Dehydrocoupling

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Catalytic Antimony–Antimony Bond Formation through Stibinidene Elimination from Zirconocene and Hafnocene Complexes**

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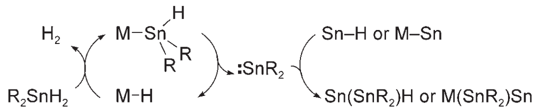
Metal-catalyzed dehydrocoupling reactions have emerged as an important synthetic method for the generation of element–element bonds and the production of new types of inorganic oligomers and polymers.[1] Current information indicates that these coupling reactions occur by a number of different mechanisms. For silane couplings catalyzed by d^0-metal complexes, σ-bond metathesis reactions appear to be important.[2] However, related catalysts mediate similar Sn–Sn bond formations and dehydropolymerizations by a mechanism that involves α-hydrogen migration and stannylene elimination, followed by rapid insertion of stannylene units into Sn–H or M–Sn bonds (Scheme 1).[3] The latter mechanism represents an unusual pathway in transition-metal chemistry and is of interest in determining how generally useful this process might be. This elimination mechanism is expected to be most favored for the heavier main-group elements, which readily form stable low-valent species. These elements should also possess weak element–hydrogen bonds which could additionally promote α-hydrogen migration. To explore the possible utility of this unusual reaction type, we investigated the dehydrocoupling of stibines. Herein, we provide two examples of metal-catalyzed Sb–Sb bond formation and evidence that these reactions occur through α-hydrogen migration with stibinidene (:SbR) elimination from d^0-metal–SbHR derivatives. For Group 15 elements, catalytic dehydrocouplings have been reported for primary phosphines[4] and Lewis acid/phosphine adducts.[5]



Scheme 1. Possible mechanism for stannane dehydrocoupling.

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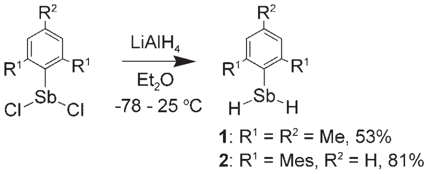
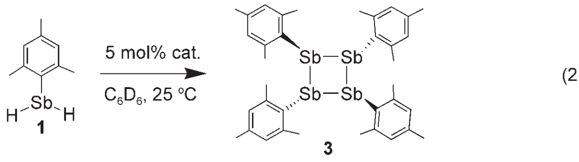
The stibines $MesSbH_2$ (**1**; Mes = mesityl) and $dmpSbH_2$ (**2**; dmp = 2,6-dimesitylphenyl) were readily prepared by reduction of the dichloro precursors using $LiAlH_4$ to afford analytically pure colorless crystals in 53 and 81 % yield, respectively [Eq. (1)].[6] As with $(2,6\text{-}Trip_2C_6H_3)SbH_2$ (Trip = $2,4,6\text{-}iPr_3C_6H_2$),[6c] stibine **2** (m.p. 174–176 °C) shows considerably greater thermal stability than **1**, which decomposes in the solid state over a period of hours at ambient temperature to insoluble products. The deuterated stibine $MesSbD_2$ ([D_2]**1**) was similarly prepared by reduction of $MesSbCl_2$ using $LiAlD_4$ in 43 % yield of the isolated product. The IR spectrum of [D_2]**1** exhibits a ν_{Sb-D} stretch (1341 cm^{-1}) that is shifted with respect to the ν_{Sb-H} stretch of **1** (1873 cm^{-1}) by the expected amount.



(1)

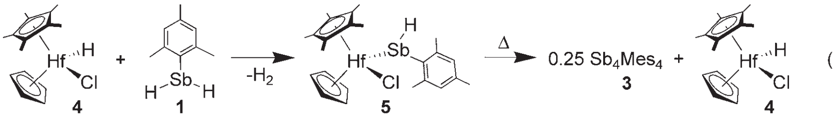
Zirconocene complexes $[Cp_2Zr(H)Cl]$ and $[Cp_2ZrMe_2]$ (Cp = cyclopentadienyl) react with 20 equivalents of stibine **1** in C_6D_6 to liberate H_2 and produce the known tetrastibene Sb_4Mes_4 (**3**) in high yield [> 95 %; Eq. (2)].[6b] It is noteworthy that these reactions occur in the dark, but ambient lighting accelerates the dehydrocoupling. Qualitatively, $[Cp_2Zr(H)Cl]$ (< 0.5 h) is a much faster catalyst than $[Cp_2ZrMe_2]$ (≈ 16 h), likely a result of a slower initial reaction of **1** with dimethyl zirconocene.[2] Intermediate species were not observed by ^1H NMR spectroscopy during the course of these reactions. Stiochiometric dehydrocoupling of phenylstibine ($PhSbH_2$) has been reported by reaction with alkyllithium reagents, sodium metal, or hydrogen traps (styrene or phenylacetylene).[7]



