Terminal stibinidene ligands. Generation of CpCp*Hf=Sb(dmp) and trapping reactions with PMe_3 and 2-butyne†

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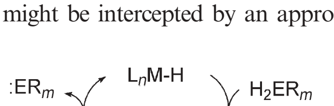
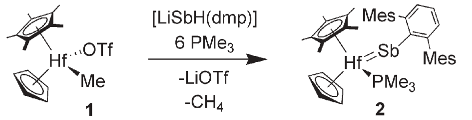
Treating CpCp*HfMe(OTf) (1) with LiSbH(dmp) results in formation of CpCp*HfMe(SbHdmp), which undergoes α-abstraction to liberate methane and generate CpCp*Hf=Sb(dmp), which is thermally unstable but can be trapped with PMe_3 or 2-butyne to give CpCp*Hf(PMe_3)=Sb(dmp) (2) and CpCp*Hf[η^2-*Sb,C*:Sb(dmp)C(Me)=C(Me)] (3), respectively.

A recently discovered mechanism for dehydrocoupling catalysis involves α-elimination, in which a low valent main group fragment is extruded from a metal center (Scheme 1). This process was first identified for stannane dehydropolymerization catalyzed by d^0 group 4 metallocene catalysts and involves α-stannylene (:SnR_2) elimination.[1] More recently, the dehydrocoupling of primary stibines with related catalysts was shown to proceed through α-stibinidene (:SbR) elimination.[2] The latter reaction system, involving elimination of a stibinidene fragment from complexes of the type CpCp*HfCl(SbHR) has heightened interest in the possible existence of terminal stibinidene complexes of hafnium and the chemical behavior of such species. To the best of our knowledge, a metal complex bearing a terminal stibinidene ligand has not been reported. Herein, we report some initial observations in this direction, including preparation and characterization of the terminal stibinidene complex CpCp*(Me_3P)Hf=Sb(dmp) (**2**, dmp = 2,6-dimesitylphenyl).

The synthetic route to **2** is based on α-hydrogen abstraction in a methyl stibide complex. Reaction of LiSbHdmp, generated in ethereal solution by treatment of dmpSbH_2 with BuLi, with an Et_2O solution of CpCp*HfMe(OTf) (**1**)[3] resulted in methane evolution and a complex mixture of products. Monitoring the reaction by ^1H NMR spectroscopy (benzene-d_6) revealed resonances consistent with formation of a hafnocene methyl complex (δ −0.50, CH_3) bearing a primary stibide ligand (δ 2.29, SbH).[2] Observation of methane in the ^1H NMR spectrum also suggested the possibility of α-abstraction to give an unstable stibinidene complex, which might be intercepted by an appropriate trapping reagent. Addition of six equivalents of PMe_3 to the initial reaction mixture afforded analytically pure brown crystals of CpCp*(Me_3P)Hf=Sb(dmp) (**2**) in 63% yield (eqn 1).‡ Complex **2** was characterized by NMR (^1H, ^{13}C, and ^{31}P), IR, and UV-vis spectroscopy. Two magnetically inequivalent *ortho* methyl groups of the dmp substituent are observed in the NMR spectra, indicating hindered rotation of the mesityl rings on the NMR time scale. Notably, features consistent with a stibide proton are absent from the ^1H NMR and IR spectra.[2] X-Ray quality crystals of complex **2** have not yet been obtained.



Scheme 1 General catalytic activation *via* α-elimination.

