Addition of H_2 to distannynes under ambient conditions†

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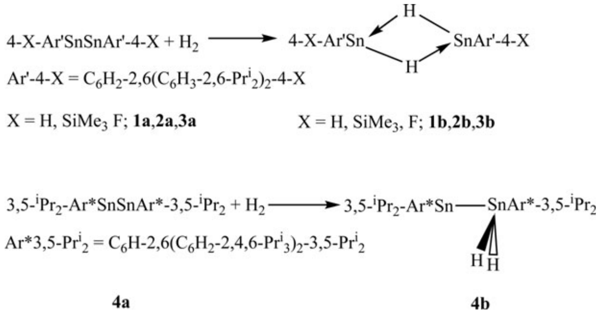
Dihydrogen reacts directly with a range of distannynes at *ca.* 25 °C under one atmosphere pressure to afford symmetric hydrogen bridged or unsymmetric stannylstannane products in high yield.

The activation of hydrogen by transition metal centers has been of long standing interest and has generated much discussion.[1–4] The initial interaction of H_2 and the metal generally involves side-on σ donation by the H–H bond and synergic back donation from filled metal d orbitals into the σ* antibonding orbital of H_2.[5–12] In contrast, there is an almost complete absence of a corresponding chemistry for main group molecular compounds. In 2005, it was shown that the reaction between the molecular species Ar′GeGeAr′ (Ar′ = C_6H_3-2,6(C_6H_3-2,6-Pr^i_2)$_2$) and H_2 at 1 atmosphere in hexane at 25 °C rapidly afforded a mixture of Ar′HGeGeHAr′, Ar′H_2GeGeH_2Ar′ and Ar′GeH_3 which represented the first example of H_2 activation by a main group element molecular species under mild conditions in the absence of a catalyst.[13,14] Recently, the groups of Bertrand and Stephan demonstrated that H_2 reacted with an alkyl amino carbene[15] or underwent reversible activation with main group compounds that incorporate frustrated Lewis acid–base pairs.[16,17] The H_2 activation by Ar′GeGeAr′ is thought to be due in part to the singlet diradical character of the ground state.[18] It is noteworthy that active sites with diradical character have also been implicated in the interaction of organic substrates with rearranged single-crystal silicon and germanium surfaces that resemble the multiple bonded molecular species since they incorporate these elements in similar bonding environments.[19–24] We now report that H_2 is activated under ambient conditions by distannynes of formula, ArSnSnAr (Ar = terphenyl ligand). In contrast to the reaction of Ar′GeGeAr′ with H_2, which yields a mixture of products these reactions cleanly afford a single tin(II) hydride product.



Scheme 1 Activation of hydrogen by a series of distannynes.

The addition of excess H_2 to dark green solutions of the distannynes **1a–4a** in ether or toluene solvent afforded the products **1b–4b** shown in Scheme 1.‡ The orange crystalline products **1b**, **2b** or **3b** precipitated from solution and are slightly soluble in benzene to yield a pale blue solution. Their ^{1}H NMR spectra revealed a diagnostic signal (*ca.* 9.13 ppm) which matches the Sn–H chemical shifts of **1b–3b** synthesized by treatment of aryltin halide precursors with various reducing agents.[25,26] X-Ray crystallography showed that they had identical structures to those previously described which feature bridging hydrides as shown for **1b–3b** in Scheme 1.[25,26] An interesting aspect of the hydrogenation of **2a** concerned its structure[27] which differs considerably from those of other distannynes in the solid state. Distannynes **1a**, **3a** and others[28,29] possess multiple bonded *trans*-bent structures with tin–tin distances near 2.67 Å and Sn–Sn–C angles in the range of 121–127°. In contrast, **2a** has a single-bonded structure featuring an Sn–Sn bond length of 3.066(1) Å and an Sn–Sn–C angle of 99.3(1)° in the solid state. Calculations indicated that there is very little singlet diradical character in the ground state of a strongly bent ArSnSnAr species and hence the reactivity of strongly bent **2a** toward H_2 might have been expected to be lower.[18] However, its reactivity is indistinguishable from that of **1a** and **3a**. This supports the view that **2a** "relaxes" to a multiple bonded form which has ground state singlet diradical character in solution and this is consistent with the calculations of Takagi and Nagase[30,31] which predicted that multiple bonded ArSnSnAr is more stable than the strongly bent forms of these molecules (*i.e.* that of **2a**) and that the greater bending in the solid state is a consequence of packing forces.

