Sulfido-Bridged Titanium−Iridium Heterobimetallic Complexes Derived from an Iridium Hydrosulfido Complex

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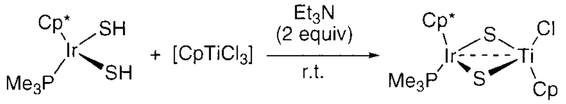
*Summary: Reactions of [Cp*Ir(SH)$_2$(PMe$_3$)] (**1**; Cp* = η^5-C$_5$Me$_5$) with [CpTiCl$_3$] (Cp = η^5-C$_5$H$_5$) and [TiCl$_4$(thf)$_2$] in the presence of triethylamine afforded the sulfido-bridged titanium−iridium heterobimetallic complexes [CpTiCl(μ_2-S)$_2$Ir(PMe$_3$)Cp*] (**2**) and [TiCl$_2$(μ_2-S)$_2$Ir(PMe$_3$)Cp*] (**3**), respectively.*

Introduction

Interest in early−late heterobimetallic (ELHB) complexes has increased in recent years because of the cooperative reactivities of the two distinct metal centers as well as their unique electronic structures originated from the gradient of d orbital energy levels of the two metals.[1] Given that hydrosulfido complexes are inorganic counterparts of thiols, they can be promising building blocks to synthesize sulfur-bridged ELHB complexes.[2] Indeed, hydrosulfido complexes of early transition metals such as [Cp$_2$Ti(SH)$_2$] (Cp = η^5-C$_5$H$_5$) and [Cp*$_2$Zr(SH)$_2$] (Cp* = η^5-C$_5$Me$_5$) react with late transition metal complexes to afford hydrosulfido- or sulfido-bridged ELHB complexes.[3−7] However, the opposite synthetic approach to sulfur-bridged ELHB complexes, i.e., the reaction of late transition metal hydrosulfido complexes with early transition metal complexes, has awaited to be developed. We have already demonstrated that the hydrosulfido-bridged dinuclear complexes of noble metals [Cp*MCl(μ_2-SH)$_2$MClCp*] (M = Ru,[8] Rh, Ir[9]) react with late transition metal complexes to afford a variety of homo- and heterometallic sulfido clusters with higher nuclearity; however, incorporation of early transition metal fragments has not yet been attained. Dobbs and Bergman[10] have synthesized the sulfido-bridged dinuclear complexes [Cp*M(PR$_3$)(μ_2-S)$_2$IrCp*] (M = Rh, R = Me; M = Ir, R = *p*-tolyl) from [Cp*M(SH)$_2$(PR$_3$)] and the iridium imido complex [Cp*Ir(NBu^t)]. In our continuing study on the synthesis and reactivities of sulfur-bridged ELHB complexes containing titanium,[3,4,11] we have now found that the hydrosulfido complex of a late transition metal [Cp*Ir(SH)$_2$(PMe$_3$)] (**1**)[12] reacts with chlorotitanium complexes to give the sulfido-bridged ELHB complexes containing titanium and iridium.

Results and Discussion

Treatment of the bis(hydrosulfido)iridium complex **1** with an equimolar amount of [CpTiCl$_3$] in the presence of 2 equiv of triethylamine afforded the sulfido-bridged titanium−iridium complex [CpTiCl(μ_2-S)$_2$Ir(PMe$_3$)Cp*] (**2**) in 80% yield (eq 1). The ^{1}H NMR spectrum of **2** shows



1 **2** (1)

only one Cp, Cp*, and PMe$_3$ resonances; no hydrosulfido resonance is observed. The absence of the hydrosulfido ligands is also deduced from the lack of the ν_{SH} bands in the IR spectrum. A related reaction of [CpTiCl$_3$] with

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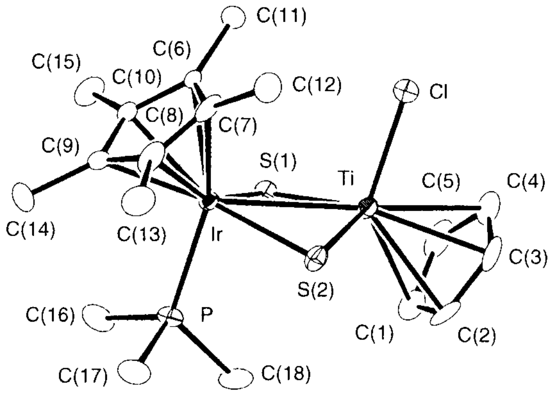