(2)

cat. (reaction time) =$[Cp_2Zr(H)Cl]$ (<0.5 h), $[Cp_2ZrMe_2]$ (16 h), [CpCp*Hf(H)Cl](8 h)

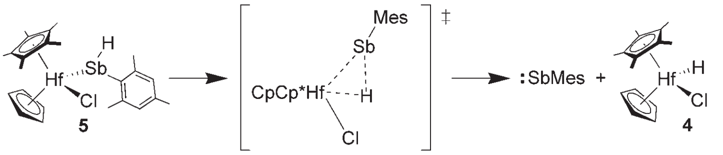
The hafnium hydride [CpCp*Hf(H)Cl] (**4**; Cp* = pentamethylcyclopentadienyl) is a much slower catalyst than $[Cp_2Zr(H)Cl]$ for the dehydrocoupling of Equation (2) (≈ 8 h), and addition of one equivalent of **1** to a solution of **4** in C_6D_6 resulted in rapid evolution of H_2 and near-quantitative formation of [CpCp*HfCl{Sb(H)Mes}] (**5**), as identified by ^1H and ^{13}C NMR spectroscopy [Eq. (3)]. The Sb–H proton of **5** resonates at $\delta = 2.46$ ppm, an upfield shift from the Sb–H resonance of **1** ($\delta = 3.12$ ppm). Installation of the stibide ligand presumably occurs through σ-bond metathesis to form H_2. The σ-bond metathesis reaction that forms stibide complex **5** is fast ($t_{1/2} < 2$ min) relative to the reaction of $[Sn(H)_2Mes_2]$ with **4** to form $[CpCp^*HfCl\{Sn(H)Mes_2\}]$ ($t_{1/2} \approx 75$ min). The facile activation of an Sb–H bond is consistent with the known, small bond-dissociation energy for SbH_3 (61 kcal mol^{-1}).[8] The isotope effect associated with the Sb–H bond activation ($k_H/k_D = 1.2(2)$) was determined by a competition experiment that involved treatment of **4** with an excess of **1** and [D_2]**1** (1:1) in C_6D_6. This isotope effect is small relative to that expected for a σ-bond metathesis mechanism;[2] however, pre-equilibrium coordination of the stibine to the Hf center could explain the observed isotope effect.[3a]



(3)

Compound **5** exhibits limited thermal stability in solution and could not be isolated as a pure solid. Thermal decomposition of **5** led to quantitative formation of tetrastibene **3** and hafnium hydride **4** [Eq. (3)], as determined by ^1H and ^{13}C NMR spectroscopy. Reaction of a solution of **4** in C_6D_6 with [D_2]**1** resulted in evolution of HD and quantitative formation of [CpCp*HfCl{Sb(D)Mes}] ([D_1]**5**), as determined by NMR spectroscopy. The thermal decomposition of [D_1]**5** provided **3** and hafnium deuteride [CpCp*Hf(D)Cl] in nearly quantitative yields.

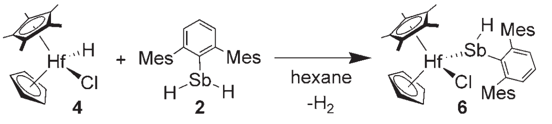
The sequence of stoichiometric reactions in Equation (3) appears to involve elementary steps that account for the catalytic dehydrocoupling of $MesSbH_2$ by **4**. Thus, the Sb–Sb bond-forming process was investigated in more detail. The decomposition of **5** follows first-order kinetics ($k = 1.02(6) \times 10^{-4}\ s^{-1}$) over approximately five half-lives, as evaluated by ^1H NMR spectroscopy. Decomposition of [D_1]**5** proceeds at a rate of $k = 2.53(5) \times 10^{-5}\ s^{-1}$, which gives a kinetic isotope effect (k_H/k_D) of 4.0 for this reaction. This relatively large isotope effect is consistent with significant Sb–H bond cleavage in the transition state. Additional evidence for an α-hydrogen migration/stibinidene elimination pathway comes from an Eyring analysis, which provided the activation parameters $\Delta H^{\neq} = 27.3(1)$ kcal mol^{-1} and $\Delta S^{\neq} = -20.0(1)$ eu (for $T = 2.2$–46.9 °C). These values are similar to those obtained for the α-stannylene elimination reaction of $[CpCp^*HfCl(SnPh_3)]$, which results in the formation of [CpCp*HfClPh] and diphenylstannylene,[3c] and are consistent with an ordered transition state [Eq. (4)].



