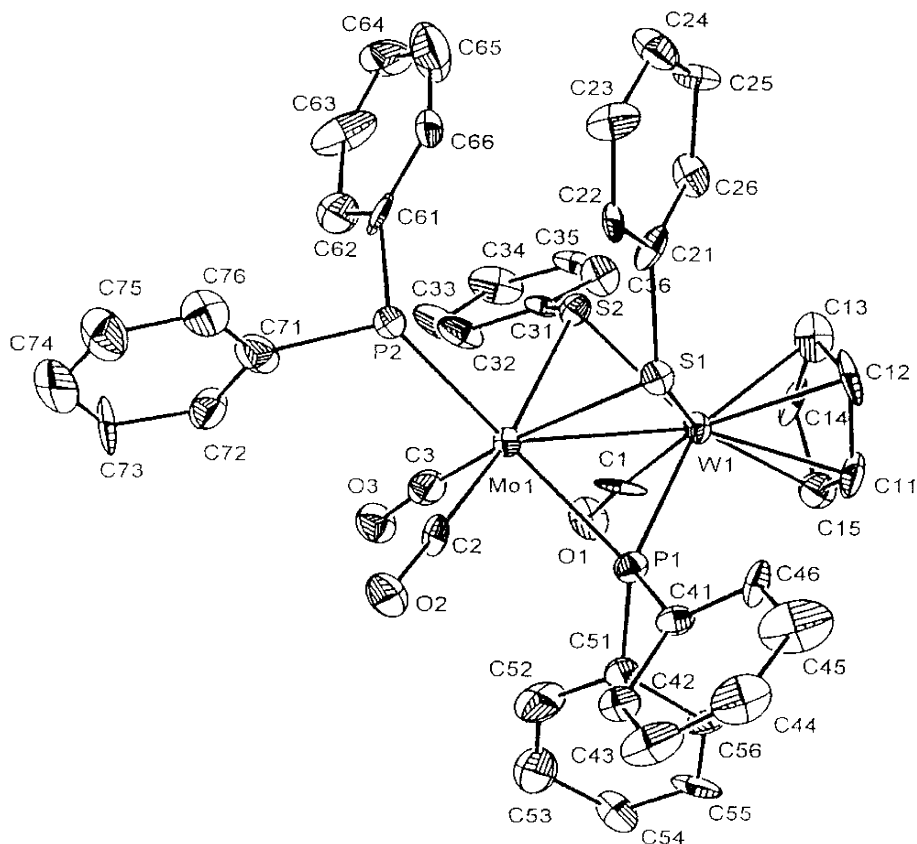
Figure 4. ORTEP drawing of **5**, with 30% thermal ellipsoids. Hydrogen atoms are omitted.
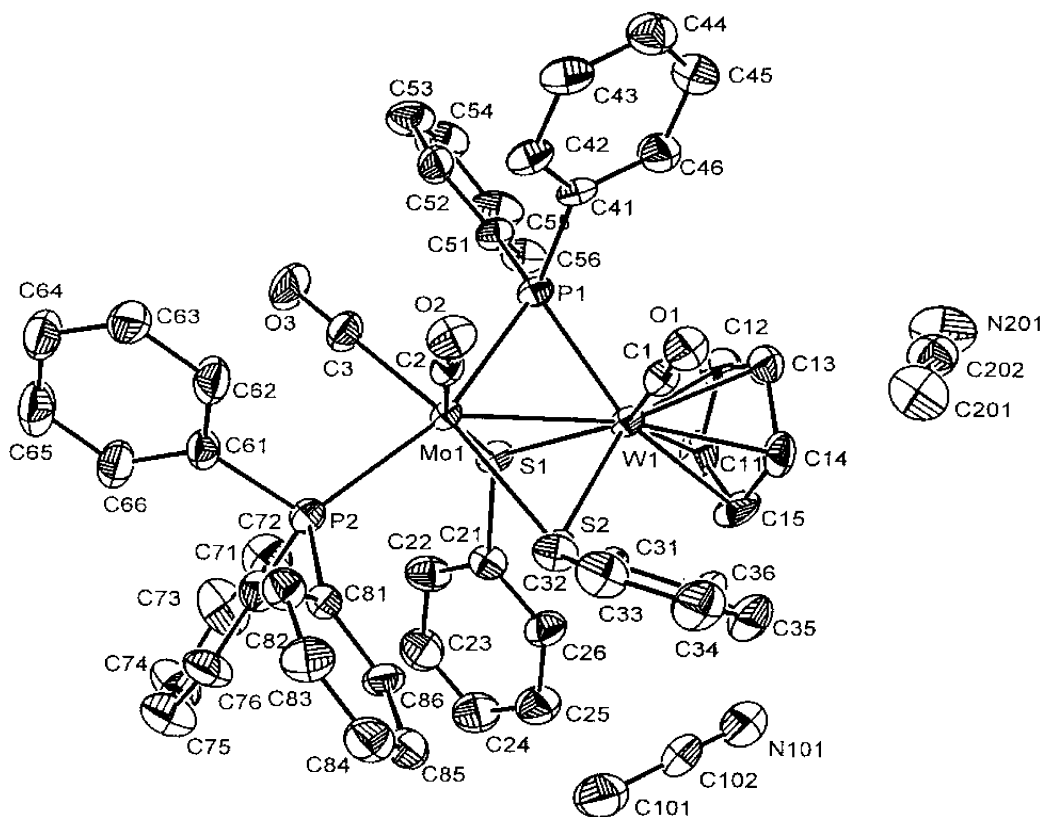
Figure 5. ORTEP drawing of **6**, with 30% thermal ellipsoids. Hydrogen atoms are omitted.

