Inorg. Chem. **2006**, *45*, 9625–9627

Inorganic Chemistry Communication

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

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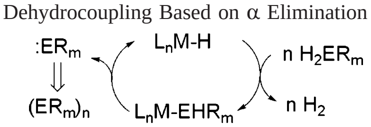
Received September 25, 2006

The bis(stibido) complex CpCp*Hf($SbMes_2$)$_2$ (**2**) was prepared and structurally characterized. Complex **2** reacts with 2 equiv of xylylisocyanide to give the bis-insertion product CpCp*Hf[C($SbMes_2$)═N(2,6-MeC_6H_3)]$_2$ (**4**). The reaction of **2** with oxidants (I_2 and O_2) or donors (carbon monoxide and diphenylacetylene) or thermolysis promotes the reductive elimination of Sb_2Mes_4.

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 diphosphanes, 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 metallocene complexes.[1,4] The latter reactions appear to operate by a mechanism involving σ-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 metallocene 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−$SnPh_3$ to Hf−Ph and :$SnPh_2$) 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, Harrod[7] and Stephan[8] have reported the catalytic dehydrocoupling of primary phosphines to cyclic oligomers. Very little is known about related antimony compounds, although $Cp_2Zr(SbPh_2)_2$ was reported in 1984.[9] More recently, we found that Cp_2ZrHCl and Cp_2ZrMe_2 are catalysts for the dehydrocoupling of $MesSbH_2$ (Mes = mesityl) to [SbMes]$_4$, and the stibido complexes CpCp*Hf(SbHAr)Cl (Ar = Mes, dmp = 2,6-$Mes_2C_6H_3$) undergo α-stibinidene elimination to give CpCp*HfHCl and [SbMes]$_4$ or dmpSb═Sbdmp.[10] The generation of CpCp*Hf[SbH(dmp)]Me results in rapid elimination of methane and the formation of the stibinidene complex CpCp*Hf═Sb(dmp), which was trapped by PMe_3 and 2-butyne.[11] To further probe the inherent chemical properties of stibido complexes of hafnium, the bis(stibido) derivative

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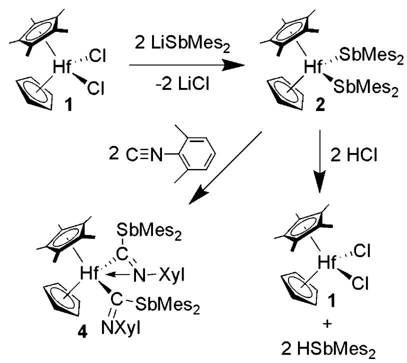
10.1021/ic061826q CCC: $33.50
Published on Web 11/03/2006

Scheme 2



CpCp*Hf(SbMes$_2$)$_2$ (**2**) has been synthesized and characterized. Preliminary results on the chemistry of this complex are reported, including reductive elimination of the distibine Mes$_2$SbSbMes$_2$.

Treatment of an ethereal slurry of CpCp*HfCl$_2$ (**1**) with 2 equiv of LiSbMes$_2$, generated in an Et$_2$O 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 ^{1}H and ^{13}C NMR, IR, and UV−vis spectroscopy. The violet color of **2** results from a ligand-to-metal charge-transfer band at 630 nm ($\epsilon = 1.5 \times 10^4$ L cm^{-1} mol^{-1}). Complex **2** shows pseudo-C_s symmetry from temperatures of −95 to +45 °C by ^{1}H and ^{13}C NMR spectroscopy. Additionally, the *o*-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 Et$_2$O 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[SbH(dmp)] [**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 SbMes$_2$ 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 a$_1$ orbital of the Cp$_2$MX$_2$ fragment.[12] These structural features are consistent with multiple-bond character in complex **2**, similar to that observed in complexes of the type Cp$_2$M(PR$_2$)$_2$ (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 LiSbMes$_2$ resulted in a mixture of **2**, unreacted **1**, and a

