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Dehydrogenative Dimerization of Di-*tert*-butyltin Dihydride Photochemically and Thermally Catalyzed by Iron and Molybdenum Complexes**

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Dehydrogenative coupling of tertiary stannanes, R_3SnH, catalyzed by a transition metal is known to produce distannanes, $R_3Sn{-}SnR_3$,[1] whereas a mixture of cyclic and linear oligo- or polystannanes is obtained from the analogous dehydrogenative coupling of secondary stannanes, R_2SnH_2.[2–4] 1,2-Dihydrodistannanes are of significant interest as bifunctional model compounds to mimic the properties of polystannanes and they are excellent precursors for further derivatization. However, until a report by Uhlig et al.[5a] there were no well-defined methodologies for the synthesis of 1,2-dihydrodistannanes.[6] The Uhlig synthesis involves a two-step reaction sequence that starts with the reaction of *tert*-butylmagnesium chloride with tin tetrachloride in an overall yield of 2.5%. We now report the photochemical and thermal dehydrogenative dimerization of $t\mathrm{Bu_2SnH_2}$ (**1**) to $t\mathrm{Bu_2HSn{-}SnH}t\mathrm{Bu_2}$ (**2**), catalyzed by the iron catalysts **3** and **4** and their molybdenum analogues **5** and **6**.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2Me]$ (**3**)
$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)Me]$ (**4**)
$[(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)Me]$; L = CO (**5**), PPh_3 (**6**)

Irradiation of a C_6D_6 solution of $t\mathrm{Bu_2SnH_2}$ in the presence of 5 mol% of **3** in a sealed Pyrex NMR tube with a medium-pressure mercury lamp resulted in the progressive formation of **2**[7] [Eq. (1)]. The photochemical reaction was monitored

$$2\,t\mathrm{Bu_2SnH_2} \xrightarrow[\mathrm{C_6D_6}]{\mathrm{catalyst}/h\nu} \mathrm{H}t\mathrm{Bu_2Sn{-}Sn}t\mathrm{Bu_2H} \qquad (1)$$

by ^{119}Sn and ^{1}H NMR spectroscopy and turned out to be a clean transformation of **1** to **2**, that is, the ^{119}Sn resonance at −118.2 ppm (**1**) transformed to a resonance at −83.4 ppm (**2**) with 80% conversion after 30 h of irradiation. However, it became clear from the NMR monitoring that catalyst **3** is slowly consumed and the rate of catalytic transformation slows and ultimately the process stops. A similar photochemical reaction of 6 h duration using the isomeric stannane, $n\mathrm{Bu_2SnH_2}$ resulted in a transformation to the corresponding distannane, $(n\mathrm{Bu_2SnH})_2$ ($\delta(^{119}\mathrm{Sn}) = -208.2$ ppm), and oligostannanes of only about 5%. However, the catalyst was completely consumed in this short time period, at a rate much greater than with the *tert*-butyltin analogue, and this poses a problem for the utility of the process.

Since the key step in the catalysis is presumably the initial photochemical expulsion of a CO ligand to form a coordinatively unsaturated 16-electron species, we surmised that a similar system could be formed thermally by use of a phosphine-substituted derivative of the catalyst, that is, complex **4**. Indeed, treatment of a C_6D_6 solution of $t\mathrm{Bu_2SnH_2}$ (**1**) in the presence of 5 mol% of **4**, in a sealed Pyrex NMR tube at 60 °C, resulted in the 100% transformation of **1** to **2**. The reaction was monitored by ^{1}H, ^{13}C, ^{119}Sn, and ^{31}P NMR spectroscopy.[8] It became clear that catalyst **4** ($\delta(^{31}\mathrm{P}) = 86.6$ ppm) was a transient species that was replaced by $[\mathrm{CpFe(CO)(PPh_3)Sn}t\mathrm{Bu_2H}]$ (**7**, Cp = $\eta^5\text{-}C_5H_5$; $\delta(^{31}\mathrm{P}) = 77.4$ ppm).[9] Complete conversion of **4** to **7** occurred with approximately 50% transformation of **1** to **2.** However, continued monitoring indicated that the process **1**→**2** continued to completion, illustrating the role of **7** as a catalyst. A separate experiment using an independently synthesized sample of **7** corroborated the efficient catalytic transformation of **1** to **2**, yielding only a single organotin product with insignificant loss of catalyst **7.** The molecular structure of **7** was determined by X-ray structure analysis and is depicted in Figure 1.[10] The complex adopts a normal three-legged piano-

