

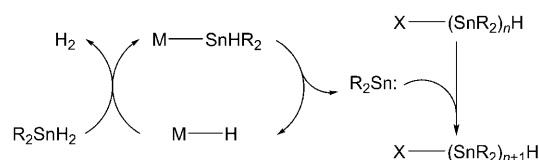
Facile Interconversion of $[\text{Cp}_2(\text{Cl})\text{Hf}(\text{SnH}_3)]$ and $[\text{Cp}_2(\text{Cl})\text{Hf}(\mu\text{-H})\text{SnH}_2]$: DFT Investigations of Hafnocene Stannyl Complexes as Masked Stannylenes**

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Electrophilic, d^0 transition-metal complexes have found use as effective catalysts for a number of chemical transformations, most prominently olefin polymerization. The reactivity associated with this catalysis involves rapid migratory insertions of the olefin substrate into d^0 metal-carbon bonds. Recently, other fundamental reaction steps have been identified for d^0 metal complexes, and some of these are useful in new catalytic reactions. For example, a novel C–H activation process, σ -bond metathesis, enables catalytic additions of C–H bonds to olefins.^[1,2] Similar σ -bond metathesis steps have been found for activation of E–H bonds (E = main-group element), and this reactivity is important in catalytic element–element (e.g., Si–Si, Sn–Sn, P–P, Sb–Sb, etc.) bond formations with d^0 metal catalysts.^[3–9]

Recent studies in d^0 transition-metal–main-group chemistry have implicated a new type of fundamental reaction step: migratory deinsertion (or α -elimination) of a low-valent main-group fragment ER_n from a $\text{M–ER}_n\text{R}'$ derivative. This process was first observed for zirconocene and hafnocene stannyl derivatives such as $[\text{CpCp}^*(\text{Cl})\text{Hf–SnPh}_3]$ ($\text{Cp} = \text{C}_5\text{H}_5$, $\text{Cp}^* = \text{C}_5\text{Me}_5$), which decomposes to $[\text{CpCp}^*(\text{Cl})\text{Hf–Ph}]$ and SnPh_2 ,^[7] and $[\text{CpCp}^*(\text{Cl})\text{Hf–SnHMe}_3]$ ($\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$), which eliminates SnMe_2 to form $[\text{CpCp}^*(\text{Cl})\text{Hf–H}]$.^[5] Eliminations of this type appear to operate in the catalytic dehydropolymerization of secondary stannanes R_2SnH_2 to polystannanes $\text{H}(\text{SnR}_2)_n\text{H}$. A likely mechanism

for the latter process involves dehydrocoupling of the stannane with a metal hydride by σ -bond metathesis to form H_2 and a Hf–SnHR_2 complex, with subsequent elimination of the stannylene SnR_2 to regenerate the metal hydride. The stannylene is then polymerized by rapid insertions into Hf–Sn or H–Sn bonds (Scheme 1).^[6] Similar reactivity leads to



Scheme 1. Mechanism proposed for the dehydrocoupling of stannanes in the presence of a hafnium hydride.^[6] The catalytic production of stannylene is followed by insertions into Hf–Sn ($\text{X} = \text{Hf}$) or H–Sn ($\text{X} = \text{H}$) bonds.

Sb–Sb bond formation by α -stibinidene elimination from a Hf–SbHR complex,^[8] and an analogous process is implicated for the formation of As–As bonds via a Zr–AsHMe derivative.^[9] In parallel, the α -elimination of methylene from $[\text{Cp}'_2\text{Ce}(\text{CH}_2\text{X})]$ ($\text{Cp}' = 1,2,4\text{-}i\text{Bu}_3\text{C}_5\text{H}_2$; $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{OMe}, \text{NMe}_2$) in the reaction of $[\text{Cp}'_2\text{CeH}]$ with CH_3X to form $[\text{Cp}'_2\text{CeX}]$ and CH_4 shows that the formation of carbene occurs in the presence of electron-withdrawing X groups.^[10]

Interestingly, then, there appears to be two fundamental processes associated with dehydrocoupling of main-group compounds as catalyzed by early transition metals: σ -bond metathesis and migratory deinsertion of low-valent species (and subsequent reinsertion into the appropriate bond). Experimentally, the mechanism of Scheme 1 may be difficult to distinguish from a mechanism involving only σ -bond metathesis steps (as proposed for silanes).^[3] To address this issue, computational studies have been carried out on Sn–Sn bond-forming reactions of the hydride $[\text{Cp}_2(\text{Cl})\text{HfH}]$ ($[\text{HfH}]\text{H}$, **1**) with SnH_4 and Ph_2SnH_2 . These calculations show that the initially formed stannyl complex $[\text{Cp}_2(\text{Cl})\text{Hf–SnH}_3]$ (**2**) exists in several isomeric forms. The most stable isomer possesses a normal Hf–Sn σ bond, and a slightly less stable isomer features the SnH_3 group bonded to Hf through one of the hydrogen atoms. The latter isomer is found to function as a stannylene source in delivering SnH_2 to SnH_4 (to form Sn_2H_6) or to **2** (to form $[\text{Cp}_2(\text{Cl})\text{HfSn}_2\text{H}_5]$), with free-energy barriers that are lower than those associated with a purely σ -bond metathesis mechanism for Sn–Sn bond formation.