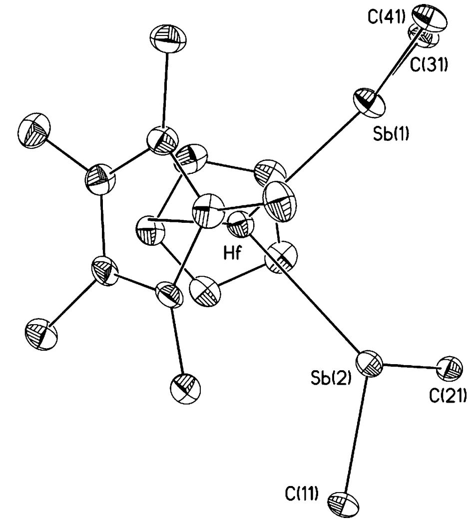


Figure 1. Perspective view of **2** with thermal ellipsoids drawn at the 35% probability level. Hydrogen atoms, solvent molecules, and mesityl rings except ipso carbon atoms have been omitted for clarity. Select bond lengths (Å) and angles (deg): Hf−Sb(1) = 2.782(1), Hf−Sb(2) = 3.013(1), Sb(1)−C(31) = 2.170(9), Sb(1)−C(41) = 2.197(9), Sb(2)−C(21) = 2.185(9), Sb(2)−C(11) = 2.199(8); Sb(1)−Hf−Sb(2) = 88.72(3), C(31)−Sb(1)−C(41)= 95.9(3), C(31)−Sb(1)−Hf = 129.4(2), C(41)−Sb(1)−Hf = 133.1(2), C(21)−Sb(2)−C(11) = 94.7(3), C(21)−Sb(2)−Hf = 109.5(2), C(11)−Sb(2)−Hf = 126.3(2).

complex tentatively assigned as CpCp*HfCl(SbMes$_2$) based on ^{1}H and ^{13}C 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 xylylisocyanide (CNxyl) afforded the insertion product CpCp*Hf[C(SbMes$_2$)=N(2,6-Me$_2$C$_6$H$_3$)]$_2$ (**4**) as analytically pure brown crystals in 85% yield (Scheme 2). Monitoring the reaction in benzene-d_6 by ^{1}H NMR spectroscopy showed quantitative conversion to **4**. Key spectroscopic features of **4** include an IR stretching vibration of ν_{CN} 1647 cm^{-1}, and the α-carbon resonance of the iminioacyl ligand appears at δ 254.7 in the ^{13}C NMR spectrum. When **2** was treated with 1 equiv of CNxyl, only a mixture of **4** and **2** was observed, with no evidence of the single insertion product. A related insertion of phenylisocyanide 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 metallocene 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 HSbMes$_2$ 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 SbMes$_2$ fragments to form tetramesityldis-

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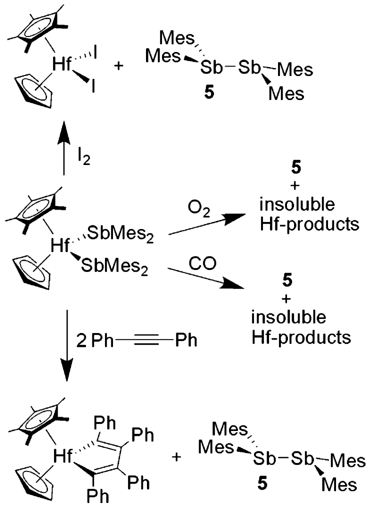
Scheme 3



tibine Sb_2Mes_4 (**5**). Treatment of a benzene-d_6 solution of **2** with ca. 1 atm of dry O_2 resulted in decolorization of the solution and precipitation of a solid. Analysis of the ^{1}H and ^{13}C NMR spectra of the reaction reveals quantitative conversion to Sb_2Mes_2, identified by comparison to an authentic sample (Scheme 3).[16] The insoluble residues consisted of an uncharacterizable hafnium product. Reaction of **2** with 1 equiv of I_2 in benzene afforded Sb_2Mes_2 and $CpCp^*HfI_2$ in 71 and 83% isolated yields, respectively, after fractional crystallization from hexane (Scheme 3).[17] This reactivity is directly analogous to that of $Cp_2Zr(SbPh_2)_2$, which reacts with I_2 to give Sb_2Ph_4 and Cp_2ZrI_2.[9] It was observed that heating benzene-d_6 solutions of **2** for >12 h at 90 °C also gives Sb_2Mes_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 Sb_2Mes_4 (Scheme 3). Heating benzene solutions of stibido complex **2** at 90 °C for 4 h in the presence of excess diphenylacetylene cleanly afforded Sb_2Mes_4 and $CpCp^*Hf(C_4Ph_4)$ in 54 and 78% isolated yields, respectively (Scheme 3). This reaction is nearly quantitative, as monitored by ^{1}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 (O_2 or I_2) also induce reductive elimination of Sb_2Mes_4 from **2** by unknown mechanisms. Presumably, the reaction of **2** with I_2 initially forms $CpCp^*Hf(I)(SbMes_2)$ and $ISbMes_2$, which then react via nucleophilic displacement of iodide by a stibido group at the antimony center of $ISbMes_2$. Group 4 metallocene derivatives are known to undergo reductive elimination, most notably alkyl hydride species, which produce the corresponding alkane.[19] Related reductive eliminations that form Si−Cl,[20] Si−H,[18] and, most recently, C−C bonds[21] have also been reported.

In summary, a new hafnium stibido complex **2** has been prepared and structurally characterized. 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 Sb_2Mes_4. Thermolysis of **2** or the addition of oxidants such as O_2 or I_2 also result in Sb−Sb bond formation to give distibine **5**.

Acknowledgment. This work was funded by the U.S. National Science Foundation and by the Miller Institute for Basic Research in Science through a Research Fellowship (R.W.).

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.

IC061826Q

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