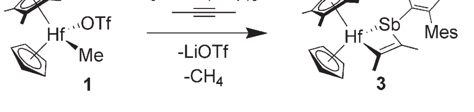


1 **2** (1)

Stibinidene complex **2** appears to be a unique example of a metal complex bearing a terminal SbR ligand, despite theoretical predictions of the possible synthesis of such complexes and the synthetic accessibility of terminal phosphinidene congeners.[4] The factors that contribute to the stability of **2** are undoubtedly similar to those for zirconocene phosphinidene complexes such as Cp*$_2$(Me_3P)Zr=P(2,4,6-^{t}Bu$_3$C$_6$H$_2$) and Cp_2(Me_3P)Zr=P(dmp).[5]

There are several reports of stibinidene ligands that bridge two metal centers.[6] These antimony centers, such as that in PhSb[Mn(CO)$_2$Cp]$_2$, are planar in the solid state, indicative of involvement of the Sb lone pair in π-bonding.[6] Additionally, two-coordinate antimony has been observed in heterocumulene complexes of the type L$_n$M=Sb=ML$_n$, for which the M–Sb–M linkage is linear.[7] Most recently in low-valent antimony chemistry, a terminal stibido (Sb^{3-}) ligand on tungsten has been prepared.[8]

Another effective trapping agent for the hafnium stibinidene species is 2-butyne. Treatment of hafnium triflate **1** with LiSbHdmp in the presence of 10 equivalents of 2-butyne gives the metallastibacyclobutene CpCp*Hf[η^2-*Sb,C*:Sb(dmp)C(Me)=C(Me)] (**3**) as analytically pure red crystals in 78% yield.‡ This formal [2 + 2]-cycloadditon of an alkyne to a stibinidene intermediate is similar to the cycloaddition reactivity observed for Zr–phosphinidene complexes.[9] Complex **3** exhibits two methyl resonances for the metallacylcobutene ligand at δ 1.93 and 1.67 in the ^1H NMR spectrum and two resonances at δ 216.2 and 148.0 in the ^{13}C NMR spectrum for the α- and β-carbon nuclei. The infrared spectrum of **3** displays a ν_{CC} stretching frequency at 1607 cm^{-1}.



1 **3** (2)

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The structure of **3** was confirmed by a single crystal X-ray diffraction study using crystals grown from concentrated pentane solution.§ The metallacycle is planar, as illustrated in Fig. 1. The Hf–Sb bond length of 2.851(3) Å is approximately 0.15 Å shorter than the Hf–Sb bond of the primary stibide complex CpCp*HfCl(SbHdmp).[2] The relatively short Hf–Sb bond of **3** is best attributed to strain in the metallacycle, as Sb is pyramidal and therefore not engaged in π-bonding with hafnium. Though this is only the second reported solid state structure of a group 4 stibide complex, zirconocene complexes bearing secondary stibide ligands are known.[10] The X-ray data and a single set of resonances in each NMR spectrum (^1H, ^{13}C) support the selective formation of a single diastereomer in this reaction.

Reaction of stibinidene complex **2** with a 5-fold excess of 2-butyne in benzene affords metallacycle **3**, indicating that the PMe_3 ligand of **2** exhibits some lability (Scheme 2). The reverse reaction, conversion of complex **3** to **2**, has not been observed at ambient temperature in benezene-d_6 or upon extended heating prior to decomposition of **3**. Treatment of stibinidene **2** with stoichiometric ethereal HCl gives, in high isolated yields, primary stibine $dmpSbH_2$ and $CpCp^*HfCl_2$. The products were identified by comparison to authentic samples.

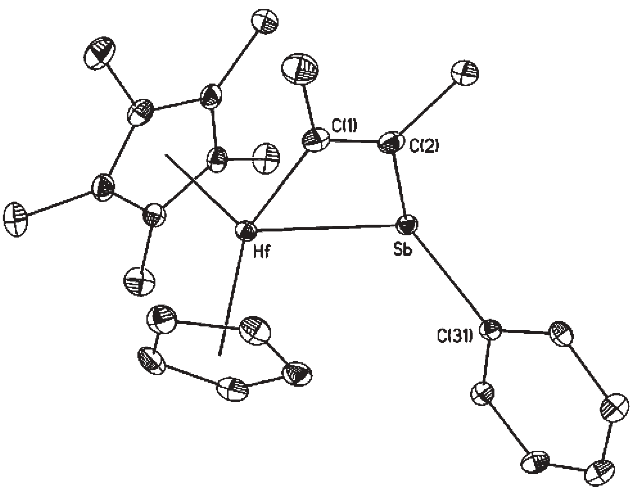
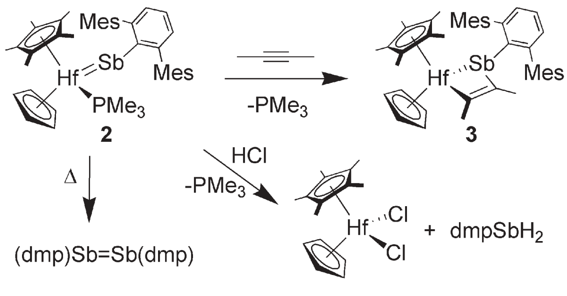