Figure 1. Molecular structure of **2** with atom-numbering scheme. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 2 and 3

	2	**3**
Ti−Ir	2.989(2)	2.899(1)
Ti−S(1)	2.249(4)	2.201(3)
Ti−S(2)	2.248(4)	2.198(3)
Ti−Cl$_A$[a]	2.333(4)	2.256(3)
Ti−Cl(2)		2.252(3)
Ir−S(1)	2.399(3)	2.378(2)
Ir−S(2)	2.403(3)	2.388(2)
Ir−P	2.285(5)	2.285(2)
Ti−S(1)−Ir	80.0(1)	78.44(8)
Ti−S(2)−Ir	79.9(1)	78.30(8)
S(1)−Ti−S(2)	100.9(1)	104.90(9)
S(1)−Ti−Cl$_A$[a]	106.7(1)	109.9(1)
S(2)−Ti−Cl$_A$[a]	105.2(1)	110.7(1)
S(1)−Ti−Cl(2)		111.4(1)
S(2)−Ti−Cl(2)		111.4(1)
Cl(1)−Ti−Cl(2)		108.5(1)

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

1,3-propanedithiol in the presence of imidazole is known to give the dithiolato complex $[\mathrm{Cp\overline{TiCl(SCH_2CH_2CH_2S})}]$.[13]

To confirm the sulfido-bridged heterobimetallic core in **2**, an X-ray analysis has been performed (Figure 1 and Table 1). The molecule has an approximate mirror plane containing the Ti, Ir, Cl, and P atoms. Both titanium and iridium centers adopt three-legged piano-stool geometries. The short Ti−Ir distance (2.989(2) Å) and the acute Ti−S−Ir angles (80.0° (mean)) suggest the presence of an interaction between these metal atoms, probably a dative bond from the d^6 Ir center to the d^0 Ti center. In the related M_4S_3 incomplete cubane-type sulfido cluster $[CpTi(\mu_3\text{-}S)_3Ir_3(\mu_2\text{-}CO)(CO)_3\{P(OMe)_3\}_3]$, two long (3.121 Å (mean)) and one short (2.815 Å (mean)) Ti−Ir distances are observed.[6c] The $TiIrS_2$ face in **2** is puckered with the dihedral angle of 154.2(2)° along the Ti−Ir vector. This distortion seems to allow a closer approach of the metal centers.[14] Complex **2** represents a hybrid of sulfido-bridged homometallic complexes $[Cp_2Ti(\mu_2\text{-}S)_2TiClCp]$[15] and $[Cp^*Ir(PMe_3)(\mu_2\text{-}S)_2IrCp^*]$:[10] the Ti−S (2.249 Å (mean)) and Ir−S (2.401 Å (mean)) distances in **2** are comparable with those found in the corresponding part of these homometallic complexes (Ti−S 2.230 Å; Ir−S 2.340 Å (mean)).

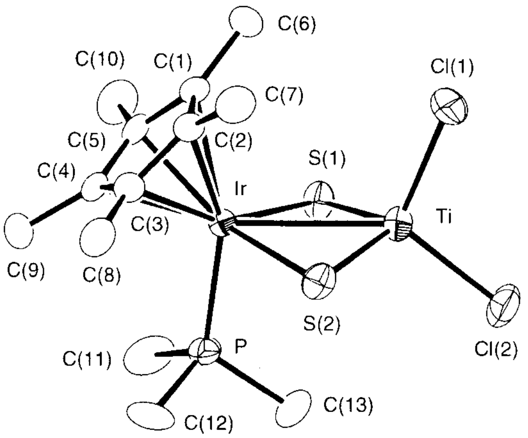
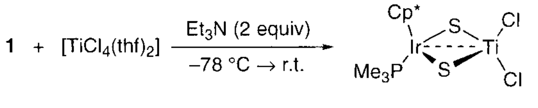


Figure 2. Molecular structure of **3** with atom-numbering scheme. Hydrogen atoms are omitted for clarity.

