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Sulfur-Bridged Early–Late Heterobimetallics Synthesized by Incorporation of Titanium, Vanadium, and Molybdenum into Bis(hydrosulfido) Templates of Group 9 Metals

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Reactions of the bis(hydrosulfido) complexes [Cp*Rh(SH)$_2$(PMe$_3$)] (**1a**; Cp* = η^5-C$_5$Me$_5$) with [CpTiCl$_3$] (Cp = η^5-C$_5$H$_5$) and [TiCl$_4$(thf)$_2$] in the presence of triethylamine led to the formation of the sulfido-bridged titanium–rhodium complexes [Cp*Rh(PMe$_3$)(μ_2-S)$_2$TiClCp] (**2a**) and [Cp*Rh(PMe$_3$)(μ_2-S)$_2$TiCl$_2$] (**3a**), respectively. Complex **3a** and its iridium analogue **3b** were further converted into the bis(acetylacetonato) complexes [Cp*M(PMe$_3$)(μ_2-S)$_2$Ti(acac)$_2$] (**4a**, M = Rh; **4b**, M = Ir) upon treatment with acetylacetone. The hydrosulfido complexes **1a** and [Cp*Ir(SH)$_2$(PMe$_3$)] (**1b**) also reacted with [VCl$_3$(thf)$_3$] and [Mo(CO)$_4$(nbd)] (nbd = 2,5-norbornadiene) to afford the cationic sulfido-bridged VM$_2$ complexes [{Cp*M(PMe$_3$)(μ_2-S)$_2$}$_2$V]$^+$ (**5a**$^+$, M = Rh; **5b**$^+$, M = Ir) and the hydrosulfido-bridged MoM complexes [Cp*M(PMe$_3$)(μ_2-SH)$_2$Mo(CO)$_4$] (**6a**, M = Rh; **6b**, M = Ir), respectively.

Current interest in early–late heterobimetallic (ELHB) complexes stems from the expectation for their unique structures and cooperative reactivities originated from the combination of electropositive early metals and electron-rich late metals.[1,2] These properties have motivated development of systematic synthetic methods for this class of compounds, exemplified by adduct formation of thiolato and phosphido complexes toward heterometal complexes having labile ligands. With regard to the preparation of sulfur-bridged ELHB complexes, recent investigations of hydrosulfido complexes[3–11] have revealed that they behave as potential sulfur metalloligands for the preparation of sulfur-bridged polynuclear complexes.[3–9] For example, the bis(hydrosulfido) complex [Cp$_2$Ti(SH)$_2$] (Cp = η^5-C$_5$H$_5$) reacts with a late

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metal complex [$(Cp^*Ru)_4(\mu_3\text{-}Cl)_4$] ($Cp^* = \eta^5\text{-}C_5Me_5$) to afford the hydrosulfido-bridged ELHB complex [$Cp_2Ti(\mu_2\text{-}SH)_2RuClCp^*$], which is further converted into the cubane-type sulfido cluster [$(CpTi)_2(Cp^*Ru)_2(\mu_3\text{-}S)_4$] upon treatment with a base.[6] Still, little is known about the incorporation reactions of group 4 and 5 metals into the M−SH functionality.[11] We recently reported that the bis(hydrosulfido)iridium complex [$Cp^*Ir(SH)_2(PMe_3)$] (**1b**) reacts with titanium complexes [$CpTiCl_3$] and [$TiCl_4(thf)_2$] in the presence of triethylamine to form the sulfido-bridged ELHB complexes [$Cp^*Ir(PMe_3)(\mu_2\text{-}S)_2TiClX$] (**2b**, X = Cp; **3b**, X = Cl).[7] To expand the scope of this synthetic method using the mononuclear bis(hydrosulfido) complex **1b**, we have investigated here the reactions of group 4−6 metal complexes with the rhodium complex [$Cp^*Rh(SH)_2(PMe_3)$] (**1a**) as well as **1b**, which led to the formation of a series of sulfur-bridged ELHB complexes containing both these early metals and group 9 metals. Formation of acetylacetonato complexes from the titanium−group 9 metal complexes **3** and acetylacetone is also described.

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of nitrogen by using standard Schlenk techniques. Solvents were dried by refluxing over Na/benzophenone ketyl (THF, toluene, benzene, and hexanes), $Mg(OMe)_2$ (methanol), or P_2O_5 (dichloromethane) and distilled before use. Triethylamine was distilled from KOH, whereas acetylacetone was used as received. Complexes **1**,[12,13] [$TiCl_4(thf)_2$],[14] [$VCl_3(thf)_3$],[14] and [$Mo(CO)_4(nbd)$] (nbd = 2,5-norbornadiene)[15] were prepared according to the literature. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL EX-270 or LA-400 spectrometer; chemical shifts are referenced to the signals of the residual nondeuterated chloroform at δ 7.26 or benzene at δ 7.16 (^1H) and PPh_3 in $CDCl_3$ at δ −5.65 (85% H_3PO_4 = δ 0.0; ^{31}P). IR spectra were recorded on a Shimadzu 8100 spectrometer. Electrochemical measurements were made with a BAS CV-50W electrochemical analyzer using a glassy carbon working electrode. Potentials were measured in dichloromethane−0.1 M $Bu^n_4NBF_4$ vs a saturated calomel electrode as reference with the scan rate of 200 mV s^{-1}. Elemental analyses were performed on a Perkin-Elmer 2400II CHN analyzer.