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 $\text{Cp} = \text{C}_5\text{H}_5$.

Supporting information for this article, including coordinates, E and G (a.u.) for all extrema, NBO analysis, and complete Gaussian 03 reference, is available on the WWW under <http://dx.doi.org/10.1002/anie.200906476>.

The pathways of Scheme 1 have been studied with DFT calculations.^[11] Unless otherwise stated, the free-energy reference G_0 represents the separated reactants (**1** along with appropriate stannanes or stannyl complexes).

As shown in Figure 1, SnH_4 reacts with **1** by σ -bond metathesis to form **2** and H_2 with a free-energy barrier of $21.1 \text{ kcal mol}^{-1}$ and a favorable free energy of reaction of $21.1 \text{ kcal mol}^{-1}$ and a favorable free energy of reaction of

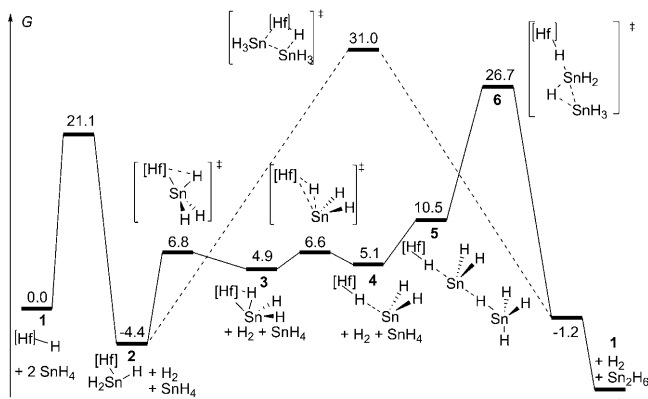


Figure 1. Free energy G in kcal mol^{-1} for the dehydrocoupling of SnH_4 by way of two successive σ -bond metathesis steps (solid and dashed lines), or by way of σ -bond metathesis and subsequent SnH_2 transfer (solid lines).

$4.4 \text{ kcal mol}^{-1}$. The transition state has the usual kite-shaped structure^[12] with no remarkable features. The subsequent reaction of **2** with SnH_4 by σ -bond metathesis to yield **1** and Sn_2H_6 has a transition state at 31 kcal mol^{-1} and a favorable energy of reaction of $9.3 \text{ kcal mol}^{-1}$. Thus, the latter metathesis reaction is associated with a significantly higher barrier than the first. The first metathesis step involves a “central” approach of SnH_4 within the H-Hf-Cl wedge, while the second step requires the “lateral” approach of SnH_4 toward the Hf-SnH_3 bond. Both reactions feature a stabilizing $\text{Cl}\cdots\text{Sn}$ interaction^[13] in the transition state (see the Supporting Information). The high barrier for the second σ -bond metathesis step suggests that alternative pathways should be considered.

The bonding of SnH_3 to Hf in **2** is that expected for an ER_3 group, where E is a Group 14 element (Figure 2). Two isomers

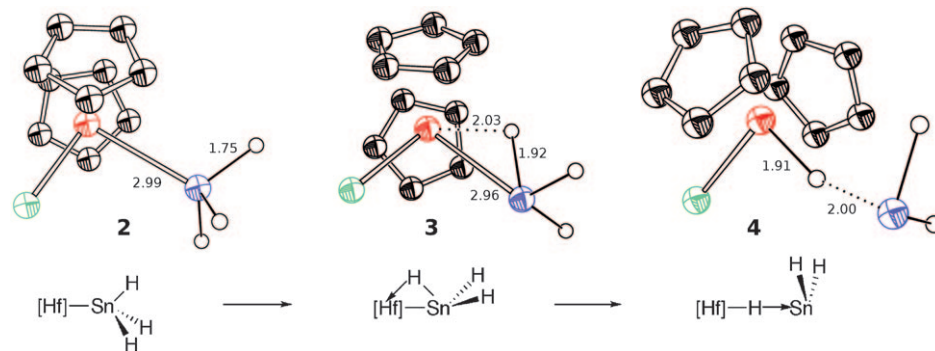


Figure 2. Optimized structures of **2**, **3**, and **4**, (distances in Å, Hf red, Sn blue, Cl green). The hydrogen atoms of C_5H_5 are omitted. Hydrogen atoms on Sn are represented as circles.

