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A New Mechanism for Metal-Catalyzed Stannane Dehydrocoupling Based on α-H-Elimination in a Hafnium Hydrostannyl Complex

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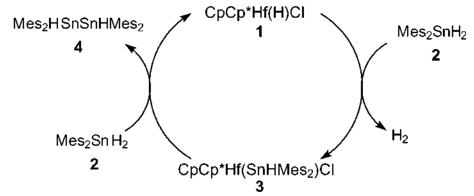
The transition metal-catalyzed dehydropolymerization of secondary stannanes by zirconocene catalysts provided the first examples of high-molecular weight polystannanes,[1] which exhibit interesting optical and electronic properties.[2] Further applications of dehydrocoupling methodologies in tin chemistry should be facilitated by knowledge of the mechanism by which the metal center mediates Sn−Sn bond formation. A possible mechanism for the d^0 metal-catalyzed dehydrocoupling of hydrostannanes involves σ-bond metathesis steps operating via concerted, four-center transition states, as described for the analogous dehydrocoupling of hydrosilanes.[3] Our efforts to probe this question have previously been thwarted by unsuccessful attempts to isolate examples of the presumed σ-bond metathesis intermediate, a d^0 metal hydrostannyl ($M-SnHR_2$) derivative. Furthermore, the low Sn−H bond strength suggests the possible operation of dehyrocoupling mechanisms involving tin-centered radicals.[4] Here we describe a metal-catalyzed dehydrocoupling of Mes_2SnH_2 to $Mes_2HSnSnHMes_2$ (Mes = 2,4,6-trimethylphenyl), for which an intermediate d^0 metal hydrostannyl complex has been isolated and studied. The dehydrocoupling in this system appears to occur by elimination of $:SnMes_2$ from CpCp*Hf(SnHMes$_2$)Cl (Cp* = η^5-C_5Me_5), with Sn−Sn bond formation proceeding via insertion of the stannylene into a Sn−H bond.

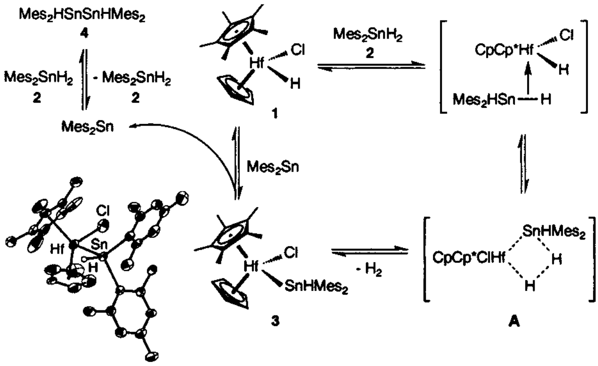
The reaction of CpCp*Hf(H)Cl[3a] (**1**) with Mes_2SnH_2 (**2**) resulted in the elimination of hydrogen and the formation of the hydrostannyl complex CpCp*Hf(SnHMes$_2$)Cl (**3**) (benzene-d_6, 10 °C, in the dark, by ^{1}H NMR spectroscopy). After 2 h the concentration of **3** reached a maximum (64% of Hf species present), and after complete conversion of the stannane **2** (12 h) the products remaining were **3** (59%) and the distannane $Mes_2HSnSnHMes_2$ (**4**, 31%). The presence of a significant amount of **1** (26%) at this point suggested that this complex might be a catalyst for the dehydrocoupling of **2** to **4**, and this was confirmed by observation of this conversion (in 98% yield) over 24 h with a catalytic amount of **1** (4 mol %, benzene-d_6, dark, 25 °C). Further investigation (vida infra) suggested that **3** is an intermediate in the catalysis, as indicated by the mechanism of Scheme 1.