Preparation of [$Cp^*Rh(PMe_3)(\mu_2\text{-}S)_2TiClCp$] (2a). To a THF (7 mL) solution of **1a** (78.3 mg, 0.208 mmol) was added triethylamine (57 μL, 0.41 mmol) and [$CpTiCl_3$] (45.1 mg, 0.206 mmol), and the mixture was stirred overnight at room temperature. After removal of the solvent in vacuo, the resultant orange solid was washed with methanol (12 mL). Subsequent recrystallization from dichloromethane−hexanes (4 mL/15 mL) afforded **2a** as orange crystals (79.1 mg, 73%). ^1H NMR (δ, $CDCl_3$): 6.31 (s, 5H, C_5H_5), 1.97 (d, $^4J_{PH}$ = 3.4 Hz, 15H, C_5Me_5), 1.20 (d, $^2J_{PH}$ = 10.7 Hz, 9H, PMe_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 6.5 (d, $^1J_{RhP}$ = 149.5 Hz). Anal. Calcd for $C_{18}H_{29}ClPRhS_2Ti$: C, 41.04; H, 5.55. Found: C, 40.76; H, 5.57.

Preparation of [$Cp^*Rh(PMe_3)(\mu_2\text{-}S)_2TiCl_2$] (3a). To a solution of **1a** (42.0 mg, 0.110 mmol) in THF (5 mL) was added triethylamine (32 μL, 0.23 mmol) and [$TiCl_4(thf)_2$] (38.0 mg, 0.114 mmol) at −78 °C, and the mixture was slowly warmed to room temperature with stirring. After removal of the solvent in vacuo, the resultant dark red residue was extracted with benzene (13 mL). The extract was evaporated to dryness in vacuo and recrystallized from dichloromethane−hexanes (2 mL/10 mL). The orange crystals that formed were filtered off and dried in vacuo (25.0 mg, 45%). ^1H NMR (δ, $CDCl_3$): 1.87 (d, $^4J_{PH}$ = 3.0 Hz, 15H, C_5Me_5), 1.41 (d, $^2J_{PH}$ = 10.7 Hz, 9H, PMe_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 5.2 (d, $^1J_{RhP}$ = 146.5 Hz). Anal. Calcd for $C_{13}H_{24}Cl_2PRhS_2Ti$: C, 31.41; H, 4.87. Found: C, 31.38; H, 4.98.

Preparation of [$Cp^*Rh(PMe_3)(\mu_2\text{-}S)_2Ti(acac)_2$] (4a). To a THF (5 mL) solution of **3a** (39.0 mg, 0.078 mmol) was added acetylacetone (20 μL, 0.20 mmol) and then triethylamine (25 μL, 0.18 mmol) at room temperature. The resultant red solution was stirred for 2 h. After removal of the solvent in vacuo, the red residue was recrystallized from toluene−hexanes (2 mL/12 mL) at −78 °C. The dark red crystals that formed were filtered off and dried in vacuo (30.8 mg, 63%). ^1H NMR (δ, C_6D_6): 5.47, 5.41 (s, 1H each, C*H*(COMe)$_2$), 1.94 (s, 3H, COMe), 1.83 (s, 9H, COMe), 1.64 (s, 15H, C_5Me_5), 1.27 (d, $^2J_{PH}$ = 10.7 Hz, 9H, PMe_3). $^{31}P\{^1H\}$ NMR (δ, C_6D_6): 6.0 (d, $^1J_{RhP}$ = 152.6 Hz). Anal. Calcd for $C_{23}H_{38}O_4PRhS_2Ti$: C, 44.24; H, 6.13. Found: C, 44.39; H, 6.19.

Preparation of [$Cp^*Ir(PMe_3)(\mu_2\text{-}S)_2Ti(acac)_2$] (4b). This complex was obtained from **3b** in a manner similar to that for **4a**. Yield: 34%. ^1H NMR (δ, C_6D_6): 5.49, 5.42 (s, 1H each, C*H*(COMe)$_2$), 1.87−1.90 (m, 9H, COMe), 1.79 (s, 3H, COMe), 1.64 (s, 15H, C_5Me_5), 1.36 (d, $^2J_{PH}$ = 10.7 Hz, 9H, PMe_3). $^{31}P\{^1H\}$ NMR (δ, C_6D_6): −31.5 (s). Anal. Calcd for $C_{23}H_{38}IrO_4PS_2Ti$: C, 38.70; H, 5.37. Found: C, 38.74; H, 5.50.

Preparation of [$\{Cp^*Rh(PMe_3)(\mu_2\text{-}S)_2\}_2V$][$BPh_4$] ($5a^+BPh_4^-$). To a solution of [$VCl_3(thf)_3$] (57.1 mg, 0.153 mmol) in THF (5 mL) was added triethylamine (90 μL, 0.65 mmol) and **1a** (116.6 mg, 0.306 mmol) at −78 °C, and the mixture was slowly warmed to room temperature with stirring. After removal of the solvent in vacuo, the dark green residue was dissolved in dichloromethane (5 mL), and then a solution of $NaBPh_4$ (53.6 mg, 0.157 mmol) in water (5 mL) was added to the dichloromethane solution. After the mixture was stirred for 3 h, the aqueous layer was removed by a syringe and the organic layer was evaporated in vacuo. Recrystallization of the residue from dichloromethane−hexanes (2 mL/10 mL) afforded dark green crystals of $\mathbf{5a}^+BPh_4^-$ (113.3 mg, 66%). ^1H NMR (δ, $CDCl_3$): 7.43−6.87 (m, 20H, BPh_4), 1.93 (d, $^4J_{PH}$ = 2.9 Hz, 30H, C_5Me_5), 1.35 (d, $^2J_{PH}$ = 10.7 Hz, 18H, PMe_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 6.8 (d, $^1J_{RhP}$ = 146.5 Hz). Anal. Calcd for $C_{50}H_{68}BP_2Rh_2S_4V$: C, 53.29; H, 6.08. Found: 52.91; H, 6.36.