of **2** (**3** and **4**) were located with free energies of 9.3 and $9.5 \text{ kcal mol}^{-1}$ above **2**. Species **2**, **3**, and **4** differ in the manner that the SnH_3 group interacts with the Hf center. In **2**, the Hf-Sn-H angles of 114° reflect sp^3 hybridization at the Sn center. Species **3** features a strongly distorted SnH_3 group with a Sn-H bond oriented away from the chloride and toward the Hf atom (Figure 2). The very acute Hf-Sn-H bond angle is 43° , and a natural bond orbital (NBO) analysis suggests the presence of a Hf-Sn-H three-center, two-electron bond. In **3**, the Sn atom has a σ lone pair with 44% 5s character, which donates electron density to an empty Hf d orbital. In **4**, a hydride bridges between the Hf and Sn atoms, as defined by a $\text{Hf}-(\mu\text{-H})\text{-Sn}$ angle of 160° and Hf-H and Sn-H bond lengths of 1.91 and 2.00 Å , respectively. In isomer **4**, the Sn σ lone pair, with 78% 5s contribution, does not interact with another atom (Figure 3). The SnH_2 fragment

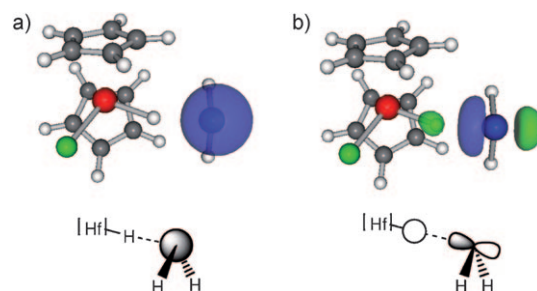


Figure 3. Frontier orbitals of **4** (calculated top, schematic bottom). a) Occupied orbital corresponding to a lone pair (78% of 5s Sn); b) low-lying empty orbital, with large 5p Sn character.

is essentially perpendicular to the $\text{Sn}-(\mu\text{-H})$ vector, as shown by an average $(\mu\text{-H})\text{-Sn-H}$ bond angle of 85° . The NBO analysis confirms that the $\mu\text{-H}$ hydride donates electron density to the 5p orbital of the SnH_2 fragment. Thus, **4** can be viewed as a donor-acceptor complex between $[\text{Hf}]\text{-H}$ and SnH_2 . The stabilizing interaction between these two species is $18.8 \text{ kcal mol}^{-1}$, and this species possesses a low-lying, empty orbital with a strong contribution from the 5p Sn orbital and substantial $(\mu\text{-H})\text{-Sn}$ antibonding character (Figure 3). The free-energy barrier for isomerization of **2** to **3** (via TS2-3) is $11.2 \text{ kcal mol}^{-1}$, and the corresponding barrier for the **3** to **4** conversion (via TS3-4) is $1.7 \text{ kcal mol}^{-1}$. The transition-state geometries show that the Hf-Sn bond is not affected by the conversion of **2** to **3**, which mainly involves a pivoting of the SnH_3 group to allow formation of the $\text{H}\cdots\text{Hf}$ interaction. After this pivoting, the isomerization from **3** to **4** involves cleavage of the Hf-Sn bond. Note that the calculated low energy barriers between **2**, **3**, and **4** suggest that these structures are accessible and can play a role in reactivity.

The transition state **6** for SnH_2 transfer from the stannyl

complex to SnH_4 was located with a free energy of $26.7 \text{ kcal mol}^{-1}$ above G_0 . It is preceded by formation of an adduct (**5**) between **4** and SnH_4 , resulting in an $\text{Sn}\cdots\text{H}$ interaction defined by a Sn-H-Sn bond angle of 132° (Figure 4). On going to TS **6**, the Sn-H-Sn angle decreases to 76° , and as the reaction

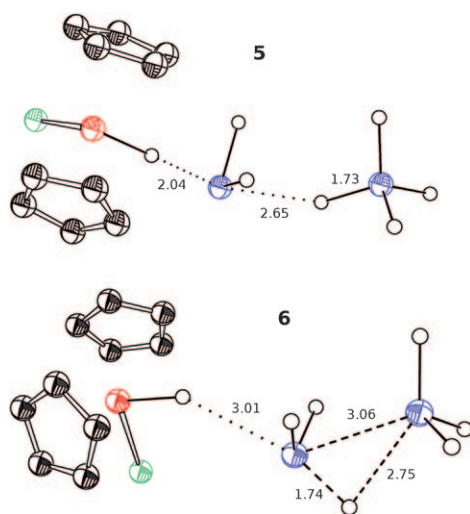


Figure 4. Structures of adduct **5** and transition state **6** (distances in Å, colors as in Figure 2).

proceeds to products, **6** transforms into $[\text{Hf}]\text{-H}$ and Sn_2H_6 . The geometry of the transition state shows that a $5p$ orbital of Sn points towards the H-Sn bond of SnH_4 , while the lone pair of Sn is not involved. This result indicates that the SnH_2 fragment in **4** has a strong electrophilic character, in agreement with the presence of a low-lying empty orbital on **4** with a large contribution from Sn (Figure 3).