data. We propose that the structures for **7**−**9** are similar to the structures of **2**, **6**, and **3**, respectively, since they have patterns in their IR and $^{31}P\{^1H\}$ spectra similar to those of **2**, **6**, and **3**. The formation of **8** indicates that

the source of R in the formation of Ph$_2$R (R = Ph, CH$_3$C$_6$H$_4$) is SR after cleavage of C−S bonds.

X-ray Structures of Compounds 2−6. The molecular structures of **2**−**6** were determined by single-crystal

Table 1. Summary of Crystal Data for Compounds 2−6

	2	**3**	**4**	**5**	**6**
formula	$C_{33}H_{25}O_4S_2$-PMoW	$C_{44}H_{37}O_2Cl_2S_4$-PMoW	$C_{39}H_{30}O_5P_2S_2$-MoW_2	$C_{44}H_{35}O_3S_2$-P_2MoW	$C_{54}H_{46}N_2O_3S_2$-P_2MoW
fw	860.44	1107.68	1168.37	1017.61	1176.83
space group	$P2_1$	$P2_1/n$	$P2_1/c$	Pc	$P\bar{1}$
a (Å)	11.4024(9)	11.9640((21)	17.565(5)	11.3696(15)	11.600(3)
b (Å)	14.2203(20)	25.768(5)	33.793(7)	18.178(3)	11.8508(24)
c (Å)	19.0087(21)	14.3079(20)	16.5990(20)	10.7818(16)	20.864(6)
α (deg)	-	-			103.130(22)
β (deg)	90.379(8)	90.157(13)	108.150(20)	117.220(16)	96.472(24)
γ (deg)					116.157(19)
V (Å^3)	3082.1(6)	4411.0(13)	9363(3)	1981.6(5)	2431.6(11)
ρ(calcd) (Mg m^{-3})	0.927	1.668	1.658	1.705	1.607
Z	2	4	8	2	2
cryst dimens (mm)	0.12 × 0.09 × 0.06	0.07 × 0.12 × 0.26	0.06 × 0.11 × 0.33	0.03 × 0.03 × 0.31	0.34 × 0.19 × 0.16
temp	room temp	room temp	room temp	room temp	room temp
λ(Mo Kα) (Å)	0.709 30	0.709 30	0.709 30	0.709 30	0.709 30
2θ range (deg)	50.0	50.0	50.0	50.0	50.0
scan type	ω	ω	ω	ω	ω
no. of rflns	5703	7793	17175	3726	8535
no. of obsd rflns	4501 ($>2.5\sigma(I)$)	5358 ($>2.5\sigma(I)$)	3419 ($>2.0\sigma(I)$)	2320 ($>2.0\sigma(I)$)	5147 ($>2.0\sigma(I)$)
no. of params refined	757	497	471	476	586
R	0.049	0.030	0.097	0.047	0.047
R_w	0.030	0.031	0.118	0.040	0.051
GOF	1.09	1.30	1.19	1.14	1.52
D_{map} min, max (e/Å^3)	−0.710, 1.930	−0.760, 1.0	−1.980, 2.610	−0.830, 1.040	−1.200, 2.490