Preparation of [$\{Cp^*Ir(PMe_3)(\mu_2\text{-}S)_2\}_2V$][$BPh_4$] ($5b^+BPh_4^-$). This complex was obtained from **1b** in a manner similar to that for $\mathbf{5a}^+BPh_4^-$. Yield: 90%. ^1H NMR (δ, $CDCl_3$): 7.44−6.90 (m, 20H, BPh_4), 2.09 (d, $^4J_{PH}$ = 2.0 Hz, 30H, C_5Me_5), 1.47 (d, $^2J_{PH}$ = 10.7 Hz, 18H, PMe_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): −25.5 (s). Anal. Calcd for $C_{50}H_{68}BIr_2P_2S_4V$: C, 46.00; H, 5.25. Found: C, 46.13; H, 5.40.

Preparation of [$Cp^*Rh(PMe_3)(\mu_2\text{-}SH)_2Mo(CO)_4$] (6a). A mixture of **1a** (96.0 mg, 0.252 mmol) and [$Mo(CO)_4(nbd)$] (83.0 mg, 0.277 mmol) in THF (10 mL) was stirred overnight at room temperature. The resultant dark red solution was evaporated to dryness, and the residue was recrystallized from dichloromethane−hexanes (4 mL/15 mL) at −78 °C. The dark red crystals that formed were filtered off and dried in vacuo (114.1 mg, 77%). ^1H NMR (δ, $CDCl_3$): 1.77 (d, $^2J_{PH}$ = 10.3 Hz, 9H, PMe_3), 1.70 (d, $^4J_{PH}$ = 2.9 Hz, 15H, C_5Me_5), −2.32 (d, $^3J_{PH}$ = 8.3 Hz, 2H, SH). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 7.9 (d, $^1J_{RhP}$ = 140.7 Hz). IR (cm^{-1}, KBr): 2552 (w,

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Table 1. X-ray Crystallographic Data for **2a**, **3a**, **4a**, **5b**$^+$BPh$_4^-$, and **6b**

	2a	**3a**	**4a**	**5b**$^+$BPh$_4^-$	**6b**
formula	$C_{18}H_{29}ClPRhS_2Ti$	$C_{13}H_{24}Cl_2PRhS_2Ti$	$C_{23}H_{38}O_4PRhS_2Ti$	$C_{50}H_{68}BIr_2P_2S_4V$	$C_{17}H_{26}IrMoO_4PS_2$
fw	526.78	497.14	624.45	1305.47	677.64
space group	*Cc* (No. 9)	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	17.275(4)	9.202(4)	12.445(4)	9.639(2)	8.562(4)
b, Å	8.371(3)	13.931(4)	20.437(5)	17.274(4)	13.406(4)
c, Å	16.143(3)	15.658(4)	11.144(3)	32.559(6)	20.309(3)
α, deg	90	90	90	82.58(2)	90
β, deg	112.95(1)	90.56(3)	90	83.45(2)	97.24(2)
γ, deg	90	90	90	85.35(2)	90
V, Å^3	2149(1)	2007(1)	2834(1)	5328(1)	2312(1)
Z	4	4	4	4	4
ρ_{calcd}, g cm^{-3}	1.628	1.645	1.463	1.627	1.946
μ(Mo Kα), cm^{-1}	15.29	17.61	10.91	53.78	65.73
R^a	0.023	0.033	0.048	0.047	0.030
R_w^b	0.033	0.032	0.047	0.047	0.031

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, $w = [\sigma_c^2(F_o) + p^2F_o^2/4]^{-1}$ (p = 0.017 (**2a**), 0.018 (**3a**), 0.020 (**4a**), 0.025 (**5b**$^+$BPh$_4^-$), 0.015 (**6b**)) with $\sigma_c(F_o)$ from counting statistics.

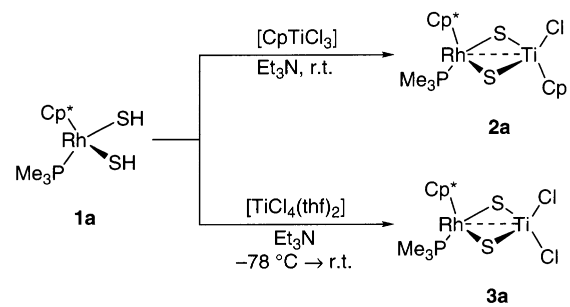
ν_{SH}), 2002, 1881, 1852, 1821 (s, ν_{CO}). Anal. Calcd for $C_{17}H_{26}MoO_4PRhS_2$: C, 34.70; H, 4.45. Found: C, 34.57; H, 4.44.

Preparation of [Cp*Ir(PMe$_3$)(μ_2-SH)$_2$Mo(CO)$_4$] (6b). This complex was obtained from **1b** in a manner similar to that for **6a**. Yield: 49%. ^{1}H NMR (δ, $CDCl_3$): 1.85 (d, $^2J_{PH}$ = 10.3 Hz, 9H, PMe$_3$), 1.76 (d, $^4J_{PH}$ = 2.0 Hz, 15H, C_5Me_5), −1.88 (d, $^3J_{PH}$ = 8.3 Hz, 2H, SH). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): −32.5 (s). IR (cm^{-1}, KBr): 2529 (w, ν_{SH}), 2004, 1879, 1864, 1817 (s, ν_{CO}). Anal. Calcd for $C_{17}H_{26}IrMoO_4PS_2$: C, 30.13; H, 3.87. Found: C, 29.97; H, 3.85.