The hafnium hydrostannyl complex **3** was isolated as thermochromic crystals (yellow $\lesssim$10 °C; orange $\gtrsim$10 °C) in 64% yield from the stoichiometric reaction between **1** and **2** (1.5 h, 10 °C, dark, benzene). The molecular structure of **3** (Scheme 2) is characterized by a Hf−Sn bond length of 3.0073(6) Å. For comparison, the other d^0 group 4 M−Sn bond lengths to be reported are 2.843(1) Å for $Cp_2Ti(SnPh_3)Cl$,[5] and 3.0231(2) (M = Zr) and 2.9956(3) Å (M = Hf) for {MeSi[SiMe$_2$N(4-CH$_3$C$_6$H$_4$)]$_3$}SnMCp$_2$Cl.[6] There is no apparent interaction between the Hf center and the Sn−H bond of **3** (the Sn−H hydrogen was located in the difference Fourier map). As expected,[7] the $^1J_{117/119\text{SnH}}$ coupling constants (918, 961 Hz) are greatly reduced from the corresponding values for the free stannane (1765, 1864 Hz), as is the ν_{SnH} stretching frequency (1728 cm^{-1}; 1864 cm^{-1} for **2**).

Scheme 1



Scheme 2



The dehydrogenative condensation of **1** and **2** is reversible, as indicated by the addition of H_2 (1 atm) to a solution of isolated **3**, which resulted in the conversion of **3** to **1** (92%) and **4** (21%) over 2 days. The expected stannane **2** was observed only in trace amounts during the reaction, since it is converted to **4** under these conditions. Thus, complex **3** appears to possess an unusually reactive metal−tin bond, as zirconium and hafnium stannyl derivatives that have been studied previously do not undergo hydrogenolysis.[8]

To probe the Hf−Sn bond-forming process of Scheme 1, the kinetics of the reaction between **1** and **2** were studied at 9.3 °C (benzene-d_6) under pseudo-first-order conditions of excess stannane. Despite the reversibility of this reaction, well-behaved kinetics were observed for ca. 75% conversion of **1** in the presence of excess **2**. The dependence of the rates on the concentration of **2** established a second-order rate law, rate = k[**1**][**2**], with k(9.3 °C) = 6.4 (2) × 10^{-3} M^{-1} s^{-1}. The activation parameters determined by an Eyring analysis (over the temperature range 0.7−33.2 °C), $\Delta H^\ddagger = 7.4$ (3) kcal mol^{-1} and $\Delta S^\ddagger = -42$ (1) eu, are consistent with a concerted σ-bond metathesis process in which severe restriction of vibrational or rotational degrees of freedom accompanies formation of the transition state.

A further probe of the mechanism involved isotopic labeling studies with deuterium. However, the kinetic isotope effect measured for the reaction of the deuterated stannane **2**-d_2 with **1**, $k_{\text{HH}}/k_{\text{HD}} = 1.2$ (1), is much lower than what might be expected for a concerted transition state **A** (Scheme 2).[9] Deuteration at hafnium (**1**-d_1) results in a small, inverse isotope effect, $k_{\text{HH}}/k_{\text{DH}} = 0.89$ (3),

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and deuteration at both Hf and Sn results in a cancellation of the previous effects: $k_{HH}/k_{DD} = 1.0$ (1). These results may be explained by a mechanism involving rate-determining coordination of the Sn−H bond of the stannane to the Hf center of **1** to form a σ-complex (Scheme 2). Cleavage of the Sn−H bond would then occur in a subsequent, relatively rapid step involving the 4-center transition state **A**. In our view, the inverse isotope effect is best explained as a secondary effect resulting from loss of the normal bending modes for the Hf−H(D) bond in the sterically crowded Sn−H σ-complex.[10] The kinetic behavior described above has not been previously observed for σ-bond metathesis processes, but it appears to reflect the highly crowded nature of the reactants **1** and **2**.

Given the sterically encumbered natures of **2** and **3**, it seemed unlikely that they could react in a concerted manner to produce the distannane. Attempts to study the kinetics of this process were complicated by the relatively rapid decomposition of **3** in solution. Interestingly, the thermal decomposition of **3** (toluene-d_8, in the dark) cleanly produced the hydride **1** (20% after 10 min), and over the course of 3 days a temperature-dependent equilibrium was established. At room temperature, the **3**/**1** ratio was 1:10, while at −30 °C complex **3** was favored by a ratio of 2:1. Thus, it appears that **3** decomposes via the elimination of dimesitylstannylene; however, ^{1}H NMR spectra of the reaction mixture suggested the presence of a number of mesityl-containing products. To facilitate their identification, the concentration of tin species in solution was increased by adding a significant amount of **2** to **3**, and analysis of this reaction mixture (13 equiv **2**, benzene-d_6, dark, 25 °C) by ^{119}Sn NMR spectroscopy revealed the presence of three tin species (δ −348.7, −316.8, −225.7). By comparison to known values for other $(R_2Sn)_n$ compounds,[1b,11] we attribute these shifts to the cyclics $(Mes_2Sn)_n$, with $n = 3$, 4, and 5. In addition, a FAB-MS analysis of this solution gave ions corresponding to the $n = 3$ and 4 cyclics; fragmentation of $(Mes_2Sn)_5$ likely prevented its detection by mass spectrometry. It therefore appears that complex **3** exists in equilibrium with **1** and a mixture of cyclic species derived from the oligomerization of :SnMes$_2$ (eq 1).