X-ray diffraction analyses. The selected bond distances and bond angles are listed in Tables 2 and 3, respectively. Two independent molecules of **2** crystallized in the asymmetric unit cell. The two independent molecules are crystallographically nonidentical and can be distinguished by the chirality of the S atom. The structures of **2**, **3**, **5**, and **6** are similar in that they all contain a WMoS$_2$P core where tungsten and molybdenum atoms are bridged by two thiolato ligands and one phosphido ligand. The W−Mo bond lengths in **2**, **3**, **5**, and **6** are 2.8427(14), 2.8589(6), 2.8063(20), and 2.8382(13) Å, respectively. On average, they are shorter by 0.37 Å compared to the W−Mo (3.2054(16) Å) bond length in the parent compound **1**.[4] The literature supports the variation in metal−metal bond distances in dinuclear compounds on the basis of the 18-electron rule, and experimental findings suggested that single, double, or triple bonds could be rationalized from the consideration of the valence electrons around each metal.[12−14] On the other hand, the metal−metal bonds become shorter when the number of bridging ligands increases.[15−25] Shortening of the W−Mo bond length in

compounds **2**, **3**, **5**, and **6** from that in **1** is expected, as the number of bridging ligands in them is increased compared to **1**. Although according to the 18-electron rule a double bond should exist between the two metal centers of the 32-electron dinuclear **3**, the W−Mo bond in **3** is not only considerably longer than reported Mo=W double bonds (2.702−2.718 Å)[26] but also longer compared to that of 34-electron **2**, **5**, and **6**. A similar trend is also noted in the reported 32-electron CpMo-(CO)(μ-SPh)$_3$Mo(CO)(SPh)$_2$ (2.8040(9) Å) and 34-electron CpMo(CO)(μ-SCH$_2$C$_6$H$_5$)$_3$Mo(CO)$_3$ (2.7791(4) Å) complexes.[27] These may be due to the repulsions of the lone pair on sulfur atoms of the terminal SPh ligands on the Mo site in **3**. Compound **4** is a unique example for comparison of metal−metal bond variation according to the number of bridging ligands, since the singly bridged Mo(μ-PPh$_2$)W unit has a Mo−W distance of 3.189(7) Å, whereas in the triply bridged Mo(μ-S)$_2$(μ-PPh$_2$)W unit the distance is 2.797(6) Å. The average values of the acute angles W−S−Mo (66.97°) and W−P−Mo (73.07°) are comparable to reported values for the structures where metal−metal interaction exists.[28]

In general, metal to bridging thiolate sulfur bonds are longer than those to terminal thiolate sulfur bonds.[29] We observed the same trend in the case of **3**: the Mo$_{br}$−S (2.5665 Å, average) distance is longer than that of Mo$_{tr}$−S (2.3402 Å, average), but the Mo$_{tr}$−S

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Table 2. Selected Bond Lengths (Å) for Compounds 2−6

Compound **2**			
W1−S1	2.505(3)	Mo1−S1	2.577(3)
W1−S2	2.469(3)	Mo1−S2	2.562(3)
W1−P1	2.389(3)	Mo1−P1	2.490(3)
W1−C4	2.018(10)	S1−C31	1.808(10)
Mo1−C1	1.947(11)	S2−C41	1.811(11)
Mo1−C2	2.000(13)	P1−C11	1.841(11)
Mo1−C3	2.013(14)	P1−C21	1.827(11)
Mo1−W1	2.8427(14)		
Compound **3**			
W1−S1	2.4525(14)	Mo1−S1	2.5738(14)
W1−S2	2.4769(15)	Mo1−S2	2.5592(15)
W1−P1	2.3850(15)	Mo1−S3	2.3782(17)
Mo1−P1	2.4809(15)	Mo1−S4	2.3033(15)
W1−C1	2.016(6)	Mo1−C2	1.977(6)
S1−C41	1.803(6)	S2−C51	1.794(5)
S3−C61	1.773(6)	S4−C71	1.774(5)
P1−C21	1.840(6)	P1−C31	1.822(6)
Mo1−W1	2.8589(6)		
Compound **4**			
W3−S3	2.486(22)	Mo2−S3	2.594(21)
W3−S4	2.510(16)	Mo2−S4	2.588(16)
W3−P3	2.354(23)	Mo2−P3	2.474(21)
W4−P4	2.363(20)	Mo2−P4	2.483(19)
W3−C101	1.95(9)	P3−C131	1.85(8)
W4−C102	2.11(8)	P3−C141	1.82(8)
W4−C103	1.80(10)	P4−C151	1.78(8)
Mo2−C104	1.93(7)	P4−C161	1.85(8)
Mo2−C105	2.00(9)	W3−Mo2	2.797(6)
W4−Mo2	3.189(7)		
Compound **5**			
W1−S1	2.474(6)	Mo1−S1	2.591(6)
W1−S2	2.464(6)	Mo1−S2	2.541(6)
W1−P1	2.393(6)	Mo1−P1	2.461(6)
W1−C1	2.06(3)	Mo1−P2	2.474(7)
Mo1−C2	1.994(23)	S1−C21	1.84(3)
Mo1−C3	1.86(3)	S2−C31	1.743(20)
P1−C41	1.850(21)	P2−C61	1.79(3)
P1−C51	1.860(24)	P2−C71	1.86(3)
W1−Mo1	2.8063(20)		
Compound **6**			
W1−S1	2.491(3)	Mo1−S1	2.611(3)
W1−S2	2.470(3)	Mo1−S2	2.525(3)
W1−P1	2.398(3)	Mo1−P1	2.457(3)
W1−C1	1.970(12)	Mo1−P2	2.559(3)
Mo1−C2	1.908(11)	S1−C21	1.794(11)
Mo1−C3	2.035(12)	S2−C31	1.803(11)
P1−C41	1.823(11)	P2−C61	1.840(12)
P1−C51	1.848(11)	P2−C71	1.838(13)
W1−Mo1	2.8382(13)	P2−C81	1.837(12)