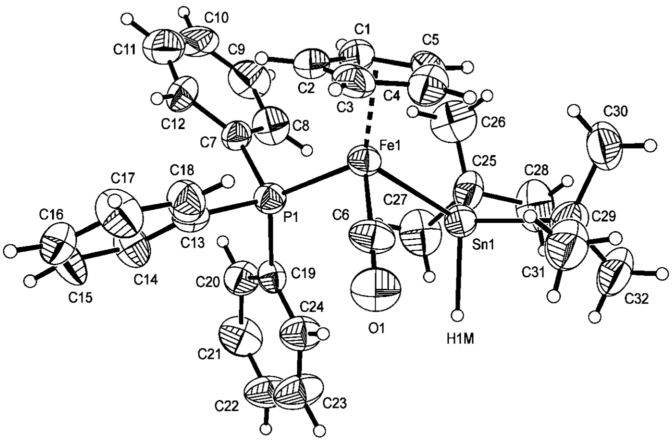

Figure 1. Molecular structure of **7**; selected distances [Å] and angles [°]: Fe1–Sn1 = 2.617(6), Sn1–H1M = 1.87(9), Fe1–C6 = 1.699(13), Fe1–P1 = 2.227(5) Å; C25-Sn1-Fe1 = 118.9(3), C29-Sn1-Fe1 = 113.3(4), C25-Sn1-C29 = 108.6(5), Sn1-Fe-P1 = 101.60(16), Sn1-Fe-C6 = 82.6(4), P1-Fe-C6 = 93.8(4).

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stool geometry in which the hydrogen atom at Sn is oriented *anti* with respect to the Cp ring to minimize steric interactions of the *t*Bu groups with PPh_3, and the P-Fe-Sn angle becomes slightly wider (101.58°) to accommodate the PPh_3 group. The Fe–Sn and Sn–H bond lengths of 2.617(6) Å and 1.87(9) Å, respectively, are intermediate between those of related transition metal tin complexes.[11]

Similar chemistry was observed using the molybdenum analogues **5** and **6** as catalysts. We could observe the formation of [CpMo(CO)$_3$Sn*t*Bu$_2$H] (**8**), synthesize it independently,[9] and demonstrate its utility as a catalyst in the photochemical transformation of **1** to **2**. The structure of this complex is illustrated in Figure 2;[10] the geometry at Mo is square pyramidal and, as with **7**, the hydrogen atom at Sn is *trans* to the Cp ring, with the Sn–H distance being slightly longer (2.14(3) Å) than in the Fe analogue **7**.

Attempts to perform the same transformation with di-*n*-butylstannane were not successful. The thermal reaction of *n*Bu$_2$SnH$_2$, using catalyst **4** at 60 °C, resulted in a complex mixture of cyclic and linear oligostannanes, H–(*n*Bu$_2$Sn)$_n$–H, with tin resonances at −202.5, −202.9, −208.1, −208.4, −209.9, and −220.5 ppm. We did not observe the transient formation of (*n*Bu)$_2$HSnSn(*n*Bu)$_2$H in high yields,[12] thus, this chemistry is not productive for the formation of tetra-*n*-butyldistannane. It is clear that the reaction is dominated by the nature of the groups on Sn: oligomeric materials are obtained for the less space-requiring *n*-butyl groups whereas dimers are formed for the bulkier *tert*-butyl groups. Recently Nakazawa et al. noted a similar dimerization of tertiary silanes using [CpFe(CO)$_2$Me] as a catalyst and dimethylformamide as solvent, and also noted that the nature of the R groups had a significant impact upon the efficiency of the process.[13]

The most probable mechanism to explain our results is related to the dimerization of tertiary stannanes and silanes reported by Braunstein et al.[1d] and Nakazawa et al.,[13,14] respectively, involving the transient formation of bis(stannyl) metal complexes (Scheme 1). The catalytic cycle involves the initial oxidative addition of *t*Bu$_2$SnH$_2$ to [CpM(CO)$_n$CH$_3$], followed by the reductive elimination of CH_4 to generate a new coordinatively unsaturated 16-electron species, [CpM(CO)$_n$(Sn*t*Bu$_2$H)]. A second oxidative addition of *t*Bu$_2$SnH$_2$ to this intermediate leads to the formation of [CpM(CO)$_n$(H)(Sn*t*Bu$_2$H)$_2$], a type of reaction that is well-established for reactions involving R_3SnH to form, for example, [CpFe(CO)(H)(SnR$_3$)$_2$].[15,16] For M = Fe, the hydridobis(stannyl)iron complex then reacts with either CO or PPh_3 to reductively eliminate the distannane and form [CpFe(CO)$_2$H] or [CpFe(CO)(H)(PPh$_3$)], respectively, a reaction similar to the reported elimination of disilanes from [CpFe(CO)(H)(SiR$_3$)$_2$] complexes.[13] The phosphine hydride complex is stable enough to persist and can regenerate the catalytically active species whereas the dicarbonyl hydride complex more rapidly forms the dimeric iron complex [{CpFe(CO)$_2$}$_2$] which stops the catalysis process. We have attempted to observe the