We have recently demonstrated that the Cp ligand on the $CpTiCl_2$ fragment in the electron-deficient ELHB cubane-type sulfido cluster $[(CpTiCl_2)(CpTi)(Cp^*Ru)_2(\mu_3\text{-}S)_4]$ is replaced by a chloride anion.[3b] Although attempts to substitute the Cp ligand in **2** in a similar manner have failed, the Cp-free titanium−iridium complex $[TiCl_2(\mu_2\text{-}S)_2Ir(PMe_3)Cp^*]$ (**3**) could be synthesized by the reaction of **1** with 1 equiv of $[TiCl_4(thf)_2]$[16] in the presence of triethylamine (eq 2). Spectroscopic data of **3** suggest the absence of hydrosulfido ligands as in the Cp analogue **2**. Furthermore, the detailed structure of **3** has been determined by X-ray crystallography (Figure 2). The titanium center is tetrahedral, and the $Cp^*Ir(PMe_3)S_2$ fragment in **3** is almost superimposable with that in **2**. As in **2**, the $TiIrS_2$ face in **3** is folded with the dihedral angle of 159.9(1)° along the Ti−Ir vector. The Ti−Ir, Ti−S, and Ti−Cl distances in **3** are much shorter than those in the Cp complex **2**, indicating that the absence of a Cp ligand enhances the electron-deficient character of the titanium atom in **3** (Table 1). Indeed, the Ti−S distances in **3** (2.200 Å (mean)) are considerably shorter than those in the related eight-electron thiolato complex $[Ti(SC_6HMe_4\text{-}2,3,5,6)_4]$ (2.292 Å (mean))[17] and even fall in the range of the Ti=S double bonds (2.111−2.217(1) Å) observed in complexes $[Et_4N]_2[Ti(=S)Cl_4]$,[18] $[\{PhC(NSiMe_3)_2\}_2Ti(=S)(py)]$,[19] $[Cp^*_2Ti(=S)(py)]$,[20] and $[Na_4(thf)_8][\{(CpTiS)_2(\mu_2\text{-}S)_2\}_2]$.[21] It is to be noted that the electron-deficient titanium atom loses THF molecules during the formation of **3**; the resultant highly electron-deficient titanium center seems to be stabilized by the Ir→Ti dative bond. Even if this dative bond is taken into consideration, the



(2)

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formal electron count of the titanium center in **3** is only 10, which is unusually small for titanium−sulfur complexes without bulky ligands. Complex **3** also provides a rare example of (chloro)(sulfido)titanium complexes without cyclopentadienyl ligands.[18,22]

In summary, we have rationally prepared sulfido-bridged titanium−iridium ELHB complexes with and without Cp ligand on the titanium atom from the mononuclear iridium hydrosulfido complex **1**. Both complexes have a dative bond from the iridium atom to the electron-deficient titanium atom, and in particular, the highly electron-deficient titanium center in the Cp-free heterobimetallic complex **3** is unique. Further studies of cooperative reactivities on the ELHB complexes **2** and **3** as well as syntheses of sulfido-bridged ELHB complexes from **1** are now in progress.

Experimental Section

General Comments. All manipulations were carried out under nitrogen atmosphere by using standard Schlenk techniques. Solvents were dried by refluxing over Na/benzophenone ketyl (THF, benzene, hexanes) and P_2O_5 (dichloromethane) and distilled before use. Triethylamine was distilled from KOH. ^{1}H NMR and ^{31}P{^{1}H} NMR spectra were recorded in $CDCl_3$ on a JEOL LA-400 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400II CHN analyzer.

Preparation of [CpTiCl(μ_2-S)$_2$Ir(PMe$_3$)Cp*] (2). To a solution of **1** (300 mg, 0.639 mmol) in THF (30 mL) was added triethylamine (178 μL, 1.28 mmol) and [CpTiCl$_3$] (140 mg, 0.638 mmol), and the mixture was stirred overnight. After removal of the solvent in vacuo, the resultant orange solid was washed with methanol. Subsequent recrystallization from dichloromethane−hexanes (10 mL/40 mL) afforded **2** as light red crystals (315 mg, 80%). ^{1}H NMR: δ 6.35 (s, 5H, C_5H_5), 2.00 (d, $^4J_{PH} = 2.0$ Hz, 15H, C_5Me_5), 1.28 (d, $^2J_{PH} = 10.7$ Hz, 9H, PMe$_3$). ^{31}P{^{1}H} NMR: δ −30.2. Anal. Calcd for $C_{18}H_{29}ClIrPS_2Ti$: C, 35.09; H, 4.74. Found: C, 34.79; H, 4.87.