(4)

Presumably, the reaction shown in Equation (4) involves the elimination of mesitylstibinidene (:SbMes), which condenses to form the observed tetrastibene **4**. An attempt to trap free :SbMes was made by addition of 2,3-dimethyl-1,3-butadiene (10–60 equiv), an effective trap for free stibinidene,[9] to solutions of **5** in C_6D_6. However, the presence of the added diene had no effect on the rates of decomposition or formation of Sb_4Mes_4 as the exclusive Sb-containing product. The inability to trap free stibinidene is consistent with a rapid Sb–Sb bond-forming event. In d^0-metal-catalyzed dehydrocoupling of secondary stannanes, stannylene fragments are difficult to trap and appear to rapidly insert into metal–hydride and metal–tin bonds.[3]

The treatment of solutions of **4** in hexane with $dmpSbH_2$ resulted in the evolution of H_2 and the formation of a red solution, from which analytically pure red crystals of [CpCp*HfCl{Sb(H)dmp}] (**6**) were obtained in 89% yield [Eq. (5)]. Complex **6** was characterized by NMR and IR spectroscopic analysis and a single-crystal X-ray diffraction study. Diagnostic spectroscopic features for **6** include a ^{1}H NMR resonance at $\delta = 2.49$ ppm for the stibide ligand proton (cf. $\delta = 2.46$ ppm for **5**) and a IR stretch at $\nu_{SbH} = 1830\ cm^{-1}$, a value $41\ cm^{-1}$ lower in energy than that for $dmpSbH_2$. The latter observation is consistent with a metal-bound stibide ligand.[10]



(5)

The solid-state structure of **6** is shown in Figure 1.[11] The Hf–Sb bond length is 3.0035(8) Å; a search of the Cambridge Structural Database provided no examples of Group 4 metals with stibine or stibide ligands. The structurally characterized complex most closely related to **6** is $[Cp_2Nb(H)_2(SbPh_2)]$, which features a Nb–Sb bond length of 2.8929(4) Å and a pyramidal Sb center (angles at Sb: $\Sigma = 306.3°$).[12] The Sb–C(11) bond of **6** is roughly coplanar with the Hf–Cp centroid vector—an arrangement likely to reduce steric interactions. However, such a geometry also allows for donation from the lone pair on the antimony center to a vacant orbital on Hf.[13] Current evidence prohibits definitive assignment of such an interaction.

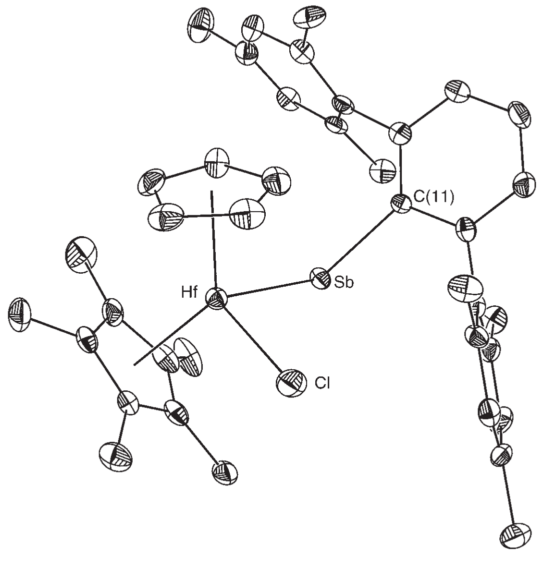
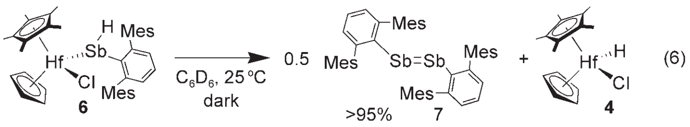


Figure 1. Perspective view of one enantiomer of [CpCp*HfCl{Sb(H)dmp}] (**6**), with thermal ellipsoids drawn at the 35% probability level. Hydrogen atoms have been omitted for clarity. Select bond lengths [Å] and angles [°]: Hf–Sb 3.0035(8), Hf–Cl 2.407(2), Sb–C(11) 2.180(8); Cl-Hf-Sb 96.62(6), C(11)-Sb-Hf 112.2(2).

Thermal decomposition of **6** proceeded smoothly in C_6D_6 to give **4** and the reported distibene (dmp)Sb=Sb(dmp) [**7**; Eq. (6)].[6b] Furthermore, **4** catalyzed the dehydrocoupling of $dmpSbH_2$ in C_6D_6 solution to form H_2 and **7** in > 95% yield, as determined by ^{1}H NMR spectroscopy. A preliminary kinetic investigation indicates that thermal decomposition proceeds with a first-order dependence on the concentration of **6** ($k = 1.29(5) \times 10^{-5}\ s^{-1}$), which is consistent with an α-hydrogen migration/stibinidene extrusion mechanism.