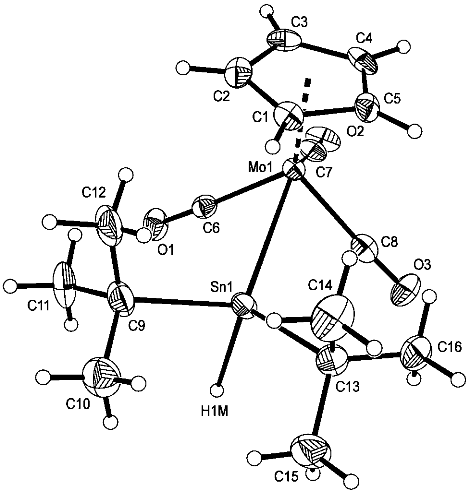
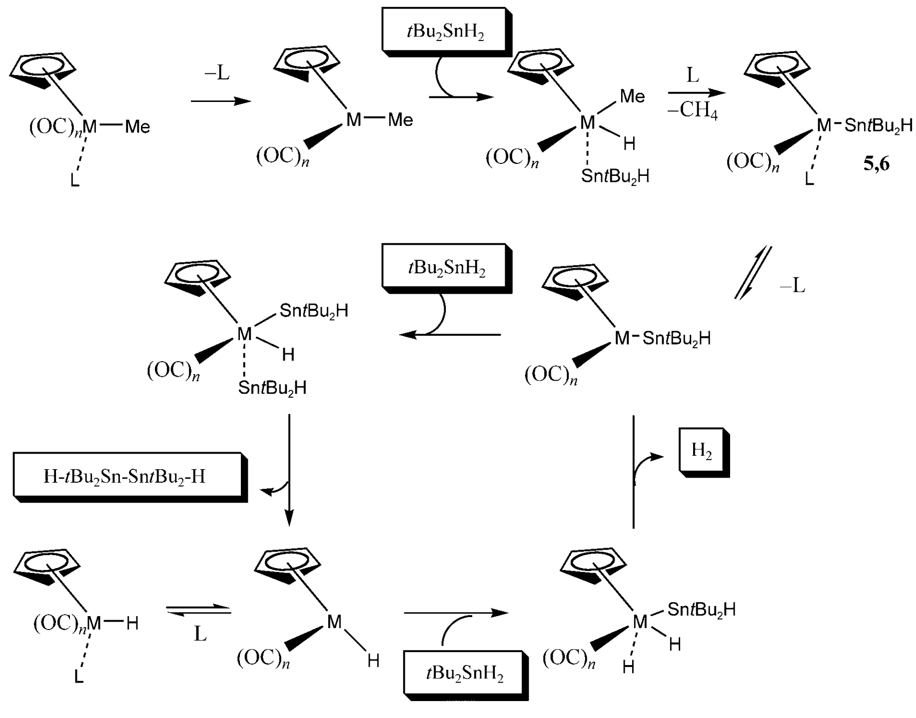


Figure 2. Molecular structure of **8**, the disorder on *t*Bu group C9 is omitted for clarity; selected distances [Å] and angles [°]: Fe1–Mo1 = 2.8565(11), Sn1–H1M = 2.14(3) Å; C9-Sn1-Mo1 = 113.65(10), C13-Sn1-Mo1 = 114.07(10), H1M-Sn1-Mo1 = 113.9(9), C13-Sn1-C29 = 112.05(14).



Scheme 1. The most probable mechanism to explain the results on stannane dimerization presented herein. *n* = 2, M = Fe, L = CO (**3**), PPh$_3$ (**4**); *n* = 3, M = Mo, L = CO (**5**), PPh$_3$ (**6**).

bis(stannyl) intermediate [CpFe(CO)(H)(SntBu$_2$H)$_2$] from the photochemical reaction of equimolar amounts of [CpFe(CO)$_2$(SntBu$_2$H)] and tBu$_2$SnH$_2$ in C$_6$D$_6$. This reaction is quite complex; however, we could identify the bis(stannyl)iron complex spectroscopically.[17]

In summary, we have established a new catalytic system involving iron and molybdenum complexes for the dehydrogenative dimerization of tBu$_2$SnH$_2$ both thermally and photochemically. The thermal catalytic process is much more efficient than the photochemical process and Mo catalysts are relatively more active than the corresponding Fe catalysts. Further studies to develop other transition metals as better catalysts with dialkyl/aryl tin hydrides are in progress.

