Masked Stannylenes

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Facile Interconversion of [$Cp_2(Cl)Hf(SnH_3)$] and [$Cp_2(Cl)Hf(\mu\text{-}H)SnH_2$]: DFT Investigations of Hafnocene Stannyl Complexes as Masked Stannylenes**

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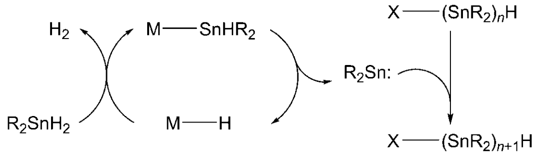
Electrophilic, d^0 transition-metal complexes have found use as effective catalysts for a number of chemical transformations, most prominently olefin polymerization. The reactivity associated with this catalysis involves rapid migratory insertions of the olefin substrate into d^0 metal-carbon bonds. 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 $M{-}ER_nR'$ derivative. This process was first observed for zirconocene and hafnocene stannyl derivatives such as [$CpCp^*(Cl)Hf{-}SnPh_3$] ($Cp = C_5H_5$, $Cp^* = C_5Me_5$), which decomposes to [$CpCp^*(Cl)Hf{-}Ph$] and $SnPh_2$,[7] and [$CpCp^*(Cl)Hf{-}SnHMes_2$] (Mes = 2,4,6-$Me_3C_6H_2$), which eliminates $SnMes_2$ to form [$CpCp^*(Cl)Hf{-}H$].[5] Eliminations of this type appear to operate in the catalytic dehydropolymerization of secondary stannanes R_2SnH_2 to polystannanes $H(SnR_2)_nH$. 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 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–AsHMes derivative.[9] In parallel, the α-elimination of methylene from [$Cp'_2Ce(CH_2X)$] ($Cp' = 1,2,4\text{-}t Bu_3C_5H_2$; X = F, Cl, Br, I, OMe, NMe_2) in the reaction of [Cp'_2CeH] with CH_3X to form [Cp'_2CeX] and CH_4 shows that the formation of carbene occurs in the presence of electron-withdrawing X groups .[10]



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 (X = Hf) or H–Sn (X = H) bonds.

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 [$Cp_2(Cl)HfH$] ([Hf]H, **1**) with SnH_4 and Ph_2SnH_2. These calculations show that the initially formed stannyl complex [$Cp_2(Cl)Hf{-}SnH_3$] (**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 [$Cp_2(Cl)HfSn_2H_5$]), 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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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 kcal mol^{-1} and a favorable free energy of reaction of 4.4 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 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 Cl···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.

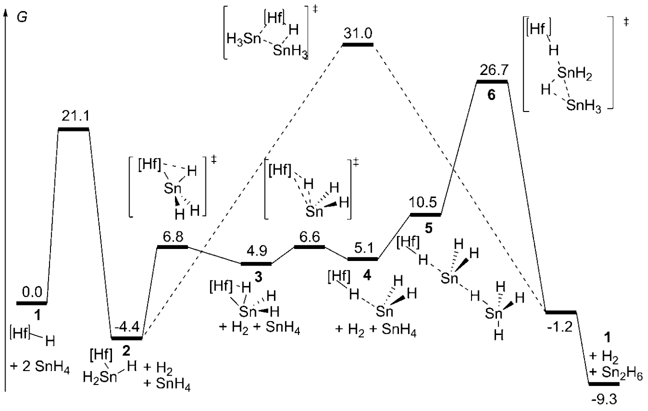

Figure 1. Free energy G in kcal mol^{-1} for the dehydrocoupling of SnH_4 by way of two successive σ-bond metathesis steps (solid and dashed lines), or by way of σ-bond metathesis and subsequent SnH_2 transfer (solid lines).

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 of **2** (**3** and **4**) were located with free energies of 9.3 and 9.5 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 Hf-(μ-H)-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 is essentially perpendicular to the Sn–(μ-H) vector, as shown by an average (μ-H)-Sn–H bond angle of 85°. The NBO analysis confirms that the μ-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 [Hf]–H and SnH_2. The stabilizing interaction between these two species is 18.8 kcal mol^{-1}, and this species possesses a low-lying, empty orbital with a strong contribution from the 5p Sn orbital and substantial (μ-H)–Sn antibonding character (Figure 3). The free-energy barrier for isomerization of **2** to **3** (via TS**2**–**3**) is 11.2 kcal mol^{-1}, and the corresponding barrier for the **3** to **4** conversion (via TS**3**–**4**) is 1.7 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 H···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.