(2.3023(15) Å) distance trans to the sulfido ligand is shorter than that of Mo_{tr}−S (2.3782(17) Å) trans to the phosphido ligand. This indicates that the sulfido ligand has a strong trans effect compared to that of the phosphido ligand. Such a short Mo_{tr}−S (2.3023(15) Å) distance trans to the sulfido ligand indicates the existence of sulfur to molybdenum π bonding.[30]

Conclusion

The paper describes the reactivity difference among metallothiolates CpM(CO)$_3$SPh (M = Mo, W), PhSH, and Ph$_2$S$_2$ toward the dinuclear phosphido-bridged

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Table 3. Selected Bond Angles (deg) for Compounds 2−6

Compound **2**			
W1−S1−Mo1	68.01(8)	S1−Mo1−C2	101.6(3)
W1−S2−Mo1	68.78(7)	S1−Mo1−C3	105.7(4)
W1−P1−Mo1	71.25(8)	S2−Mo1−P1	106.23(11)
S1−W1−S2	75.27(10)	S2−Mo1−C1	100.4(4)
S1−W1−P1	77.14(10)	S2−Mo1−C2	167.9(3)
S1−W1−C4	139.2(3)	S2−Mo1−C3	86.1(4)
S2−W1−P1	112.55(10)	P1−Mo1−C1	97.7(4)
S2−W1−C4	81.8(3)	P1−Mo1−C2	81.6(3)
P1−W1−C4	81.3(3)	P1−Mo1−C3	166.7(4)
S1−Mo1−S2	72.46(10)	C1−Mo1−C2	87.4(5)
S1−Mo1−P1	74.06(10)	C1−Mo1−C3	84.8(5)
S1−Mo1−C1	166.5(4)	C2−Mo1−C3	85.5(5)
Compound **3**			
W1−S1−Mo1	69.28(4)	S1−Mo1−P1	71.10(5)
W1−S2−Mo1	69.16(4)	S1−Mo1−C2	105.04(16)
W1−P1−Mo1	71.94(4)	S2−Mo1−S3	87.36(5)
S1−W1−S2	75.32(5)	S2−Mo1−S4	89.84(5)
S1−W1−P1	74.84(5)	S2−Mo1−P1	106.25(5)
S1−W1−C1	143.33(17)	S2−Mo1−C2	175.14(16)
S2−W1−P1	112.05(5)	S3−Mo1−S4	109.48(6)
S2−W1−C1	83.65(17)	S3−Mo1−P1	148.59(6)
P1−W1−C1	86.09(16)	S3−Mo1−C2	88.78(16)
S1−Mo1−S2	71.85(4)	S4−Mo1−P1	98.94(6)
S1−Mo1−S3	87.28(5)	S4−Mo1−C2	94.23(16)
S1−Mo1−S4	154.87(6)	P1−Mo1−C2	75.76(16)
Compound **4**			
W3−S3−Mo2	66.8(6)	S3−Mo2−C105	177.2(22)
W3−S4−Mo2	66.5(4)	S4−Mo2−P3	72.7(6)
W3−P3−Mo2	70.8(7)	S4−Mo2−P4	86.3(6)
W4−P4−Mo2	82.3(6)	S4−Mo2−C104	156.2(19)
S3−W3−S4	75.2(6)	S4−Mo2−C105	110.8(22)
S3−W3−P3	114.9(6)	P3−Mo2−P4	142.0(7)
S3−W3−C101	85.0(3)	P3−Mo2−C104	97.1(21)
S4−W3−P3	76.1(6)	P3−Mo2−C105	74.1(22)