The asymmetric tin(II) hydride (3,5-^{i}Pr$_2$-Ar*)SnSn(H)$_2$ (Ar*3,5-^{i}Pr$_2$) **4b** was previously synthesized by the reaction of (3,5-^{i}Pr$_2$Ar*)SnCl with HAlBu$^i_2$ which gave a deep blue solution from which small dark blue, plate-like crystals could be obtained. Calculations have shown that the asymmetric structure becomes more favored with increased ligand size.[25] Thus, it was of interest to investigate hydrogenation of the more hindered distannyne **4a** to see if the asymmetric Sn hydride **4b** was indeed formed. It was found that the hydrogenation of **4a** proceeds more slowly than **1a–3a** possibly as a result of the greater steric hindrance of the 3,5-^{i}Pr$_2$-Ar* ligand.

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† Electronic supplementary information (ESI) available: CIF for **4b**, details of the synthesis of **1b–4b** and DFT calculations. CCDC 698896. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/b813442a

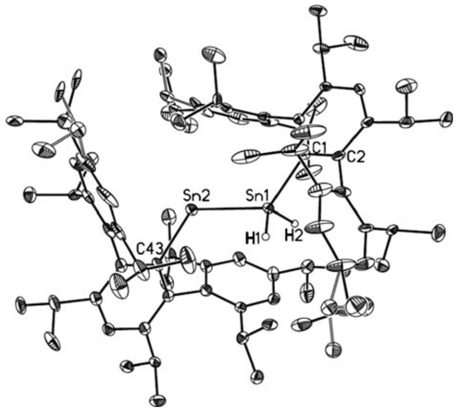

Fig. 1 Thermal ellipsoid (30%) plot of the tin hydride **4b**. H atoms (except Sn–H) are not shown. Selected bond distances (Å) and angles (°): Sn(1)–C(1) 2.197(5), Sn(2)–C(43) 2.250(5), Sn(1)–Sn(2) 2.9242(7), Sn(1)–H(1) 1.59(2), Sn(1)–H(2) 1.56(2), Sn(2)–Sn(1)–C(1) 125.77(14), Sn(2)–Sn(1)–H(1) 108(2), Sn(2)–Sn(1)–H(2) 100(2), Sn(1)–Sn(2)–C(43) 109.87(13).

The ^{1}H NMR and IR spectroscopy identified the product of hydrogenation as the same as the asymmetric tin(II) hydride obtained by reduction of (3,5-$\text{Pr}^i{}_2$Ar*)SnCl. A broad singlet at 7.92 ppm was observed in the ^{1}H NMR spectrum which corresponds to terminal hydrogens and there were two strong bands at 1810 and 1783 cm^{-1} in the IR spectrum corresponding to the two Sn–H stretching modes. Blue needle like crystals of **4b** were obtained from benzene and a new X-ray data set enabled the terminal Sn–H moieties to be located for the first time (Fig. 1). The terminal Sn–H distances are about 1.58(2) Å which are significantly shorter than the *ca.* 1.9 Å Sn–H distances in the bridging species.[25]

DFT calculations were performed on several model species (see ESI for more detailed computational results†) to determine the energies involved in the addition of one or two equivalents of H_2 to the distannynes.