Fig. 1 View of the molecular structure of **3** with *ortho* mesityl groups and hydrogen atoms omitted for clarity. Thermal ellipsoids shown at the 35% probability level. Selected metrical parameters: Hf–Sb = 2.851(2) Hf–C(1) = 2.188(5), Sb–C(2) = 2.259(5), Sb–C(31) = 2.204(5) Å; Sb–Hf–C(1) = 77.5(1), Hf–C(1)–C(2) = 29.5(2), C(1)–C(2)–Sb = 123.4(4), C(2)–Sb–Hf = 62.3(1)°.



Scheme 2

Heating stibinidene complex **2** in benzene-d_6 results in liberation of PMe_3 (*ca.* 0.9 equiv.) and formation of (dmp)Sb=Sb(dmp)[11] in 80% yield (with respect to **2**) by ^1H NMR spectroscopy (Scheme 2). A complex mixture of hafnium-containing products are observed, but the majority of metal-containing products precipitate from solution and could not be characterized. Thermolysis of **2** in the presence of 20 equivalents of $dmpSbH_2$ or $MesSbH_2$ did not alter the product distribution, and no evidence for catalytic dehydrocoupling was observed. The thermal decomposition of **2** appears to be similar to the conproportionation of the stibabismuthene (Bbt)Sb=Bi(Bbt) (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]phenyl) to distibene (Bbt)Sb=Sb(Bbt) and (Bbt)Bi=Bi(Bbt) observed by Tokito and coworkers.[12,13] Further investigations of early transition-metal–antimony chemistry are on-going.