S4−W3−C101	145.5(25)	P4−Mo2−C104	112.8(19)
P3−W3−C101	86.0(3)	P4−Mo2−C105	84.8(22)
S3−Mo2−S4	72.0(6)	C104−Mo2−C105	85.0(3)
S3−Mo2−P3	107.2(7)	P4−W4−C102	84.0(18)
S3−Mo2−P4	95.4(7)	P4−W4−C103	105.0(3)
S3−Mo2−C104	91.4(22)	C102−W4−C103	76.0(3)
Compound **5**			
W1−S1−Mo1	67.24(15)	S1−Mo1−C2	105.3(7)
W1−S2−Mo1	68.19(15)	S1−Mo1−C3	163.8(9)
W1−P1−Mo1	70.62(18)	S2−Mo1−P1	107.77(21)
S1−W1−S2	77.22(19)	S2−Mo1−P2	86.70(21)
S1−W1−P1	74.95(20)	S2−Mo1−C2	170.4(6)
S1−W1−C1	135.5(9)	S2−Mo1−C3	94.3(9)
S2−W1−P1	112.63(20)	P1−Mo1−P2	154.50(22)
S2−W1−C1	81.1(8)	P1−Mo1−C2	80.6(6)
P1−W1−C1	78.4(7)	P1−Mo1−C3	102.6(9)
S1−Mo1−S2	73.80(19)	P2−Mo1−C2	83.8(6)
S1−Mo1−P1	71.75(20)	P2−Mo1−C3	97.0(8)
S1−Mo1−P2	93.29(20)	C2−Mo1−C3	88.3(11)
Compound **6**			
W1−S1−Mo1	67.55(7)	S1−Mo1−C2	162.3(3)
W1−S2−Mo1	69.25(8)	S1−Mo1−C3	96.7(4)
W1−P1−Mo1	71.52(8)	S2−Mo1−P1	106.88(10)
S1−W1−S2	78.02(10)	S2−Mo1−P2	90.71(10)
S1−W1−P1	76.19(10)	S2−Mo1−C2	98.6(3)
S1−W1−C1	140.7(3)	S2−Mo1−C3	166.7(4)
S2−W1−P1	110.59(10)	P1−Mo1−P2	161.61(10)
S2−W1−C1	82.6(3)	P1−Mo1−C2	93.8(3)
P1−W1−C1	79.3(3)	P1−Mo1−C3	79.7(3)
S1−Mo1−S2	74.86(9)	P2−Mo1−C2	88.7(3)
S1−Mo1−P1	73.00(10)	P2−Mo1−C3	82.0(4)
S1−Mo1−P2	107.59(10)	C2−Mo1−C3	92.4(5)

complex **1**. During the reaction between CpMo(CO)$_3$SPh and **1** under mild conditions, thiolato ligand transfer occurred and a mixed thiolato- and phosphido-bridged **2** was formed. In the case of CpW(CO)$_3$SPh, not only **2** but also the mixed-metal trinuclear **4**, a C−S bond

cleavage product, was observed. Under similar reaction conditions the C−S bond in PhSH or Ph_2S_2 could not be cleaved during treatment with **1**, but cleavage of the C−S bond in both PhSH and Ph_2S occurred when the same reactions were carried out at higher temperature. The ease of C−S bond cleavage in the case of CpW-$(CO)_3$SPh over that in the free thiols under mild conditions is attributed to the μ_3-SR bridging mode, which reduces the BDE of the C−S bonds.