(6)

In summary, Group 4 metal complexes have been shown to catalytically dehydrocouple stibines. These dehydrocoupling reactions with the hafnium catalyst [CpCp*Hf(H)Cl] show first-order dependence on the hafnium stibide species, a large primary kinetic isotope effect, and activation parameters that are consistent with a mechanism that involves α-hydrogen migration and elimination of a stibinidene fragment (α-stibinidene elimination). Efforts to extend this chemistry, which involves elimination of low-valent fragments, to catalytic reactions of additional stibines, other elements, and new processes are ongoing.

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[1] a) F. Gauvin, J. F. Harrod, H. G. Woo, *Adv. Organomet. Chem.* **1998**, *42*, 363–405; b) J. Y. Corey, *Adv. Organomet. Chem.* **2004**, *51*, 1–52; c) T. D. Tilley, *Comments Inorg. Chem.* **1990**, *10*, 37–46.
[2] T. D. Tilley, *Acc. Chem. Res.* **1993**, *26*, 22–29.
[3] a) N. R. Neale, T. D. Tilley, *J. Am. Chem. Soc.* **2002**, *124*, 3802–3803; b) N. R. Neale, T. D. Tilley, *Tetrahedron* **2004**, *60*, 7247–7260; c) N. R. Neale, T. D. Tilley, *J. Am. Chem. Soc.* **2005**, *127*, 14745–14755.
[4] a) N. Etkin, M. C. Fermin, D. W. Stephan, *J. Am. Chem. Soc.* **1997**, *119*, 2954–2955; b) M. C. Fermin, D. W. Stephan, *J. Am. Chem. Soc.* **1995**, *117*, 12645–12646; c) V. P. W. Böhm, M. Brookhart, *Angew. Chem.* **2001**, *113*, 4832–4834; *Angew. Chem. Int. Ed.* **2001**, *40*, 4694–4696.
[5] C. A. Jaska, I. Manners in *Inorganic Chemistry in Focus II* (Eds: G. Meyer, D. Naumann, L. Wesemann), Wiley-VCH, Weinheim, **2005**, pp. 53–64.
[6] a) Primary stibine $dmpSbH_2$ is novel; synthesis of $MesSbH_2$ has been reported recently: H. J. Breunig, M. E. Ghesner, E. Lork,

Z. Anorg. Allg. Chem. **2005**, *631*, 851–856; b) M. Ates, H. J. Breunig, A. Soltani-Neshan, M. Z. Tegeler, *Z. Naturforsch. B* **1986**, *41*, 321–326; c) B. Twamley, C. D. Sofield, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1999**, *121*, 3357–3367.

[7] a) K. Issleib, A. Balszuweit, *Z. Anorg. Allg. Chem.* **1975**, *418*, 158–166; b) K. Issleib, A. Balszuweit, *Z. Anorg. Allg. Chem.* **1976**, *419*, 87–91.

[8] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, **1999**, p. 88.

[9] T. Sasamori, Y. Arai, N. Takeda, R. Okazaki, N. Tokitoh, *Chem. Lett.* **2001**, 42–43.

[10] H.-G. Woo, J. F. Walzer, T. D. Tilley, *J. Am. Chem. Soc.* **1992**, *114*, 7047–7055.

[11] Crystal structure analysis of **6**: $C_{39}H_{45}ClHfSb$, $M_r = 849.44$, triclinic, $P\bar{1}$, $a = 9.070(2)$, $b = 11.309(2)$, $c = 18.282(3)$ Å, $\alpha = 83.691(4)$, $\beta = 80.809(3)$, $\gamma = 71.477(3)°$, $V = 1751.7(5)$ Å^3, $Z = 2$, $\rho = 1.611\ \mathrm{g\,cm^{-3}}$, $\mu = 3.833\ \mathrm{mm^{-1}}$, $F(000) = 838$, $\theta = 1.13$–$26.39°$. Final $R1 = 5.20\,\%$, $wR2 = 11.55\,\%$, GOF = 0.963 for 379 parameters and 11448 reflections (of which 6913 with $I > 2\sigma(I)$), max positive and negative peaks in DF map 3.777 and $-1.298\ \mathrm{e\,Å^{-3}}$. Data were collected at 163(2) K Bruker Platform goniometer ($Mo_{K\alpha}$ radiation, 0.71073 Å) equipped with a CCD detector (Smart Apex). A Patterson search was used to locate the Hf and Sb atoms; all non-H atoms were converted and refined anisotropically. Hydrogen atoms were refined isotropically, fixed at calculated positions. Despite large residual electron density proximal to the Sb center, a stable hydrogen atom could not be refined at that location. CCDC-285852 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] G. I. Nikonov, L. G. Kuzmina, J. A. K. Howard, *Organometallics* **1997**, *16*, 3723–3725.

[13] R. T. Baker, J. F. Whitney, S. S. Wreford, *Organometallics* **1983**, *2*, 1049–1051.