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Notes and references

‡ **Experimental data: CpCp*(Me$_3$P)Hf=Sb(dmp) (2)**. A 10 mL Et_2O solution of $dmpSbH_2$ (136 mg, 0.311 mmol) was treated with BuLi (0.19 mL, 1.6 M) at −78 °C, then warmed slowly to 0 °C for 2 h. The stibide solution was transferred on to a solution of CpCp*HfMe(OTf) (154 mg, 0.283 mmol) and PMe_3 (0.15 mL, 1.70 mmol) in 5 mL E_2O at −78 °C. After 2 h at ambient temperature, the volitile materials were distilled, and the residue was crystalized from Et_2O (174 mg, 0.196 mmol, 63%). ^1H (C_6D_6, 400.1 MHz): δ 7.158 (t, $C_6Mes_2\mathit{H}_3$, 1 H), 7.088 (s, $C_6Me_3\mathit{H}_2$, 4 H), 6.698 (d, $C_6Mes_2\mathit{H}_3$, 2 H), 5.277 (s, $C_5\mathit{H}_5$, 5 H), 2.463 (s, $C\mathit{H}_3$, 6 H), 2.392 (s, $C\mathit{H}_3$, 6 H), 2.190 (s, $C\mathit{H}_3$, 6 H), 1.711 (s, $C_5(C\mathit{H}_3)_5$, 15 H) 0.429 (d, $C\mathit{H}_3$, 9 H). ^{13}C (C_6D_6, 100.6 MHz): δ 150.3 (s, *Ar*), 144.7 (s, *Ar*), 136.6 (d, *Ar*), 134.7 (s, *Ar*), 129.1 (s, *Ar*), 128.4 (s, *Ar*), 127.5 (s, *Ar*), 125.9 (s, *Ar*), 112.6 (s, C_5Me_5), 100.9 (s, C_5H_5), 23.0 (s, $\mathit{C}H_3$), 22.7 (s, $\mathit{C}H_3$), 20.8 (s, $\mathit{C}H_3$), 20.3 (d, $\mathit{C}H_3$, J_{PC} = 24 Hz), 13.4 (s, C_5Me_5). ^{31}P (C_6D_6, 161.97 MHz): δ 14.0 (s, $\mathit{P}Me_3$). UV-vis (hexane): 488 nm (4719), 348 (22786). Anal. calcd for $C_{42}H_{54}HfPSb$: C, 56.67; H, 6.11. Found: C, 56.30; H, 6.14. **CpCp*Hf[*Sb,C*:η^2-Sb(dmp)CMe=C(Me)] (3)**. Prepared as above from $dmpSbH_2$ (132 mg, 0.302 mmol), BuLi (0.226 mL, 1.6 M), and CpCp*HfMe(OTf) (164 mg, 0.302 mmol), substituing 2-butyne (0.084 mL) for PMe_3. Here, the residue was crystalized from pentane to give red crystals of the title compound (204 mg, 0.236 mmol, 78%). ^1H (C_6D_6, 400.1 MHz): δ 7.125 (t, $C_6Mes_2\mathit{H}_3$, 1 H), 6.934 (d, $C_6Mes_2\mathit{H}_3$, 2 H), 6.854 (s, $C_6Me_3\mathit{H}_2$, 4 H), 5.475 (s, $C_5\mathit{H}_5$, 5 H), 2.425 (s, $C\mathit{H}_3$, 6 H), 2.381 (s, $C\mathit{H}_3$, 6 H), 2.272 (s, $C\mathit{H}_3$, 6 H), 1.932 (s, $C\mathit{H}_3$, 3 H), 1.670 (s, $C\mathit{H}_3$, 3 H), 1.628 (s, $C_5(C\mathit{H}_3)_5$, 15 H). ^{13}C (C_6D_6, 100.6 MHz): δ 216.2 (s, Hf*C*Me), 147.9 (s, Sb*C*Me), 144.0 (s, *Ar*), 142.2 (s, *Ar*), 136.6 (d, *Ar*), 136.3 (s, *Ar*), 129.0 (s, *Ar*), 128.9 (s, *Ar*), 128.7 (s, *Ar*), 126.4 (s, *Ar*), 116.9 (s, C_5Me_5), 108.6 (s, C_5H_5), 22.3 (s, $\mathit{C}H_3$), 21.9 (s, $\mathit{C}H_3$), 21.1 (s, $\mathit{C}H_3$), 18.7 (s, $\mathit{C}H_3$), 18.6 (s, $\mathit{C}H_3$), 12.2 (s, C_5Me_5). IR (KBr, Nujol): 1607 (s, ν_{CC}) cm^{-1}. Anal. calcd for $C_{43}H_{51}HfSb$: C, 59.49; H, 5.92. Found: C, 59.15; H, 5.92.

§ Crystal data: for **3**, $C_{43}H_{51}HfSb$, M = 868.08, monoclinic, $P2_1/n$, a = 12.046(1), b = 16.500(1), c = 18.075(1) Å, β = 93.404(1)°, Z = 4, V = 3586.2(5) $Å^3$, T = 123 K, μ(Mo Kα) = −3.675 mm^{-1}. Of 15986 total reflections (red block, 3.15 = θ = 24.73°), 6075 were independent (R_{int} = 3.31%). A semi-empirical absorption correction was performed using psi-scans. Patterson methods were used to locate the heavy atoms Hf and Sb. All non-hydrogen atoms were converted to and refined anisotropically. Hydrogen atoms were refined isotropically and fixed at calculated positions. No anomalous bond lengths or angles were observed. Integration of the data at 0.80 Å resolution provided a high quality data set and solution despite the relatively low value of θ = 24.73°. $R(F)$ = 3.47%, $R(wF)$ = 6.26%, GoF = 1.236. CCDC 614367. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b609773a

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