Experimental Section

General Procedures. All reactions and other manipulations were performed by use of standard Schlenk techniques under an atmosphere of nitrogen. 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. The compounds CpM$(CO)_3$SPh (M = Mo, W) and CpW$(CO)_2(\mu$-PPh$_2)$Mo$(CO)_5$ were prepared following the reported procedures.[2f,g,4] Infrared spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. 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. Electron impact (EI) and fast-atom-bombardment (FAB) mass spectra were recorded on a VG 70-2505 or a JEOL JMS-HX 100 mass spectrometer. GC-MS spectra were obtained on a HP6890 (GC) and HP5973 (MS) GC-MS. Microanalyses were performed by use of a Perkin-Elmer 2400 CHN analyzer.

Reactions of 1 with CpM$(CO)_3$SPh (M = Mo, W). To a solid mixture of **1** (0.50 g, 0.68 mmol) and CpW$(CO)_3$SPh (0.60 g, 1.35 mmol) was added dichloromethane (50 mL) and the mixture kept at reflux for 60 h. The reaction mixture was evaporated to dryness. The residue was then dissolved in dichloromethane (10 mL) and the solution was subjected to silica gel chromatographic workup. Compound **2** was eluted as a greenish brown band by dichloromethane and hexane (1:1) following a band of unreacted purple **1**. Compound **4** was then isolated as a brown band using net dichloromethane. Unreacted **1**: yield 0.21 g (41%). Compound **2**: yield 0.08 g (21%). Anal. Calcd for $C_{33}H_{25}O_4PS_2$MoW: C, 46.02; H, 2.90. Found: C, 46.37; H, 2.97. IR (CH_2Cl_2, ν_{CO}): 1997 vs, 1971 vs, 1930 s, 1857 s cm^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): δ 7.75−7.02 (m, 20H, C_6H_5), 6.22 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR (THF): δ 138.5 (s). MS (FAB): m/z 861 (M$^+$ + 1). Compound **4**: yield 0.052 g (7%). Anal. Calcd for $C_{39}H_{30}O_5P_2S_2$MoW$_2$: C, 40.07; H, 2.57. Found: C, 39.91; H, 2.74. IR (CH_2Cl_2, ν_{CO}): 1980 s, 1932 vs, 1914 vs, 1863 vs cm^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): δ 7.49−6.91 (m, 20H, C_6H_5), 5.95 (s, 5H, C_5H_5), 5.44 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR (THF): δ 155.96 (d), 135.86 (d, $^2J_{P-P} = 15.97$ Hz). When a reaction between CpMo$(CO)_3$SPh (0.14 g, 0.40 mmol) and **1** (0.15 g, 0.20 mmol) was carried out by following the above procedure, compounds **2** and unreacted **1** were isolated in 18% (0.031 g) and 34% (0.051 g) yields, respectively.

Reaction of 1 with CpW$(CO)_3$SPh in CH_2Cl_2. To a solid mixture of **1** (0.050 g, 0.07 mmol) and CpW$(CO)_3$SPh (0.060 g, 0.14 mmol) was added CH_2Cl_2 (5 mL) and the mixture kept at reflux for 60 h. The volatiles were separated from the reaction mixture by collecting them in a liquid nitrogen trap and analyzed by GC-MS.

Reactions of 1 with PhSH and Ph_2S_2 in Dichloromethane. To a dichloromethane solution (50 mL) of **1** (0.20 g, 0.275 mmol) was added PhSH (0.09 g, 0.81 mmol) and the mixture kept at reflux for 30 h. The reaction mixture was evaporated to dryness. The residue was then dissolved in dichloromethane (10 mL) and the solution was subjected to silica gel column chromatography. Elution with dichloromethane and hexane (1:1) collected three bands. The first, greenish brown band contained **2**. The second, violet, and the third, reddish orange, bands were compounds **5** and **3**, respectively. Compound **2**: yield 0.097 g (41%). Compound **3**: yield 0.022 g (8%). Anal. Calcd for $C_{43}H_{35}O_2PS_4$MoW: C, 50.49; H, 3.42. Found: C, 50.09; H, 3.57. IR spectrum (CH_2Cl_2, ν_{CO}): 1990 vs, 1903 vs cm^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): δ 7.69−6.83 (m, 30H, C_6H_5), 6.18 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR (THF): δ 141.8 (s). Compound **5**: yield 0.006 g, 2%. Anal. Calcd for $C_{44}H_{35}O_3P_2S_2$MoW: C, 51.86; H, 3.44. Found: C, 51.96; H, 3.71. IR (CH_2Cl_2, ν_{CO}): 1961 s, 1915 vs, 1816 cm^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): δ 8.79−6.84 (m, 30H, C_6H_5), 6.02 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR (THF): δ 20.59 (d), 122.88 (d, $^2J_{P-P} = 23.87$ Hz, J_{P-H} 232.3, PPh$_2$H). When the reaction was carried out in a similar fashion with **1** (0.2 g, 0.275) and Ph_2S_2 (0.09 g, 0.41 mmol), compounds **2** and **3** were isolated in 49% (0.115 g) and 5% (0.014 g) yields, respectively.