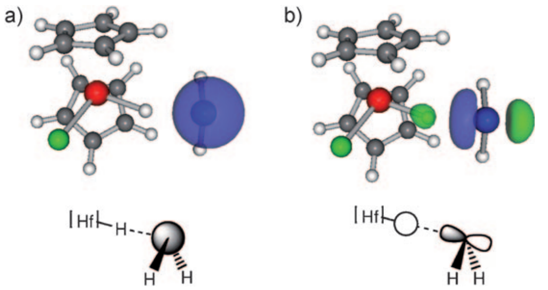

Figure 3. Frontier orbitals of **4** (calculated top, schematic bottom). a) Occupied orbital corresponding to a lone pair (78 % of 5s Sn); b) low-lying empty orbital, with large 5p Sn character.

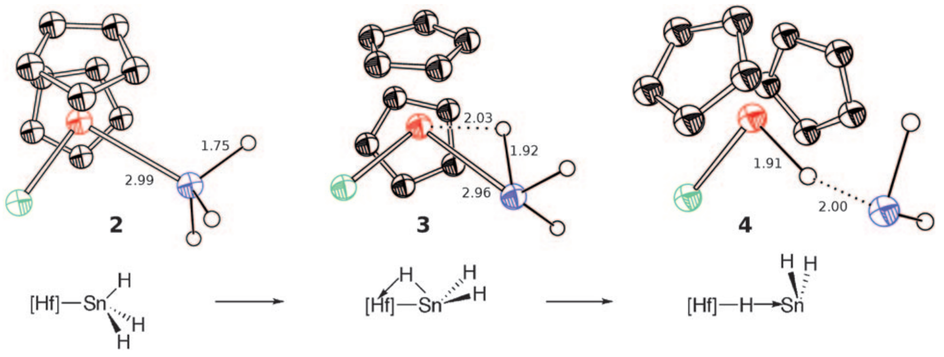

Figure 2. Optimized structures of **2**, **3**, and **4**, (distances in Å, Hf red, Sn blue, Cl green). The hydrogen atoms of C_5H_5 are omitted. Hydrogen atoms on Sn are represented as circles.

The transition state **6** for SnH_2 transfer from the stannyl complex to SnH_4 was located with a free energy of 26.7 kcal mol^{-1} above G_0. It is preceded by formation of an adduct (**5**) between **4** and SnH_4, resulting in an Sn···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 proceeds to products, **6** transforms into [Hf]−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).

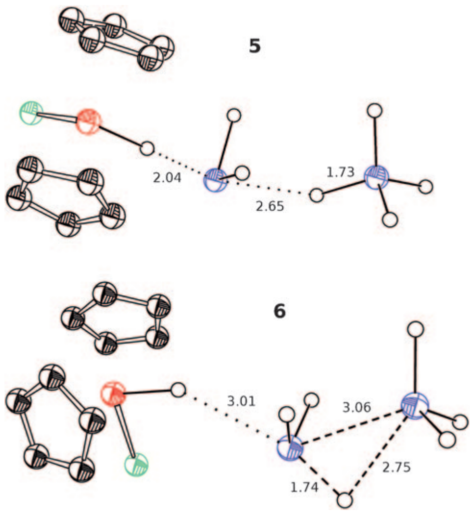

Figure 4. Structures of adduct **5** and transition state **6** (distances in Å, colors as in Figure 2).

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 [Hf]Sn_2H_5, was located, with a free energy of 19.4 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 Sn−(μ-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 of transition state **8** compared to that of **6** (19.4 and 26.7 kcal mol^{-1}).

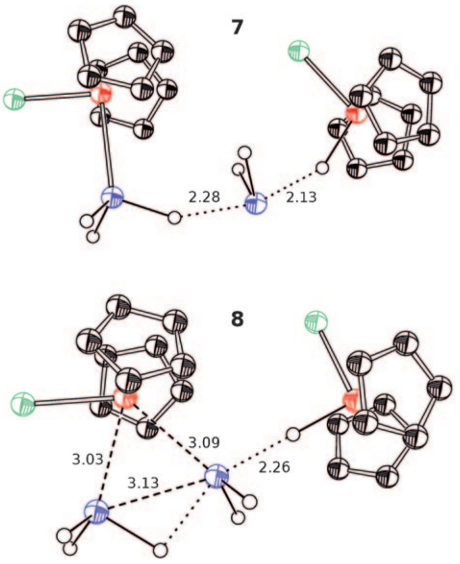

Figure 5. Structures of adduct **7** and transition state **8** (distances in Å, colors as in Figure 2).

This study shows that the least favorable pathway for reaction of [Hf]−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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