X-ray Diffraction Studies. Single crystals suitable for X-ray analyses were sealed in glass capillaries under an inert atmosphere and mounted on a Rigaku AFC7R four-circle diffractometer equipped with a graphite-monochromatized Mo Kα source (λ = 0.710 69 Å). Orientation matrixes and unit cell parameters were determined by least-squares treatment of 25 machine-centered reflections with 25° < 2θ < 40°. The data collection was performed at 294 K using the $\omega-2\theta$ scan (except for **5b**$^+$BPh$_4^-$) or ω-scan (for **5b**$^+$BPh$_4^-$) technique at a rate of 32° min^{-1} to a maximum 2θ value of 55°. The intensities of three check reflections were monitored every 150 reflections during data collection, which revealed no significant decay except for **3a**. For **3a**, a steady decrease (6.07%) of the intensities was observed, and a correction of the decay was applied. Intensity data were corrected for Lorentz−polarization effects and for absorption (ψ scans). Details of crystal and data collection parameters are summarized in Table 1.

Structure solution and refinements were carried out by using the teXsan program package.[16] The heavy-atom positions were determined by a Patterson method program (DIRDIF92-PATTY[17]), and the remaining non-hydrogen atoms were found by subsequent Fourier syntheses. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques (based on *F*). The hydrosulfido hydrogen atoms in **6b** were found in the final difference Fourier map, whereas all other hydrogen atoms were placed at calculated positions; they were included in the final stages of the refinements with fixed parameters. The absolute structures of **2a** and **4a** were determined on the basis of the Flack absolute structure parameters.[18] The atomic scattering factors were taken from ref 19, and anomalous dispersion effects were included; the values of $\Delta f'$ and $\Delta f''$ were taken from ref 20.

Scheme 1



Results and Discussion

Synthesis of Sulfido-Bridged Titanium−Rhodium Complexes 2a and 3a. To elucidate the synthetic versatility of the bis(hydrosulfido) complexes **1** for sulfido-bridged ELHB complexes, we first examined the reactions of the bis(hydrosulfido)rhodium complex **1a** with chlorotitanium complexes. As observed for the iridium analogue **1b**,[7] the reactions of **1a** with [CpTiCl$_3$] and [TiCl$_4$(thf)$_2$] smoothly took place to afford the sulfido-bridged titanium−rhodium complexes [Cp*Rh(PMe$_3$)(μ_2-S)$_2$TiClX] (**2a**, X = Cp; **3a**, X = Cl), respectively (Scheme 1). Use of triethylamine is necessary to suppress the formation of the chloride-transfer product [Cp*RhCl$_2$(PMe$_3$)]. Complexes **2a** and **3a** have been shown to possess essentially the same structures as their iridium analogues **2b** and **3b** by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy along with X-ray crystallography (Figure 1 and Table 2); the structural details will be discussed below. The absence of the hydrosulfido groups in **2a** and **3a** has been confirmed by IR spectroscopy. The synthetic application of **1a** for mixed-metal complexes has been limited in the literature; the only reactant reported so far is an imido complex [Cp*Ir(≡NBu^t)], which gives the sulfido-bridged rhodium−iridium complex [Cp*Rh(PMe$_3$)(μ_2-S)$_2$IrCp*] with elimination of *tert*-butylamine.[13]

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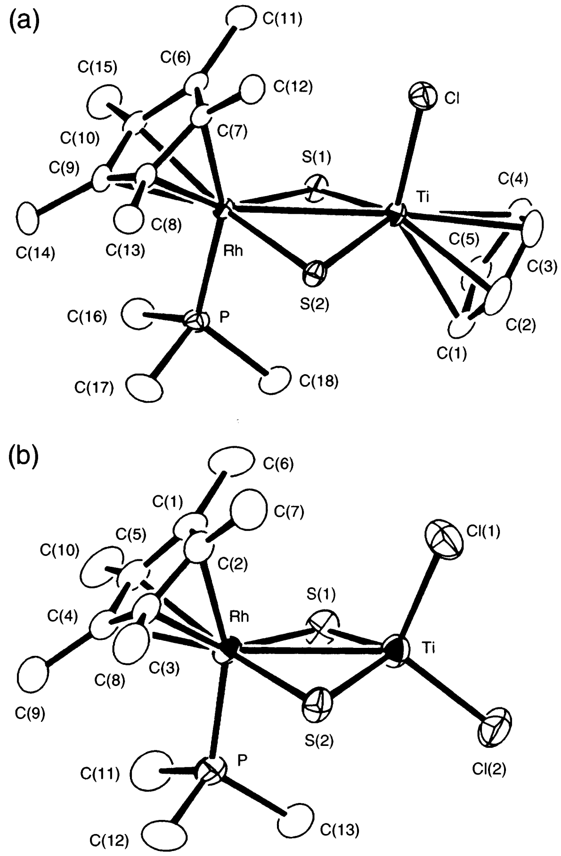


Figure 1. Structures of (a) **2a** and (b) **3a**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

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

	2a	3a
Ti–Rh	2.9930(9)	2.927(1)
Ti–S(1)	2.248(2)	2.191(1)
Ti–S(2)	2.246(2)	2.195(2)
Ti–Cl_A[a]	2.335(2)	2.261(2)
Ti–Cl(2)		2.257(2)
Rh–S(1)	2.397(1)	2.382(1)
Rh–S(2)	2.391(1)	2.387(1)
Rh–P	2.280(2)	2.295(1)
Ti–S(1)–Rh	80.16(5)	79.49(4)
Ti–S(2)–Rh	80.34(5)	79.31(4)
S(1)–Ti–S(2)	100.35(6)	104.19(5)
S(1)–Ti–Cl_A[a]	105.17(7)	110.89(6)
S(2)–Ti–Cl_A[a]	106.72(7)	109.94(6)
S(1)–Ti–Cl(2)		111.16(6)
S(2)–Ti–Cl(2)		112.52(6)
Cl(1)–Ti–Cl(2)		108.15(7)

[a] Cl_A = Cl (**2a**) or Cl(1) (**3a**).