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[7] a) In a catalytic experiment, a 5 mm Pyrex NMR tube was charged with a mixture of tBu$_2$SnH$_2$ (0.5–1.0 mmol) and 3–5 mol % of catalyst in 1.0 mL of degassed C$_6$D$_6$, and the tube was flame-sealed under vacuum. The sealed NMR tube was either irradiated with a 450 W medium-pressure mercury lamp at room temperature or suspended in an oil bath at 60 °C, and the reaction was periodically monitored by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy. After completion of the reaction, distannane **2** was separated from the catalyst by flash chromatography in hexanes and was isolated in 80–90 % yield. **Caution: When breaking the seal of the NMR tube, sometimes the tube shattered with a minor explosion. Therefore, it is recommended to cool the NMR tube in liquid N$_2$ before breaking the seal**. b) Photolysis of tBu$_2$SnH$_2$ in benzene in the absence of the catalyst for 24 h produced distannane **2** in 1 % yield.

[8] The ^{119}Sn NMR spectral changes associated with the conversion of **1** to **2** in the presence of catalyst **4** are presented in Figure 1 of the Supporting Information.

[9] For the synthesis and spectral data of **7** and **8**, see the Supporting Information.

[10] Single crystals of **7** or **8** were mounted on a Bruker APEX CCD diffractometer equipped with monochromatic Mo$_{K\alpha}$ radiation. Data collection was done with SMART [G. M. Sheldrick, SMART Bruker AXS, Madison, WI, USA, **2000**]. Cell refinement, data reduction, and incident beam and decay corrections were carried out with SAINT-Plus [G. M. Sheldrick, SAINT-Plus 6.23c Bruker AXS, Madison, WI, USA, **2000**]. The structure was solved by direct methods and refined by full-matrix least-squares techniques in SHELXTL [G. M. Sheldrick, SHELXTL 6.10 Bruker AXS, Madison, WI, USA, **2000**]. Hydrogen atoms were generated in calculated positions and constrained with the use of a riding model with the exception of the hydride that was located in the difference Fourier map. Crystal data for **7**: C$_{32}$H$_{39}$FeOPSn, $M = 645.14$, space group $P\bar{1}$, $a = 10.60(2)$, $b = 11.80(3)$, $c = 13.26(3)$ Å, $\alpha = 93.74(4)$, $\beta = 94.12(4)$, $\gamma = 114.42(3)°$. Cell volume $= 1499(6)$ Å^3, $T = 298(2)$ K, $Z = 2$, 14419 reflections collected, 5264 unique [$R_{\text{int}} = 0.1254$]. Completeness to $2\theta = 50°$: 99.5 %. $R1 = 0.0780$, $wR2 = 0.1985$ [$I > 2\sigma(I)$]. Crystal data for **8**: C$_{16}$H$_{24}$MoO$_3$Sn, $M = 478.98$, space group $P21/n$, $a = 6.720(4)$, $b = 28.689(15)$, $c = 9.545(5)$ Å, $\beta = 94.154(6)°$. Cell volume $= 1835.5(17)$ Å^3, $T = 100(2)$ K, $Z = 4$, 18400 reflections collected, 3716 unique [$R_{\text{int}} = 0.0365$]. Completeness to $2\theta = 52.70°$: 99.3 %. $R1 = 0.0313$, $wR2 = 0.1101$ [$I > 2\sigma(I)$]. CCDC 723088 (**7**) and CCDC 734347 (**8**) contain 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.

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[16] A σ-bond metathesis is possible, despite the fact that such mechanisms are generally associated with early transition metal complexes where formation of 16e$^-$ systems (and oxidation) is not so facile (or possible). However, many previous reports have

concluded that the species $CpFe(CO)CH_3$ is often involved in oxidative addition reactions, see for example: a) R. J. Kazlauskas, M. S. Wrighton, *Organometallics* **1982**, *1*, 602; b) R. H. Hooker, A. J. Rest, I. Whitwell, *J. Organomet. Chem.* **1984**, *266*, C27; c) B. A. S. Mohamed, M. Kikuchi, H. Hashimoto, K. Ueno, H. Tobita, H. Ogino, *Chem. Lett.* **2004**, *33*, 112; d) W. Adam, U. Azzena, F. Prechtl, K. Hindahl, W. Malisch, *Chem. Ber.* **1992**, *125*, 1409.

[17] Spectral data for the bis(stannyl)iron complex $[CpFe(CO)(H)(Sn\mathit{t}Bu_2H)_2]$: ^{119}Sn NMR ($C_6D_6$): $\delta = 126.0$ ppm; ^{1}H NMR: $\delta = -12.85$ (Fe-H), 1.38 (*t*Bu), 4.41 (Cp), 5.22 ppm (Sn-H); IR (hexane): $\tilde{\nu}(CO) = 1928\ cm^{-1}$.