Preparation of [TiCl$_2$(μ_2-S)$_2$Ir(PMe$_3$)Cp*] (3). To a solution of **1** (250 mg, 0.532 mmol) in THF (25 mL) was added triethylamine (150 μL, 1.08 mmol) and [TiCl$_4$(thf)$_2$] (180 mg, 0.539 mmol) at −78 °C, and the mixture was slowly warmed to room temperature with stirring. After removal of the solvent in vacuo, the resultant reddish brown residue was extracted with benzene. The extract was evaporated to dryness in vacuo and recrystallized from dichloromethane−hexanes (5 mL/25 mL). The light red needles that formed were filtered off and dried in vacuo (180 mg, 56%). ^{1}H NMR: δ 1.90 (d, $^4J_{PH} = 1.5$ Hz, 15H, C_5Me_5), 1.47 (d, $^2J_{PH} = 10.3$ Hz, 9H, PMe$_3$). ^{31}P{^{1}H} NMR: δ −29.6. Anal. Calcd for $C_{13}H_{24}Cl_2IrS_2Ti$: C, 26.63; H, 4.12. Found: C, 26.45; H, 4.16.

X-ray Diffraction Studies. Single crystals suitable for X-ray analyses were sealed in glass capillaries under an argon atmosphere and mounted on a Rigaku AFC7R four-circle diffractometer equipped with a graphite-monochromatized Mo Kα source ($\lambda = 0.7107$ Å). Orientation matrixes and unit cell parameters were determined by least-squares treatment of 25 machine-centered reflections with $25° < 2\theta < 40°$. The data collection was performed at 294 K using the ω−2θ scan technique at a rate of 32 deg min^{-1} ($5° < 2\theta < 55°$). The intensities of three check reflections were monitored every 150 reflections, which showed no significant decay during data collection. Intensity data were corrected for Lorentz−polarization effects and for absorption (ψ scans). A correction for secondary extinction was applied. Details of crystals and data collection parameters are summarized in Table 2.

Table 2. X-ray Crystallographic Data for 2 and 3

	2	3
formula	$C_{18}H_{29}ClIrPS_2Ti$	$C_{13}H_{24}Cl_2IrPS_2Ti$
fw	616.09	586.45
cryst syst	monoclinic	orthorhombic
space group	*Cc* (No. 9)	$P2_12_12_1$ (No. 19)
cryst color	orange	orange
cryst dimens, mm	0.7 × 0.4 × 0.1	0.3 × 0.2 × 0.2
a, Å	17.268(4)	13.640(2)
b, Å	8.368(4)	15.875(2)
c, Å	16.145(4)	9.366(2)
β, deg	112.92(2)	90
V, Å^3	2148(1)	2028.1(4)
Z	4	4
D_c, g cm^{-3}	1.905	1.920
F(000), e	1200	1128
μ(Mo Kα), cm^{-1}	69.68	75.04
no. of reflns measd	$+h, +k, \pm l$	$+h, +k, +l$
no. of unique reflns	2474	2639
transmsn factors	0.2046−0.9994	0.6558−0.9976
no. data used ($I > 3\sigma(I)$)	2279	2201
no. of variables	219	183
R^a	0.033	0.026
$R_w{}^b$	0.034	0.020
GOF^c	2.19	1.24
max/min residuals, e Å^{-3}	3.29/−2.70	0.65/−0.46

[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 = 0.015 (**2**), 0.007 (**3**)) with $\sigma_c(F_o)$ from counting statistics. [c] GOF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parms})]^{1/2}$.

Structure solution and refinements were carried out by using the teXsan program package.[23] The heavy atom positions were determined by the direct method program (SIR92,[24] for **2**) or Patterson method program (PATTY94,[25] for **3**), and 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 hydrogen atoms were placed at calculated positions and included in the final stages of the refinements with fixed parameters. The absolute structures of **2** and **3** were determined on the basis of the Flack absolute structure parameters.[26] The atomic scattering factors were taken from ref 27, and anomalous dispersion effects were included; the values of $\Delta f'$ and $\Delta f''$ were taken from ref 28.

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Supporting Information Available: A listing of atomic coordinates, anisotropic thermal parameters, and full bond lengths and angles for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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