Reactions of 3 with Acetylacetone To Give Acetylacetonato Complexes 4. When the ELHB complexes **3** having a Cp-free titanium center were treated with acetylacetone in the presence of an excess of triethylamine, the bis(acetylacetonato) complexes **4** were obtained (eq 1). In the ^1H NMR spectra, the acac ligands in **4** give rise to two singlets with an equal intensity in the vinyl region and ill-resolved singlets in the methyl region. Signals ascribed to the Cp* and PMe_3 ligands are also observed. These spectral features suggest that two chemically inequivalent acac ligands bind to the sulfido-bridged heterobimetallic core in **4** at the titanium center, as expected from the oxophilic nature of titanium.

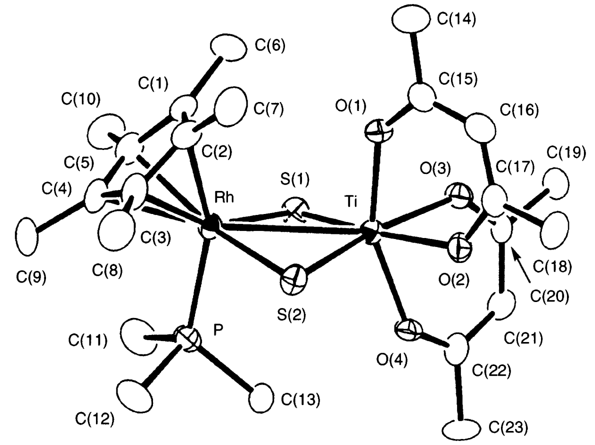
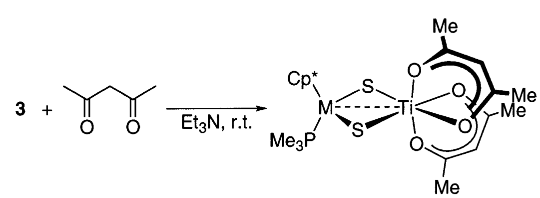


Figure 2. Structure of **4a**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **4a**

Ti–Rh	3.025(2)	Ti–O(3)	2.152(6)
Ti–S(1)	2.273(3)	Ti–O(4)	2.035(7)
Ti–S(2)	2.266(3)	Rh–S(1)	2.373(3)
Ti–O(1)	2.009(7)	Rh–S(2)	2.378(3)
Ti–O(2)	2.134(8)	Rh–P	2.274(3)
Ti–S(1)–Rh	81.22(10)	S(2)–Ti–O(3)	170.5(2)
Ti–S(2)–Rh	81.2(1)	S(2)–Ti–O(4)	94.4(2)
S(1)–Ti–S(2)	99.4(1)	O(1)–Ti–O(2)	82.5(3)
S(1)–Ti–O(1)	98.2(2)	O(1)–Ti–O(3)	81.8(3)
S(1)–Ti–O(2)	168.5(2)	O(1)–Ti–O(4)	156.3(3)
S(1)–Ti–O(3)	89.4(2)	O(2)–Ti–O(3)	79.3(3)
S(1)–Ti–O(4)	97.6(2)	O(2)–Ti–O(4)	78.5(3)
S(2)–Ti–O(1)	100.3(2)	O(3)–Ti–O(4)	80.8(3)
S(2)–Ti–O(2)	91.8(2)		

The octahedral *cis*-{TiX_2(*β*-diketonato)$_2$}-type core has been well-documented;[21] typical examples include a dithiolato complex [$Ti(S_2C_6H_3Me\text{-}4)(acac)_2$].[22] On the other hand, complexes **2** having a Cp ligand at the titanium atom did not react with acetylacetone under the same conditions.



(1)

4a: M = Rh; **4b**: M = Ir

To elucidate the detailed structure of the acetylacetonato complexes **4**, an X-ray analysis of the titanium–rhodium complex **4a** has been carried out; the molecular structure of **4a** is depicted in Figure 2, and selected interatomic distances are listed in Table 3. In contrast to the parent complexes **3**, the coordination geometry of the titanium center with two acac ligands in **4a** is distorted octahedral with the O(1)–Ti–O(4) angle of 156.3(3)°, for example. The bite angles of the two chelating acac ligands are 82.5(3) and 80.8(3)°. It is to be noted that the Ti–O distances trans to the Ti–S

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(22) Douek, J. A.; Spickett, J. T. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1470–1472.

bonds (2.143 Å (mean)) are much longer than the other Ti−O distances (2.022 Å (mean)), indicating the stronger trans influence of the bridging sulfido ligands. Similar distortion from the regular octahedral geometry as well as the trans influence of the bridging ligands is observed in a related oxo-bridged complex [{(acac)$_2$Ti}$_2$(μ_2-O)$_2$].[23,24] Within the acac ligands in **4a**, significant C−C and C−O bond alternation is not observed. The structural details of the Ti(μ_2-S)$_2$-Rh core in **4a** along with those in **2a** and **3a** will be described in the following section.