Previously reported experimental data suggest the possibility for Sn-Sn bond formation by insertion of a free stannylene into a Hf-Sn bond (Scheme 1).^[6] Accordingly, the transition state **8** for SnH_2 transfer from **4** to a stannyl complex, to form $[\text{Hf}]\text{Sn}_2\text{H}_5$, was located, with a free energy of $19.4 \text{ kcal mol}^{-1}$ above G_0 . Transition state **8** is preceded by formation of an adduct **7** between **4** and **2**, where the stannylene is almost midway (ca. 2.20 Å) between HfH and SnH hydrogen atoms of the two metal fragments (Figure 5). The stannylene is oriented with its $5p$ orbital pointing toward the hydrogen atom of the stannyl group. On proceeding to **8**, the stannylene rotates by 180° about the $\text{Sn}-(\mu\text{-H})$ direction and approaches Hf at a distance of 3.09 Å , which is similar to the other Hf-Sn separation of 3.03 Å . At transition state **8**, the stannylene directs a $5p$ orbital towards a Sn-H bond, as in **7**, and its σ lone pair towards Hf . An NBO analysis of **8** confirms the donor-acceptor interaction between the stannyl and stannylene fragments and from the stannylene to Hf (see the Supporting Information). This result contrasts with the stannylene insertion into SnH_4 (transition state **6**), in which the stannylene primarily plays the role of an electron-acceptor group. In the latter case, the absence of an appropriate empty orbital on the stannane prevents the stannylene from using its σ lone pair for bonding in the transition state. This situation accounts for the lower energy

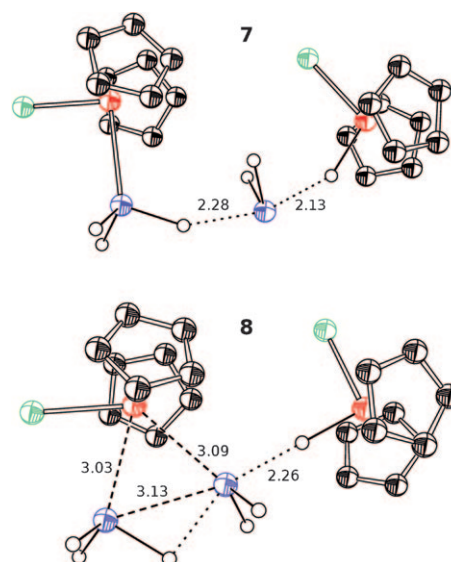


Figure 5. Structures of adduct **7** and transition state **8** (distances in Å, colors as in Figure 2).

of transition state **8** compared to that of **6** (19.4 and $26.7 \text{ kcal mol}^{-1}$).

This study shows that the least favorable pathway for reaction of $[\text{Hf}]\text{-SnH}_3$ (**2**) with SnH_4 is σ -bond metathesis, and that the most favorable mechanism involves SnH_2 transfer into the Hf-Sn bond of a stannyl complex. Calculations of representative extrema with Ph_2SnH_2 in place of SnH_4 gave similar results. The calculations are therefore in good agreement with experiment, in that insertion into the Hf-Sn bond is preferred for unhindered stannanes (such as SnH_4 and Ph_2SnH_2). Although bulky stannanes were not considered, it is likely that σ -bond metathesis would be even more disfavored in such cases. The calculated activation barriers are also in agreement with the need to run the experiments at room temperature or above.^[5,6]

It is remarkable that the dehydrocoupling of SnH_4 to Sn_2H_6 may occur by transfer of a stannylene unit without the need for complete α -elimination of the free stannylene. The comparison between complete elimination of a “free” stannylene and the transfer mechanism described herein will be the topic of a future study. The stannylene-transfer reaction is energetically feasible owing to the dynamic behavior of the stannyl complex, which readily isomerizes to a species possessing a reactive stannylene unit. Interestingly, the stannylene is intramolecularly stabilized by a hafnium hydride fragment. Such structures may only be accessible for the heavier main-group elements, as they appear to be associated with the presence of a stable lone pair with a high degree of s character and a low-lying empty orbital (e.g., the empty $5p$ orbital on SnH_2 ; Figure 3).^[14] Whether or not this reactivity is possible for additional main-group elements, and in particular lighter elements such as silicon, remains to be explored.

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