Antimony–Antimony Bond Formation by Reductive Elimination from a Hafnium Bis(stibido) Complex

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The bis(stibido) complex CpCp*Hf(SbMes)₂ (2) was prepared and structurally characterized. Complex 2 reacts with 2 equiv of xyllylisocyanide to give the bis-insertion product CpCp*Hf[C(SbMes)]=N(2,6-MeC₆H₃)₂ (4). The reaction of 2 with oxidants (I₂ and O₂) or donors (carbon monoxide and diphenylacetylene) or thermolysis promotes the reductive elimination of Sb₂Mes₄.

There has been considerable recent interest in the use of transition-metal reagents and catalysts for the formation of bonds between the heavier elements.¹⁻⁸ The development of this field has resulted in the discovery of numerous compounds with metal–main group element bonds and the identification of several chemical pathways for element–element bond formation. For example, rhodium complexes catalyze the dehydrocoupling of primary and secondary phosphines to diphenosphines, probably by a simple mechanism involving oxidative additions and reductive eliminations.² Similar dehydrocoupling reactions produce Si–Si bonds,³ and extended chains of silicon atoms (polysilanes) are obtained by dehydrocoupling reactions of primary silanes catalyzed by group 4 metalloocene complexes.¹⁴ The latter reactions appear to operate by a mechanism involving α-bond metathesis steps, which break Si–H bonds and form Si–Si bonds via concerted, four-centered transition states.⁵ The dehydrocoupling of hydrostannanes to polystannanes is also catalyzed by group 4 metalloocene complexes, and mechanistic work has implicated a process involving α elimination of a low-valent main-group fragment, which then undergoes catenation via insertions into Sn–H or M–Sn bonds (Scheme 1).⁶ The α-stannylene elimination step of this dehydrocoupling process involves migration of hydrogen to the metal, and related aryl and alkyl migrations (e.g., Hf–SnPh₃ to Hf–Ph and :SnPh₂) have also been observed.⁶b,c The latter observations suggest that early-metal complexes of the heavier elements might be convenient sources of low-valent species and may provide new routes to catenated compounds.

Scheme 1. Dehydrocoupling Based on α Elimination

In search of new routes to Sb–Sb-bonded species, we have investigated the chemistry of stibido complexes of zirconium and hafnium. For related phosphorus systems, Harrod⁷ and Stephan⁸ have reported the catalytic dehydrocoupling of primary phosphines to cyclic oligomers. Very little is known about related antimony compounds, although Cp₂Zr(SbPh₂)₂ was reported in 1984.⁹ More recently, we found that Cp₂ZrHCl and Cp₂ZrMe₂ are catalysts for the dehydrocoupling of MesSbH₂ (Mes = mesityl) to [SbMes]₄, and the stibido complexes Cp₂Hf(SbHaRCl) (Ar = Mes, dmp = 2,6-Mes₂C₆H₃) undergo α-stibinidene elimination to give Cp₂Hf(SbH(dmp))Me results in rapid elimination of methane and the formation of the stibinidene complex Cp₂Hf=Sb(dmp), which was trapped by PMe₃ and 2-butyne.¹¹ To further probe the inherent chemical properties of stibido complexes of hafnium, the bis(stibido) derivative

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CpCp*Hf(SbMes2)2 (2) has been synthesized and characterized. Preliminary results on the chemistry of this complex are reported, including reductive elimination of the distibine Mes2SbMes2.

Treatment of an ethereal slurry of CpCp*HfCl2 (1) with 2 equiv of LiSbMes2, generated in an Et2O solution, resulted in a green solution that over a period of ca. 30 min evolved to a violet color. From this solution, analytically pure purple crystals of 2 were obtained in 63% isolated yield (Scheme 2). Characterization of complex 2 followed from 1H and 13C NMR, IR, and UV–vis spectroscopy. The violet color of 2 results from a ligand-to-metal charge-transfer band at 630 nm (ε = 1.5 × 104 L cm⁻¹ mol⁻¹). Complex 2 shows pseudo-C₂ symmetry from temperatures of -95 to +45 °C by 1H and 13C NMR spectroscopy. Additionally, the α-methyl substituents of the mesityl rings are equivalent, indicating rapid Sb–C rotation throughout this temperature range.

Single crystals of 2 were grown from a concentrated Et₂O solution cooled to -35 °C. An X-ray diffraction study was performed, and the molecular structure of complex 2 is shown in Figure 1. Notably, two crystallographically unique antimony centers were located. One antimony center, Sb(2), is pyramidal with the sum of the angles about Sb(2) being 330.4°. The Sb(2)–Hf bond length of 3.014(1) Å is slightly longer than that for CpCp*HfCl(SbMes2) [3; 3.0035(8) Å],10. The slight lengthening in the Sb–Hf bond of 2 is likely a result of greater steric congestion associated with the SbMes2 ligand. The other antimony center is essentially planar [Σ angles at Sb(1) = 358.4°] and has a considerably shortened Sb(1)–Hf bond length of 2.782(1) Å, which is 0.22 Å shorter than the Sb(2)–Hf bond of 3. Additionally, the plane of this stibido ligand [C(31)–Sb(1)–C(41)] is approximately orthogonal to the Hf–Sb(1)–Sb(2) plane, which allows for lone-pair donation into the vacant α orbital of the Cp₂MX₂ fragment.12 These structural features are consistent with multiple-bond character in complex 2, similar to that observed in complexes of the type Cp₂M(PR₃)₂ (M = Hf, Zr; R = Et, Cy) and related derivatives observed first by Baker and co-workers.13

The reaction of hafnocene dichloride 1 with 1 equiv of LiSbMes2 resulted in a mixture of 2, unreacted 1, and a complex tentatively assigned as CpCp*HfCl(SbMes2) based on 1H and 13C NMR spectra. Efforts to separate the two stibido complexes have thus far failed, and variation of the reaction conditions (e.g., solvent, temperature, addition rate) has not yet favored the monosubstituted hafnocene product.

