

Supporting Information

Calculations

Theoretical calculations were performed on model tin (II) and tin (IV) hydride species with ligands of increasing size to determine the relative stabilities of forms **I**, **II**, and **III** (Figure S1). The ligands used for the computations were Me, Ph, Ar (Ar = 2,6-Ph₂C₆H₃) and Ar' (Ar' = C₆H₃-2,6-(C₆H₃-2,6-Prⁱ)₂). For all the ligands used, the optimized geometries of Sn (II) hydride species do not show any significant differences with the change of the basis sets used in these calculations (see experimental DFT section). All the computations for the dihydrogenated tin species are in agreement with the recent computations by Nagase et al. Some very small differences were found in the computed bond lengths and bond angles and somewhat larger differences were obtained in the overall energies

due to the use of a slightly different functional. For verification purposes, the geometries of forms **I**, **II**, and **III** with Ar' ligand were also optimized at [4333111/433111/43]/B3PW91 level of theory, and the obtained geometrical features were in perfect agreement with Nagase's results. The hydrogenation energies computed as $\Delta E_{\text{hydrogenation}} = (E_{\text{RSnHSnHR}} - (E_{\text{RSnSnR}} + E_{\text{H}_2}))$, exhibit a thermodynamical trend, which is always in favor of the hydrogenated species, independent of the size of the ligand used.

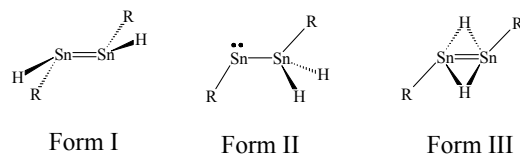


Figure S1. DFT optimized isomer forms of (RSnH)₂

For the calculations where R = Ar' (modeling **1a** & **1b**), the most stable gas-phase structure is the asymmetric form **II**. As in the case of Nagase's calculations, the hydride bridge form **III** is predicted to be the least stable isomer (by about 10 kcal mol⁻¹) even though this form is adopted by (Ar'SnH)₂ in the solid state. Due to the small energy differences between each of these isomers, factors such as crystal packing forces will determine which structure is more favored upon crystallization. The importance of packing forces is underlined by the structure of 4-Me₃Si-Ar'SnSnAr'-4-SiMe₃, in which trimethylsilyl substituted at the *para*-position of the central phenyl induces a single bonded structure for **2a** instead of the multiply bonded structure like that in **1a**. The optimized structure of the hydride-bridged isomer [Ar'Sn(μ-H)]₂ corresponds reasonably well to the structure of **1b** determined by X-ray crystallography. The calculated Sn-Sn separation (3.224Å) which is ca. 0.1 Å longer than that in **1b** [3.1260(11) Å] and the C_{ipso}-Sn-Sn (98.9°) is nearly identical to the one in **1b** (98.11° (15)). Also the central phenyl ring orthogonal to the Sn₂H₂ core is reproduced by the calculation data.

For the more bulky tin (II) hydride [(3,5-ⁱPr₂-Ar*)SnH]₂, the asymmetric form **II** was predicted. The

presence of the auxiliary ⁱPr₂ groups at the 3, 5 positions of the central phenyl ring destabilizes both the Sn-Sn bonded form **I** and the hydride-bridged form **III**. Apparently, the bulky ligand influences the geometry of the solid state form obtained upon crystallization, which is reflected by the X-ray structure of **4b**.

31. Gaussian 03

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision D.1*; Gaussian, Inc.: Pittsburgh, PA, 2003

Experimental

‡All reactions were performed with the use of modified Schlenk techniques under an atmosphere of hydrogen or nitrogen or in a Vacuum Atmospheres Nexus Drybox. Solvents were dried and collected using Grubbs-type solvent purification system manufactured by Glass Contour and degassed three times (freeze-pump-thaw method) prior to use. [4-H-Ar']Li (4-H-Ar' = Ar' = C₆H₃-2,6-(C₆H₃-2,6-ⁱPr₂)₂), (Ar'-SnCl)₂ and [3,5-ⁱPr₂-Ar*]Li (3,5-ⁱPr₂-Ar* = 3,5-ⁱPr₂-C₆H₂-2,6-(C₆H₂-2,4,6-ⁱPr₃)₂), were prepared according to literature procedures. 2,6-dichloro-4-trimethylsilyl-benzene was also synthesized as described in the literature. n-BuLi (2.5M solution in hexane), anhydrous SnCl₂, K, graphite, H₂ gas were purchased from commercial sources and used as received. ¹H and ¹³C{¹H} NMR spectra were obtained on a Varian Mercury 300MHz spectrometer (300.1 and 75.5MHz, respectively) and referenced internally to residual protio benzene C₆D₆ solvent. Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer 1430 instrument. Melting points were measured obtained in sealed glass capillaries under nitrogen using a Mel-Temp II apparatus and are uncorrected.