Reactions of 1 with PhSH and Ph_2S_2 in Benzene. To a benzene solution (50 mL) of **1** (0.50 g, 0.68 mmol) was added PhSH (0.22 g, 2.0 mmol), and the mixture was refluxed for 20 h and then evaporated to dryness. The residue was dissolved in dichloromethane and concentrated to 10 mL. Four bands were collected by silica gel column chromatography using dichloromethane and hexane (1:1). The first band contained **2**. The second, violet, the third, greenish orange, and the fourth, reddish orange, bands were compounds **5**, **6**, and **3**, respectively. Compound **2**: yield 0.206 g (36%). Compound **3**: yield 0.104 g (15%). Compound **5**: yield 0.047 g (7%). Compound **6** was obtained in a trace amount. Similarly, the reaction between compound **1** (0.40 g, 0.55 mmol) and Ph_2S_2 (0.18 g, 0.82 mmol) for 12 h afforded compounds **2**, **3**, and **6** in 38% (0.177 g), 34% (0.191 g), and 4% (0.026 g) yields, respectively. Data for compound **6** are as follows. Anal. Calcd for $C_{50}H_{40}O_3P_2S_2$MoW: C, 54.84; H, 3.65. Found: C, 54.75; H, 4.01. IR (CH_2Cl_2, ν_{CO}): 1961 s, 1903 vs, 1815 s cm^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): δ 7.85−6.55 (m, 35H, C_6H_5), 5.99 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR (THF): δ 42.06 (d), 124.09 (d, $^2J_{P-P} = 17.18$ Hz).

Reaction of 1 with $(CH_3C_6H_4)_2S_2$ in Benzene. To a benzene solution (50 mL) of **1** (0.50 g, 0.68 mmol) was added $(CH_3C_6H_4)_2S_2$ (0.255 g, 1.0 mmol), and the mixture was refluxed for 17 h and then evaporated to dryness. The residue was dissolved in dichloromethane and concentrated to 10 mL. Chromatographic workup using dichloromethane and hexane (1:1) isolated three bands. The first, greenish orange, the second, reddish brown, and the third, reddish orange, bands were compounds **7**−**9**, respectively. Compound **7**: yield 0.287 g (45%). Anal. Calcd for $C_{35}H_{29}O_4PS_2$MoW: C, 47.30; H, 3.27. Found: C, 47.46; H, 3.40. IR (CH_2Cl_2, ν_{CO}): 1996 vs, 1970 vs, 1928 s, 1856 s cm^{-1}. ^{1}H NMR (CD$_3$Cl): δ 7.60−6.85 (m, 18H), 5.78 (s, 5H, C_5H_5), 2.22 (s, 3H), 2.17 (s, 3H). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$): δ 135.6(s). Compound **8**: yield 0.024 g (3%). Anal. Calcd for $C_{53}H_{46}O_3P_2S_2$MoW: C, 55.99; H, 4.05. Found: C, 55.93; H, 4.14. IR (CH_2Cl_2, ν_{CO}): 1959 s, 1900 vs, 1813 s cm^{-1}. ^{1}H NMR (CD$_3$Cl): δ 7.55−6.33 (m, 32H), 5.72 (s, 5H, C_5H_5), 2.30 (s, 3H), 2.14 (s, 3H), 2.10 (s, 3H). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$): δ 41.19 (d), 124.59 (d, $^2J_{P-P} = 19.20$ Hz). Compound **9**: yield 0.208 g (28%). Anal. Calcd for $C_{47}H_{43}O_2PS_4$MoW: C, 52.32; H, 3.99. Found: C, 52.15; H, 4.24. IR (CH_2Cl_2, ν_{CO}): 1986 vs, 1899 vs cm^{-1}. ^{1}H NMR (CD$_3$Cl): δ 7.42−6.78 (m, 26H), 5.75 (s, 5H, C_5H_5), 2.37 (s, 3H), 2.29 (s, 3H), 2.23 (s, 3H), 2.21 (s, 3H). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$): δ 142.7 (s)

Reaction of 1 with PhSH in C_6D_6. To a C_6D_6 solution (5 mL) of **1** (0.150 g, 0.21 mmol) was added PhSH (0.07 g, 0.63 mmol) and the mixture kept at reflux for 20 h and then evaporated to dryness. The residue was dissolved in 5 mL of dichloromethane and subjected to chromatographic workup using dichloromethane and hexane (1:1). Compounds **2**, **3**, and **5** were isolated in 23% (0.041 g), 12% (0.027 g), and 20% (0.046 g) yields, respectively. A trace amount of **6** was also obtained.