$$\underset{\mathbf{3}}{\mathrm{CpCp^*Hf(SnHMes_2)Cl}} \underset{+1}{\overset{-1}{\rightleftharpoons}} \mathrm{Mes_2Sn} \rightleftharpoons \underset{n = 3,\, 4,\, 5}{1/n\,(\mathrm{Mes_2Sn})_n} \qquad (1)$$

Further evidence in support of the α-H-elimination of stannylene from **3** was obtained by a trapping experiment in which **3** was allowed to decompose in the presence of the trapping agent 2,3-dimethylbutadiene (23 equiv), which resulted in a 92% yield (by ^{1}H NMR spectroscopy) of the stannylene-trapped product 1,1-dimesityl-3,4-dimethylstannacyclopent-3-ene (**5**). An attempt to measure the rate of this α-H-elimination using the highly efficient stannylene trap 1,2-bis(methylene)cylcopentane[12] indicated that the first-order rate constant was 2×10^{-3} s^{-1} (200 equiv, −25 °C, toluene-d_8). However, doubling the amount of the diene from 200 to 400 equiv led to an increase of the apparent rate constant by a factor of 1.7. The lack of an efficient trap for :SnMes$_2$ has prevented us from directly probing the kinetics of α-elimination, although it seems clear that this process is quite rapid.

Insight into the mechanism for Sn−Sn bond formation was derived from the reaction of **3** with the dideuteriostannane Mes$_2$SnD$_2$ (**2**-d_2, 1.0 equiv) in benzene-d_6. At room temperature, **2**-d_2 was completely consumed in less than 100 min and was converted to the dideuteriodistannane Mes$_2$DSnSnDMes$_2$ (**4**-d_2) and the monodeuteriodistannane Mes$_2$HSnSnDMes$_2$ (**4**-d_1) in 67 and 6% yields, respectively (the remaining tin species were **3** (8%) and $(Mes_2Sn)_n$ (19%)). However, when **4** was mixed with **2**-d_2 (1.2 equiv), **4**-d_1 (21%), **2**-d_1 (39%), and **2** (13%) were formed over the course of 11 days (benzene-d_6, by ^{1}H NMR spectroscopy), suggesting that this distannane may also exist in equilibrium with **2** and :SnMes$_2$. This elimination and reinsertion of stannylene has previously been observed for distannanes.[13] Thus, the observed **4**-d_1 was most likely formed from scrambling via the equilibria of Scheme 2. These data lead us to believe that Sn−Sn bond formation results from stannylene insertion into the Sn−H bond of the stannane (Scheme 2). Similar stannylene insertions have been proposed for related Sn−Sn bond-formations,[14] including the stepwise synthesis of linear chains up to 15 Sn atoms in length.[14f]

In summary, isolation of a reactive d^0 metal hydrostannyl complex has allowed mechanistic studies on a metal-catalyzed Sn−Sn bond formation which features an α-H-elimination process. This elimination produces the free stannylene :SnMes$_2$, which appears to insert into a Sn−H bond to produce the distannane. Interestingly, the experimental data may be interpreted as evidence for coordination of a σ bond prior to a σ-bond metathesis step. Future efforts will focus on establishing whether this mechanism may be operative in metal-catalyzed dehydropolymerizations of secondary stannanes to polystannanes. In addition, we have begun to explore α-elimination as a general decomposition mode for compounds containing d^0 metal−main group element bonds.

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Supporting Information Available: Experimental details of the synthesis of compounds **2**, **3**, **4**, and **5**, kinetic measurements, tables and plots of kinetic data, and tables of crystal, data collection, and refinement parameters, bond distances and angles, and anisotropic displacement parameters for **3** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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