1b: [Ar'Sn(μ-H)]₂: A solution of Ar'SnSnAr' (1.0g, 1mmol) in Et₂O (50ml) was stirred at room temperature for 2h under a H₂ atmosphere to give a

green-brown solution over a tan precipitate. The mixture was then filtered and dried under vacuum (0.56g, 0.55mmol) to give an orange solid that was identified as **1** on the basis of NMR spectroscopy. Yield: 55%. ^1H NMR (C_6D_6): δ 9.13 (s, 1H, $^1J_{\text{Sn-H}} = \text{ca.}$ 89Hz, Sn-H), 7.30 (t, 2H, $J_{\text{HH}} = 7.5\text{Hz}$, *p*-Dipp), 7.10 (m, overlap ArH), 7.03 (d, 4H, $^3J_{\text{HH}} = 7.5\text{Hz}$, ArH), 3.00 (overlap septets, 4H, $\text{CH}(\text{CH}_3)_2$), 1.11 (d, 6H, $^3J_{\text{HH}} = 6.6\text{Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.04 (d, 6H, $^3J_{\text{HH}} = 6.6\text{Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.02 (d, 6H, $^3J_{\text{HH}} = 6.6\text{Hz}$, $\text{CH}(\text{CH}_3)_2$), 0.93 (d, 6H, $^3J_{\text{HH}} = 6.6\text{Hz}$, $\text{CH}(\text{CH}_3)_2$). The Sn-H stretching band is likely obscured by ligand vibrations.

2b: $[\text{4-Me}_3\text{Si-Ar'Sn}(\mu\text{-H})_2]$: A solution of 4-Me₃Si-Ar'SnSnAr'-4-SiMe₃ (0.3g, 0.3mmol) in Et₂O (50ml) was stirred at room temperature under H₂ for 0.5h to give a green-brown solution over a tan precipitate. The mixture was then filtered and dried under vacuum (0.2g, 0.17mmol) to give an orange solid that was identified as **2** on the basis of NMR spectroscopy. Yield: 56%. ^1H NMR (C_6D_6): δ 9.12 (s, 1H, $^1J_{\text{Sn-H}} = \text{ca.}$ 87Hz, Sn-H), 7.33 (d, 2H, *m*-C₆H₂), 7.04 (d, 4H, $^3J_{\text{HH}} = 7.5\text{Hz}$, DippH), 3.01 (septets, 4H, $\text{CH}(\text{CH}_3)_2$), 1.15 (d, 12H, $^3J_{\text{HH}} = 6.6\text{Hz}$, $\text{CH}(\text{CH}_3)_2$), 0.85 (d, 12H, $^3J_{\text{HH}} = 6.6\text{Hz}$, $\text{CH}(\text{CH}_3)_2$), 0.22 (s, 9H, Si(CH₃)₃). The Sn-H stretching band is likely obscured by ligand vibrations.

3b: $[\text{4-F-Ar'Sn}(\mu\text{-H})_2]$: A solution of 4-F-Ar'SnSnAr'-4-F (0.18g, 0.17mmol) in Toluene (50ml) was stirred at room temperature for 0.5h under H₂ to give a reddish-brown solution. The mixture was concentrated to ca 10ml under vacuum to give orange crystals (0.08g, 0.075mmol) in a -18°C freezer which were characterized by ^1H NMR spectroscopy. Yield: 44%. ^1H NMR (C_6D_6): δ 9.12 (s, 1H, $^1J_{\text{Sn-H}} = \text{ca.}$ 87Hz, Sn-H), 7.81 (d, 2H, *m*-C₆H₂), 7.05 (d, 4H, $^3J_{\text{HH}} = 7.5\text{Hz}$, DippH), 2.95 (septets, 4H, $\text{CH}(\text{CH}_3)_2$), 1.21 (d, 12H, $^3J_{\text{HH}} = 6.6\text{Hz}$, $\text{CH}(\text{CH}_3)_2$), 0.93 (d, 12H, $^3J_{\text{HH}} = 6.6\text{Hz}$, $\text{CH}(\text{CH}_3)_2$). The Sn-H stretching band is likely obscured by ligand vibration.

4b: $(\text{3,5-}^i\text{Pr}_2\text{-Ar}^*)\text{SnSn}(\text{H})_2(\text{3,5-}^i\text{Pr}_2\text{-Ar}^*)$: A solution of $(\text{3,5-}^i\text{Pr}_2\text{-Ar}^*)\text{SnSn}(\text{3,5-}^i\text{Pr}_2\text{-Ar}^*)$ (0.37g, 0.3mmol) in toluene (50ml) was sealed in a Schlenk under a H₂ atmosphere and stirred at room temperature for 3 weeks to give a bluish-green solution over a teal precipitate. The precipitate was filtered off and dried under vacuum (0.2g, 0.17mmol) to give a bluish-green solid that was identified as **4** on the basis of NMR and IR spectroscopy. Yield: 54%. ^1H NMR (C_6D_6): δ 7.92 (s, 2H, $^1J_{\text{Sn-H}} = \text{ca.}$ 528Hz, Sn-H), 7.43 (s, 2H, *p*-C₆H), 7.11 (s, 8H, *m*-Trip), 2.93 (overlapping septets, 12H, $\text{CH}(\text{CH}_3)_2$), 2.54 (septet, 4H, $^3J_{\text{HH}} = 6.6\text{Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.36 (d, 48H, $^3J_{\text{HH}} = 6.9\text{Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.19 (d, 48H, $^3J_{\text{HH}} = 6.9\text{Hz}$, $\text{CH}(\text{CH}_3)_2$). IR (Nujol, cm⁻¹): 1810(m) and 1783(m) [Sn-H stretches]. The product was dissolved in 5ml of benzene which yielded dark-blue crystals of **4** upon storage of the solution at ca 7°C for 3 days.