Reaction of 2 with CpW$(CO)_3$SPh. To a mixture of CpW-$(CO)_3$SPh (0.052 g, 0.12 mmol) and **2** (0.10 g, 0.12 mmol) was added dichloromethane (50 mL), and the solution was refluxed for 60 h and then concentrated to 5 mL. Chromatographic

workup using dichloromethane and hexane (1:1) recovered 76% (0.036 g) of CpW(CO)$_3$SPh and 89% (0.089 g) of **2** as the first, orange and the second, greenish brown bands, respectively.

Reaction of 2 with 1. To a mixture of **2** (0.1 g, 0.12 mmol) and **1** (0.087 g, 0.12 mmol) was added dichloromethane (50 mL), and the solution was refluxed for 60 h and then filtered through Celite and concentrated to 5 mL. This solution was subjected to chromatographic workup using dichloromethane and hexane (1:1) and recovered 75% (0.065 g) of **1** and 95% (0.095 g) of **2** as the first, violet, and the second, greenish brown, bands, respectively.

Reactions of 2 with PhSH and Ph$_2$S$_2$. To a benzene solution (50 mL) of **2** (0.20 g, 0.232 mmol) was added PhSH (0.051 g, 0.47 mmol), and the mixture was refluxed for 16 h. The solution was evaporated to dryness. The residue was then dissolved in dichloromethane and this solution concentrated to 10 mL. Silica gel column chromatography using dichloromethane and hexane (1:1) gave three bands. The first band was unreacted **2**. The second and third bands contained compounds **5** and **3**, respectively. Unreacted **2**: yield 0.043 g (21%). Compound **3**: yield 0.057 g (31%). Compound **5**: yield 0.080 g (5%). We isolated two bands when a reaction between compound **2** (0.10 g, 0.116 mmol) and Ph$_2$S$_2$ (0.025 g, 0.116 mmol) was carried out in the above way for 22 h. The first band was unreacted **2**, and the second band was compound **3**. Unreacted **2**: yield 0.023 g (23%). Compound **3**: yield 0.056 g (61%).

Synthesis of 5 from 2 by PPh$_2$H. To a benzene solution (50 mL) of **2** (0.10 g, 0.116 mmol) was added PPh$_2$H (0.022 g, 0.18 mmol), and the mixture was refluxed for 3 h. The solution was evaporated to dryness. The residue was dissolved in dichloromethane (10 mL). Silica gel chromatography using dichloromethane and hexane (1:1) gave compound **5** in 89% (0.105 g) yield.

Synthesis of 6 from 2 by PPh$_3$. To a benzene solution (50 mL) of **2** (0.10 g, 0.116 mmol) was added PPh$_3$ (0.032 g, 0.12 mmol), and the mixture was refluxed for 4 h. The solution was evaporated to dryness. The residue was dissolved in dichloromethane and the solution concentrated to 10 mL. Silica gel chromatography using dichloromethane and hexane (1:1) gave compound **6** in 83% (0.113 g) yield.

Crystal Structure Determination of 2−6. The single crystals of **2−5** for X-ray diffraction analyses were grown by slow evaporation of their respective dichloromethane solutions layered with hexane, whereas those of **6** were obtained from slow evaporation of its dichloromethane solution layered with acetonitrile at 0 °C. Crystals of **2−6** were mounted on a glass fiber for data collection by using Mo Kα radiation on an Enraf-Nonius CAD4 diffractometer at room temperature. Details of the data collection parameters are given in Table 1.

Cell parameters were refined from 25 reflections in 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 on the basis of azimuthal scans of three reflections. The structures were solved by direct methods. The Flack parameters of **2** and **5** are −0.004(13) and 0.014(11), confirming that the correct absolute structures have been refined. The atomic and isotropic thermal parameters for all hydrogen atoms were fixed. The NRCSDP[31] program was used on a VAX workstation for structure refinement.

Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and all bond distances and angles for **2−6**; these data are also available in electronic form as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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