Structural Comparison of Sulfido-Bridged Titanium−Rhodium Complexes 2a−4a. It is of interest to compare the Ti(μ_2-S)$_2$Rh core structures in **2a**−**4a**, because the titanium centers in these complexes have different coordination geometries and formal electron counts. As listed in Tables 2 and 3, the bond distances around the titanium center lie in the order of **3a** < **2a** < **4a**. In particular, the Ti−S distances in **3a** (2.193 Å (mean)) are much shorter than those in a related tetrahedral thiolato complex [Ti(SC$_6$HMe$_4$-2,3,5,6)$_4$] (2.292 Å (mean))[25] and comparable to the Ti=S double-bond lengths (2.111−2.217(1) Å).[26] The Ti−S distances in **2a** and **4a** (2.247 and 2.270 Å (mean)) are somewhat longer than these double bond lengths but still indicate some donation of lone pair electrons from the sulfur atoms. With regard to the Ti−Cl bonds, the Ti−Cl lengths in the tetrahedral complex **3a** (2.259 Å (mean)) are shorter than that in the three-legged piano-stool complex **2a** (2.335(2) Å). The Ti−Rh distances of **2a**−**4a** (2.927(1)−3.025(2) Å) fall in the range of those found in related sulfur-bridged titanium−rhodium complexes (2.8779(7)−3.056(1) Å)[27] and suggest the presence of an Rh→Ti dative bond. Due to these Ti−Rh interactions, the Ti−S−Rh angles are acute (mean angles: 80.3 (**2a**), 79.4 (**3a**), 81.2° (**4a**)). When the dative bonds are taken into consideration, the formal electron count of the titanium center is 10 (**3**) or 14 (**2** and **4**). The short bond distances around the titanium atom in **3a** are thus explained by significantly electron-deficient nature of the titanium atom.

The TiRhS$_2$ faces in **2a**−**4a** are slightly folded around the Ti−Rh vector. The dihedral angles (**2a**, 153.96(9); **3a**, 160.47(7); **4a**, 158.5(1)°) are comparable to those found in the corresponding iridium complexes **2b** and **3b** (154.2(2) and 159.9(1)°).[7]

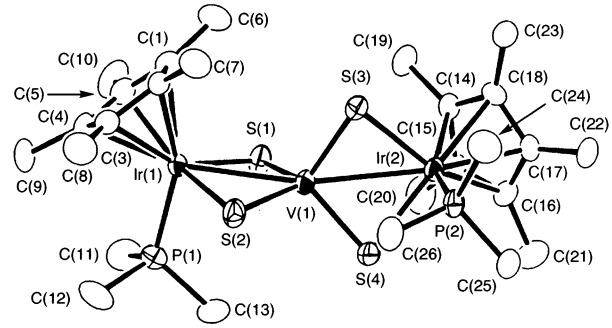
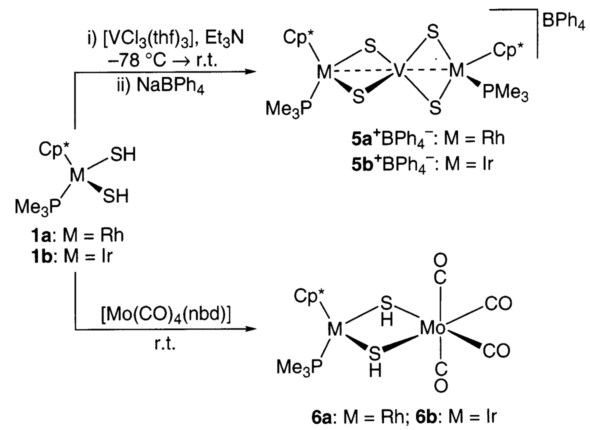


Figure 3. Structure of one of the two crystallographically independent **5b**$^+$ cations (cation 1). Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Scheme 2



Synthesis and Structures of Sulfido-Bridged Vanadium−Group 9 Metal Complexes 5$^+$. Unlike the formation of dinuclear complexes **2** and **3**, the cationic, linear trinuclear complexes [{Cp*M(PMe$_3$)(μ_2-S)$_2$}$_2$V]$^+$ (**5a**$^+$, M = Rh; **5b**$^+$, M = Ir) were exclusively formed when complexes **1** were treated with [VCl$_3$(thf)$_3$] at any molar ratio (Scheme 2). As expected, the reaction carried out in a V:M ratio of 1:2 and subsequent anion metathesis using NaBPh$_4$ gave analytically pure BPh$_4$ salt **5**$^+$BPh$_4$$^-$ in good yield. During the formation of **5**$^+$, vanadium is oxidized from V(III) to V(V). Indeed, hydrogen gas evolution has been confirmed by a GC analysis of the reaction mixture, although the yield was low (ca. 10%). An X-ray analysis of **5b**$^+$BPh$_4$$^-$ has established the trinuclear structure of **5**$^+$. The unit cell contains two crystallographically independent **5b**$^+$ cations, whose structures are essentially identical. The structure of one of these cations is shown in Figure 3, and selected interatomic distances and angles are listed in Table 4. The cation has an approximate C_2 axis passing through the vanadium atom, which adopts a distorted tetrahedral geometry with the S−V−S angles of 105.6(1)−114.2(1)°. The mean V−S distance of 2.170 Å is comparable to that found in thiovanadate anion (2.154 (ammonium salt)[28] and 2.157 Å (lithium salt)[29]). The V−Ir distances (2.850 Å