Treatment of a benzene solution of bis(stibido) complex 2 with 2 equiv of xylylisoxyamine (CNxy) afforded the insertion product CpCp*Hf[C(SbMes2)=N(2,6-Me₂C₆H₃)H]₂ (4) as analytically pure brown crystals in 85% yield (Scheme 2). Monitoring the reaction in benzene-δ₆ by 1H NMR spectroscopy showed quantitative conversion to 4. Key spectroscopic features of 4 include an IR stretching vibration of νCN 1647 cm⁻¹, and the α-carbon resonance of the iminoacyl ligand appears at δ 254.7 in the 13C NMR spectrum. When 2 was treated with 1 equiv of CNxy, only a mixture of 4 and 2 was observed, with no evidence of the single insertion product. A related insertion of phenylisoxyamine into the Hf–As bond of a hafnocene–arsenido complex has been reported by Hey-Hawkins and co-workers.14 Double insertions of the type observed for 2 are quite rare for group 4 metalocene derivatives,15 and this may reflect a high reactivity for Hf–Sb bonds.

Complex 2 reacted with 2 equiv of ethereal HCl to give quantitatively the secondary stibine HSBMes2 and dichloride 1 (Scheme 2). These two products can be separated by fractional crystallization from hexane in 77% and 89% yields, respectively.

The reaction chemistry of 2 is dominated by a reductive coupling of the SbMes2 fragments to form tetrasmetyldi-...
tibine $\text{Sb}_2\text{Mes}_4$ ($5$). Treatment of a benzene-$d_6$ solution of $2$ with ca. 1 atm of dry $\text{O}_2$ resulted in decolorization of the solution and precipitation of a solid. Analysis of the $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of the reaction reveals quantitative conversion to $\text{Sb}_2\text{Mes}_2$, identified by comparison to an authentic sample (Scheme 3). The insoluble residues consisted of an uncharacterizable hafnium product. Reaction of $2$ with 1 equiv of $\text{I}_2$ in benzene afforded $\text{Sb}_2\text{Mes}_2$ and $\text{CpCp*Hf(C_4Ph_4)}$ in 71 and 83% isolated yields, respectively (Scheme 3). This reaction is nearly quantitative, as monitored by $^1\text{H}$ NMR spectroscopy (Scheme 3). Heating benzene-$d_6$ solutions of $2$ for $>12$ h at $90\,^\circ\text{C}$ also gives $\text{Sb}_2\text{Mes}_4$ and a complex mixture of hafnium-containing products, some of which were insoluble. These reactions point to a reductive elimination process; therefore, additional evidence for a resulting hafnium(II) product was sought.

Treatment of complex $2$ with carbon monoxide (ca. 2 equiv, 1 atm) gave a complex mixture of hafnium-containing products, most of which were insoluble, and $\text{Sb}_2\text{Mes}_4$ (Scheme 3). Heating benzene solutions of stibide complex $2$ at $90\,^\circ\text{C}$ for 4 h in the presence of excess diphenylacetylene cleanly afforded $\text{Sb}_2\text{Mes}_4$ and $\text{CpCp*Hf(C_4Ph_4)}$ in 54 and 78% isolated yields, respectively (Scheme 3). This reaction is nearly quantitative, as monitored by $^1\text{H}$ NMR spectroscopy (benzene-$d_6$). The successive fractional crystallization steps to separate products and unreacted diphenylacetylene gave reduced isolated yield. Products were identified by comparison to authentic samples prepared by literature methods.$^{16,18}$

These studies indicate that the reductive elimination of distibine from $2$ is relatively facile and may occur by an associative, ligand-induced mechanism.$^{19}$ Oxidants ($\text{O}_2$ or $\text{I}_2$) also induce reductive elimination of $\text{Sb}_2\text{Mes}_4$ from $2$ by unknown mechanisms. Presumably, the reaction of $2$ with $\text{I}_2$ initially forms $\text{CpCp*Hf(I)(SbMes}_2$ and $\text{ISbMes}_2$, which then react via nucleophilic displacement of iodide by a stibido group at the antimony center of $\text{ISbMes}_2$. Group 4 metalloocene derivatives are known to undergo reductive elimination, most notably alkyl hydride species, which produce the corresponding alkane.$^{19}$ Related reductive eliminations that form $\text{Si–Cl}$,$^{20}$ $\text{Si–H}$,$^{18}$ and, most recently, $\text{C–C}$ bonds$^{21}$ have also been reported.

In summary, a new hafnium stibido complex $2$ has been prepared and structurally characterized. $\text{CNxyl}$ reacts rapidly with $2$ to insert into the Hf–Sb bond, but other ligands such as carbon monoxide or diphenylacetylene induce reductive elimination of $\text{Sb}_2\text{Mes}_4$. Thermolysis of $2$ or the addition of oxidants such as $\text{O}_2$ or $\text{I}_2$ also result in $\text{Sb}_2\text{Mes}_4$ bond formation to give distibine $5$.

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Supporting Information Available: X-ray crystallographic data (CIF) and experimental details for the synthesis and characterization of new compounds, tables of unit cell, data collection, and refinement parameters for $2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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