Geometry optimizations on the model species RSnSnR and $\text{R(H)}_n\text{SnSn(H)}_n\text{R}$ (R = Me, Ph, 2,6-Ph_2-C_6H_3 and Ar*) were performed using density functional theory with a hybrid B3LYP functional combined with either 3-21g* basis set for all atoms or a combination of the [4333111/433111/43] basis set for tin and the 6-31g(d) basis set for the remaining atoms. To ensure flexibility in the description of the metals, the [4333111/433111/43] basis set was appended with two d polarization functions using d exponents of 0.253 and 0.078, as previously reported.[32] All the geometry optimizations as well as the determination of the electronic structure were performed with the Gaussian 03 package (full reference in the ESI†). For the addition of one equivalent of H_2 to the distannynes, the calculations are in agreement with recent computations,[25] in which the differences in energies computed as $\Delta E_{\text{hydrogenation}} = (E_{\text{Ar}'\text{SnHSnHAr}'} - (E_{\text{Ar}'\text{SnSnAr}'} + E_{\text{H}_2}))$ are favorable for hydrogenation. It is clear, however, that there are only small differences in stability between the three $(\text{SnHR})_2$ isomers (Fig. 2). The addition of a second equivalent of H_2 to yield the distannane $\text{R(H)}_2\text{SnSn(H)}_2\text{R}$ is also favored. However, this addition has not been experimentally observed even in the presence of a large excess of H_2.

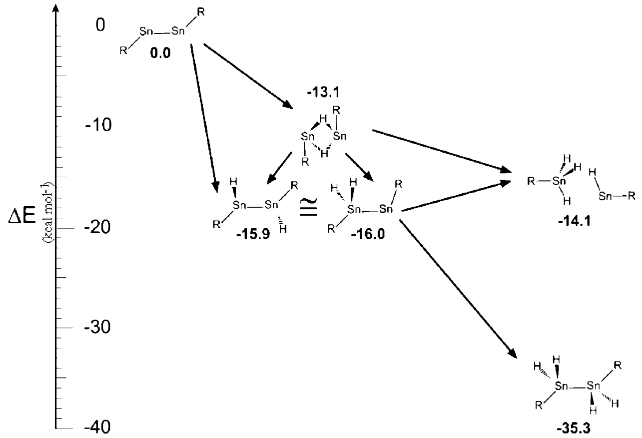

Fig. 2 Schematic diagram with computed energy differences in kcal mol^{-1} for the hydrogenation process of the Ar′SnSnAr′ species.

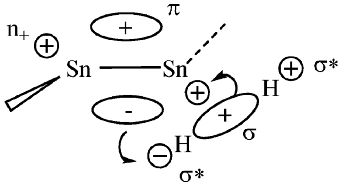

Fig. 3 Possible orbital overlaps during the activation of H_2.

The mechanism of H_2 activation by distannynes remains an open question. One possibility (Fig. 3) involves the interaction of H_2 with the LUMO (n_+, "virtual lone-pair") and HOMO (π) orbitals at a single tin center which would yield an asymmetric product like **4b** initially. This could then rearrange to the symmetric structure like **1b–3b** with less bulky substituents. The first step of H_2 activation involves a synergic donor interaction of the H–H σ-bond to the empty "lone pair" n_+ combination[26] and an acceptor interaction from the Sn–Sn π orbital to the H–H σ*-orbital from the Sn–Sn π-level. The extent of these interactions is related to the energy separation of the π and n_+ levels which are related to the singlet diradical character in the ground state of the molecule.[18]

In conclusion, H_2 is readily activated by distannynes. Furthermore, the reaction provides a clean synthetic route to the tin(II) hydride derivatives as demonstrated by the ready synthesis of **1b–4b**. Centrosymmetric bridging dimers of the general form [4-X-Ar′Sn(μ-H)]$_2$ were observed when less bulky, electronically modified ligands 4-X-Ar′ (X = H, SiMe_3, F) were used. However with the more sterically encumbered ligand 3,5-$^i\text{Pr}_2$-Ar*, the asymmetric structure (3,5-$^i\text{Pr}_2$-Ar*)SnSn(H_2)(Ar*-3,5-$^i\text{Pr}_2$) was obtained.[26]

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Notes and references

‡ Full experimental details of the synthesis of **1b–4b** are provided in the ESI.† Crystal data for **4b** at 90 K with MoKα (λ = 0.71073 Å)

radiation: $a = 17.622(2)$ Å, $b = 17.264(2)$ Å, $c = 31.149(4)$ Å, $\beta = 93.417(2)°$, monoclinic, space group $P2_1/n$, $Z = 4$, $R_1 = 0.0649$ for 10 638 ($I > 2(\sigma)I$) data.