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Table 4. Selected Bond Distances and Angles for $\mathbf{5b}^+BPh_4^-$

cation 1		cation 2	
Bond Distances (Å)			
V(1)−Ir(1)	2.852(2)	V(2)−Ir(3)	2.851(2)
V(1)−Ir(2)	2.849(2)	V(2)−Ir(4)	2.846(2)
V(1)−S(1)	2.173(3)	V(2)−S(5)	2.166(3)
V(1)−S(2)	2.181(3)	V(2)−S(6)	2.167(3)
V(1)−S(3)	2.174(3)	V(2)−S(7)	2.168(3)
V(1)−S(4)	2.161(3)	V(2)−S(8)	2.172(3)
Ir(1)−S(1)	2.373(3)	Ir(3)−S(5)	2.370(2)
Ir(1)−S(2)	2.369(3)	Ir(3)−S(6)	2.371(3)
Ir(2)−S(3)	2.384(3)	Ir(4)−S(7)	2.370(3)
Ir(2)−S(4)	2.373(3)	Ir(4)−S(8)	2.383(3)
Ir(1)−P(1)	2.270(3)	Ir(3)−P(3)	2.278(3)
Ir(2)−P(2)	2.298(3)	Ir(4)−P(4)	2.291(3)
Bond Angles (deg)			
Ir(1)−V(1)−Ir(2)	164.13(6)	Ir(3)−V(2)−Ir(4)	159.25(7)
V(1)−S(1)−Ir(1)	77.57(9)	V(2)−S(5)−Ir(3)	77.74(9)
V(1)−S(2)−Ir(1)	77.50(9)	V(2)−S(6)−Ir(3)	77.69(9)
V(1)−S(3)−Ir(2)	77.23(9)	V(2)−S(7)−Ir(4)	77.5(1)
V(1)−S(4)−Ir(2)	77.71(9)	V(2)−S(8)−Ir(4)	77.2(1)
S(1)−V(1)−S(2)	106.4(1)	S(5)−V(2)−S(6)	106.2(1)
S(1)−V(1)−S(3)	114.2(1)	S(5)−V(2)−S(7)	113.5(1)
S(1)−V(1)−S(4)	108.3(1)	S(5)−V(2)−S(8)	108.6(1)
S(2)−V(1)−S(3)	110.9(1)	S(6)−V(2)−S(7)	111.4(1)
S(2)−V(1)−S(4)	110.1(1)	S(6)−V(2)−S(8)	111.5(1)
S(3)−V(1)−S(4)	106.9(1)	S(7)−V(2)−S(8)	105.6(1)

(mean)) as well as the acute V−S−Ir angles (77.5° (mean)) indicate the presence of Ir→V dative bonds. The Ir(μ_2-S)$_2$V(μ_2-S)$_2$Ir core deviates from the linearity with the Ir−V−Ir angles of 161.7° (mean), and the $VIrS_2$ faces are folded by 159.3° (mean) along the V−Ir vectors. The geometric parameters around the three-legged piano-stool iridium centers in $\mathbf{5b}^+$ do not differ significantly from those in **2b** and **3b**.[7] Recently, a thiolato-bridged linear trinuclear complex [V{Ir(aet)$_3$}$_2$](ClO$_4$)$_3$ (aet = 2-aminoethanethiolato) containing an octahedral V(III) center has been reported;[30] the triply bridged V−Ir distances are 2.7754 Å (mean).

In agreement with the solid-state structure described above, the ^{1}H and ^{31}P{^{1}H} NMR spectra of $\mathbf{5}^+$ exhibit only one set of signals for the Cp* and PMe_3 ligands. The ^{1}H NMR as well as IR spectra also shows the absence of hydrosulfido ligands in $\mathbf{5}^+$. The cyclic voltammograms of the cationic complexes $\mathbf{5}^+$ are featured by a reversible one-electron reduction wave at −1.15 V ($\mathbf{5a}^+$) or −1.24 V ($\mathbf{5b}^+$) vs saturated calomel electrode. It is to be noted that most of the trinuclear complexes with linear M_3(μ_2-S)$_4$ cores reported thus far are derived from tetrathiomolybdate and tetrathiotungstate anions,[31] and the only precedent for these types of complexes having vanadium as the central atom is (Me_4N)$_3$[{Cl_2Fe(μ_2-S)$_2$}$_2$V],[28] which is synthesized from tetrathiovanadate anion.

Synthesis and Structures of Hydrosulfido-Bridged Molybdenum−Group 9 Metal Complexes 6. To extend the metals captured by **1** to group 6 metals, we next attempted the synthesis of sulfur-bridged molybdenum−group 9 metal complexes. Although we could not isolate any sulfido-bridged ELHB complex from the reactions of **1** with [MoCl$_3$(thf)$_3$], the metalladithiol adducts of molybdenum [Cp*M(PMe$_3$)(μ_2-SH)$_2$Mo(CO)$_4$] (**6a**, M = Rh; **6b**, M = Ir) were successfully obtained when complexes **1** were treated with a molybdenum(0) complex [Mo(CO)$_4$(nbd)] (Scheme 2). In contrast to the sulfido-bridged complexes **2**−$\mathbf{5}^+$, the ^{1}H NMR spectra of **6** exhibit hydrosulfido resonances around −2 ppm as a doublet coupled with the phosphorus nucleus; the $^3J_{PH}$ value of 8.3 Hz is comparable to those reported for other hydrosulfido complexes.[3] No fluxional behavior of the hydrosulfido ligands in solution was observed from −60 °C to room temperature. The presence of the hydrosulfido ligands is also supported by the IR spectra, which display an S−H stretching band at 2552 (**6a**) or 2529 (**6b**) cm^{-1}.