1 P. J. Brothers, *Prog. Inorg. Chem.*, 1981, **28**, 1.
2 G. J. Kubas, *Adv. Inorg. Chem.*, 2001, **56**, 127.
3 J. Halpern, *Adv. Inorg. Chem.*, 1956, **11**, 301.
4 J. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc. A*, 1966, 1711.
5 G. J. Kubas, R. R. Ryan, B. L. Swanson, P. J. Vergamini and H. Wasserman, *J. Am. Chem. Soc.*, 1984, **106**, 451.
6 G. J. Kubas, *Acc. Chem. Res.*, 1988, **21**, 120.
7 R. H. Crabtree, *Acc. Chem. Res.*, 1990, **23**, 95.
8 P. G. Jessop and R. H. Morris, *Coord. Chem. Rev.*, 1982, **121**, 155.
9 D. M. Heinekey and W. J. Oldham, *Chem. Rev.*, 1993, **93**, 913.
10 R. H. Crabtree, *Modern Coordination Chemistry*, Royal Society of Chemistry, Cambridge, 2002, p. 31.
11 S. E. Clapham, A. Hadzovic and R. H. Morris, *Coord. Chem. Rev.*, 2004, **248**, 2201.
12 D. M. Heinekey, A. Lledas and J. M. Lluch, *Chem. Soc. Rev.*, 2004, **33**, 175.
13 G. H. Spikes, J. C. Fettinger and P. P. Power, *J. Am. Chem. Soc.*, 2005, **127**, 12232.
14 A. L. Kenward and W. E. Piers, *Angew. Chem., Int. Ed.*, 2008, **47**, 38.
15 G. D. Frey, V. Lavallo, B. Donnadieu, W. W. Schoeller and G. Bertrand, *Science*, 2007, **316**, 439.
16 G. C. Welch, R. R. San Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124.
17 D. W. Stephan and G. C. Welch, *J. Am. Chem. Soc.*, 2007, **129**, 1880.
18 Y. Jung, M. Brynda, P. P. Power and M. Head-Gordon, *J. Am. Chem. Soc.*, 2006, **128**, 7185.
19 H. N. Waltenburg and J. T. Yates, *Chem. Rev.*, 1995, **95**, 1589.
20 R. J. Hamers and Y. Wang, *Chem. Rev.*, 1996, **96**, 1261.
21 J. A. Kubby and J. J. Boland, *Surf. Sci. Rep.*, 1996, **26**, 61.
22 R. J. Hamers, S. K. Coulter, M. D. Ellison, J. S. Hovis, D. F. Padowitz, M. P. Schwartz, C. M. Greenlief and J. N. Russell, *Acc. Chem. Res.*, 2000, **33**, 617.
23 S. F. Bent, *J. Phys. Chem. B*, 2002, **106**, 2830.
24 J. M. Buriak, *Chem. Rev.*, 2002, **102**, 1271.
25 B. E. Eichler and P. P. Power, *J. Am. Chem. Soc.*, 2000, **122**, 8785.
26 E. Rivard, R. C. Fischer, R. Wolf, Y. Peng, W. A. Merrill, N. D. Schley, Z. Zhu, L. Pu, J. C. Fettinger, S. J. Teat, I. Nowik, R. H. Herber, N. Takagi, S. Nagase and P. P. Power, *J. Am. Chem. Soc.*, 2007, **129**, 16197.
27 R. C. Fischer, L. Pu, J. C. Fettinger, M. A. Brynda and P. P. Power, *J. Am. Chem. Soc.*, 2006, **128**, 11366.
28 A. D. Phillips, R. J. Wright, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2002, **124**, 5930.
29 Y. Peng, R. C. Fischer, L. Pu, J. C. Fettinger, M. A. Brynda and P. P. Power, unpublished work.
30 N. Takagi and S. Nagase, *Organometallics*, 2007, **26**, 469.
31 N. Takagi and S. Nagase, *Organometallics*, 2007, **26**, 3627.
32 S. Huzinaga, in *Physical Science Data, Vol. 2: Gaussian basis sets for molecular calculations*, Elsevier, Amsterdam, 1985.