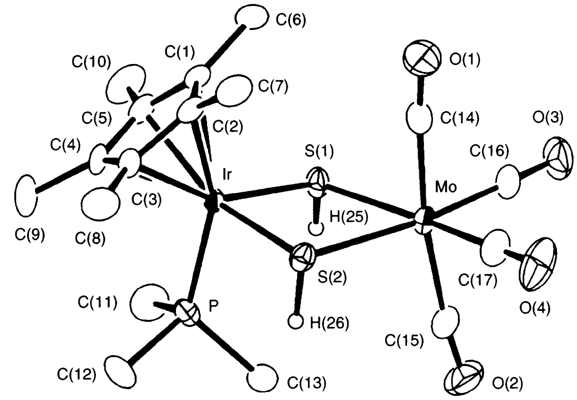

Figure 4. Structure of **6b**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms except for the hydrosulfido hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Distances (Å) and Angles (deg) for **6b**

Mo−Ir	3.796(1)	C(15)−O(2)	1.145(8)
Mo−S(1)	2.603(2)	C(16)−O(3)	1.165(8)
Mo−S(2)	2.629(2)	C(17)−O(4)	1.150(8)
Mo−C(14)	2.007(7)	Ir−S(1)	2.387(2)
Mo−C(15)	2.028(7)	Ir−S(2)	2.390(2)
Mo−C(16)	1.944(7)	Ir−P	2.281(2)
Mo−C(17)	1.955(8)	S(1)−H(25)	1.10
C(14)−O(1)	1.148(8)	S(2)−H(26)	1.18
Mo−S(1)−Ir	98.94(5)	C(14)−Mo−C(15)	171.9(3)
Mo−S(2)−Ir	98.15(5)	C(14)−Mo−C(16)	85.6(3)
S(1)−Mo−S(2)	76.25(5)	C(14)−Mo−C(17)	89.1(3)
S(1)−Mo−C(14)	88.1(2)	C(15)−Mo−C(16)	87.1(3)
S(1)−Mo−C(15)	96.5(2)	C(15)−Mo−C(17)	87.1(3)
S(1)−Mo−C(16)	98.4(2)	C(16)−Mo−C(17)	88.1(3)
S(1)−Mo−C(17)	172.6(2)	Mo−S(1)−H(25)	104.1
S(2)−Mo−C(14)	89.4(2)	Mo−S(2)−H(26)	100.5
S(2)−Mo−C(15)	98.2(2)	Ir−S(1)−H(25)	107.9
S(2)−Mo−C(16)	172.9(2)	Ir−S(2)−H(26)	99.6
S(2)−Mo−C(17)	96.9(2)		

The molecular structure has been confirmed by an X-ray analysis of **6b** (Figure 4; Table 5). The iridium center retains a three-legged piano-stool geometry, whereas the molybdenum center is octahedral. The Mo−Ir distance of 3.796(1) Å as well as the obtuse Mo−S−Ir angles (98.5° (mean)) precludes any metal−metal bonding interaction. The $MoIrS_2$ face in **6b** is slightly flattened in comparison with the Ti−Rh and V−Ir complexes described above; the dihedral angle around the Mo−Ir vector is 163.65(7)°. The two Mo−CO bonds that lie in this $MoIrS_2$ plane (1.950 Å (mean)) are

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slightly shorter than the other Mo−CO bonds (2.018 Å (mean)). The hydrosulfido hydrogen atoms have been found in the final difference Fourier map. In agreement with the ^{1}H NMR spectrum, they lie in mutually syn positions with respect to the $MoIrS_2$ face with the S−H distances of 1.10 and 1.18 Å, which are typical in hydrosulfido complexes (1.0−1.4 Å).[3]

Integration of a $Mo(CO)_4$ moiety into bis(hydrosulfido) or bis(thiolato) templates has some precedents.[32−34] For example, $[Cp_2Ti(SH)_2]$ and $[Cp^*Ir(SPh)_2(CO)]$ react with $[Mo(CO)_4(nbd)]$ to afford the hydrosulfido- and thiolato-bridged heterobimetallic complexes $[Cp_2Ti(\mu_2\text{-SH})_2Mo(CO)_4]$ (**7**)[32] and $[Cp^*Ir(CO)(\mu_2\text{-SPh})_2Mo(CO)_4]$ (**8**),[33] respectively. Unlike **6**, the syn−anti isomerization of the hydrosulfido ligands is observed for the hydrosulfido complex **7**. The IR stretching frequencies for the carbonyl ligands in **6** are comparable to those in the IrMo complex **8** (2011−1827 cm^{-1}) but much lower than those in the TiMo complex **7** (2014 and 1903 cm^{-1}), suggesting that the dative interaction from the d^6 Mo(0) center to the d^0 Ti(IV) center in **7** reduces the electron density on the molybdenum atom.

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In summary, we have revealed that the bis(hydrosulfido) complexes **1** behave as bidentate metalloligands to afford sulfur-bridged ELHB complexes containing group 4−6 and group 9 metals. It is of particular interest that the highly electron-deficient group 4 and 5 metal halides without auxiliary ligands can be used for the synthesis of sulfido-bridged ELHB complexes without formation of polymeric and insoluble sulfides, although the products depend on the metal complexes captured and are not necessarily predictable. In addition, the titanium-centered reactivity of **3** toward acetylacetone has been elicited. Further study will be directed to the development of cooperative reactivities of the metal centers in these ELHB complexes as well as further accumulation of heterometals onto these ELHB complexes, which would provide a rational way to heterotrimetallic sulfido complexes containing three very distinct metals.[8]

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Supporting Information Available: X-ray crystallographic files in CIF format (for **2a**, **3a**, **4a**, **5b**$^{+}BPh_4^{-}$, and **6b**). This material is available free of charge via the Internet at http://pubs.acs.org.

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