J. Am. Chem. Soc. **2000,** *122,* 8785−8786

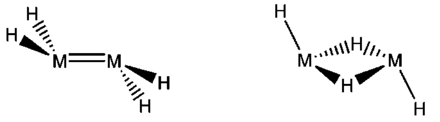
[2,6-Trip$_2$H$_3$C$_6$Sn(μ-H)]$_2$ (Trip = C$_6$H$_2$-2,4,6-*i*-Pr$_3$): Synthesis and Structure of a Divalent Group 14 Element Hydride

Barrett E. Eichler and Philip P. Power*

Department of Chemistry, University of California
Davis, One Shields Avenue, Davis, California, 95616

Received January 18, 2000

Organotin hydrides, particularly tributyltin hydride, are extremely important reducing agents in organic synthesis.[1] As with all tin hydrides reported to date, they involve tin in the +4 oxidation state. Currently, there are no stable well-characterized tin +2 hydrides, and in fact no hydride derivatives of divalent group 14 elements have been reported as stable molecules. Their apparent lack of stability may be contrasted with that of the neighboring group 15 and 16 hydrides where lower valent species (e.g. P(III) or S(II)) are common. Theoretical studies on the hypothetical MH$_2$ (M = Si−Pb) monomers show that they have the expected V-shaped geometries.[2] However, calculations for the dimers (MH$_2$)$_2$ indicate that for silicon and germanium the trans-bent M−M bonded dimeric structure **1** (Figure 1) is the most stable, whereas for tin and lead, the trans dihydrogen bridged structure **2** (Figure 1) is preferred.[2a] Although these species are unknown as stable molecules, there is now a relatively large body of data that shows that related lower valent organic derivatives of the group 14 elements can be stabilized by large substituents.[3] It therefore seemed a possibility that large organic substituents might also stabilize the corresponding lower valent hydride derivatives. In this paper it is shown that the use of a bulky terphenyl substituent[4] enables the synthesis, characterization, and structure of the first example of an Sn(II) hydride, [2,6-Trip$_2$H$_3$C$_6$Sn(μ-H)]$_2$ (Trip = 2,4,6-triisopropylphenyl) (**4**) along with its deuterium analogue [2,6-Trip$_2$H$_3$C$_6$Sn(μ-D)]$_2$ (**5**).



1 (M= Si, Ge) **2**(M= Sn, Pb)

Figure 1. Depictions of M−M bonded M$_2$H$_4$ (**1**) and hydride bridged M$_2$H$_4$ (**2**).

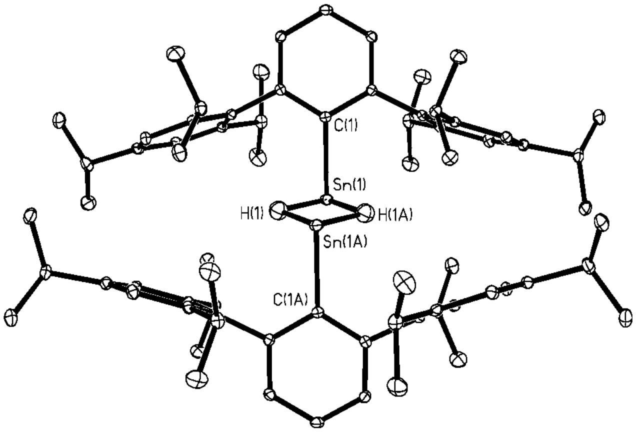


Figure 2. Thermal ellipsoid (30%) plot of **4**. Hydrogen atoms except for H(1) and H(1a) are not shown for clarity. Selected interatomic distances (Å) and angles (deg): Sn(1)···Sn(1a) = 3.1192(3), Sn(1)−C(1) = 2.210(2), Sn(1)−H(1) = 1.89(3), Sn(1)−H(1a) = 1.95(3), C(1)−Sn(1)−Sn(1a) = 93.28(5), Sn(1)−H(1)−Sn(1a) = 108.7(9), H(1)−Sn(1)−H(1a) = 71.3(9), C(1)−Sn(1)−H(1) = 91.7(9), C(1)−Sn(1)−H(1a) = 93.6(9).

Compound **4** was synthesized[5] by the dropwise addition of a diisobutylaluminum hydride (DIBAL) solution to 2,6-Trip$_2$C$_6$H$_3$SnCl[6] (**3**) in diethyl ether at −78 °C. Initially, the orange solution became green, but upon warming to ca. −30 °C, the color became dark blue. After the solution was warmed to room temperature, the diethyl ether was removed and the remaining blue solid was extracted with benzene. Filtration and concentration of the blue solution produced orange crystals of **4**. Its X-ray crystal structure[7] shows that it is dimeric in the solid state as illustrated in Figure 2. It crystallizes in the space group $P\bar{1}$ and features two 2,6-Trip$_2$H$_3$C$_6$SnH units which are related by a center of symmetry and linked by bridging hydrides which were located on the difference map and refined isotropically without restraints. The Sn···Sn separation is 3.1192(3) Å. The structure of **4** resembles that of the aryltin chloride [2,6-Mes$_2$H$_3$C$_6$Sn(μ-Cl)]$_2$ (**6**, Mes = 2,4,6-trimethylphenyl),[8] which is dimerized through Cl$^-$ bridges and has a tin−tin distance of 3.997(1) Å. The tin−tin separations in both **4** and **6** are much larger than the intermetallic bond distance of 2.81 Å in gray tin.[9] The difference in radii between hydrogen (0.32 Å) and chlorine (0.99 Å) accounts for the much smaller Sn···Sn distance in **4**, and there seems little doubt that there is very little interaction between the tin atoms. The Sn−C bond length of 2.210(2) Å in **4** is slightly longer than the sum of the covalent radii of tin and carbon (1.40 Å + 0.77 Å = 2.17 Å).[9] The sum of the interligand angles at tin, 256.6°, underlines the highly pyramidalized tin geometry and indicates the presence of a lone pair at the metal. The distances to the bridging hydrogens

---

(1) (a) Davies, A. G. *Organotin Chemistry*; VCH: New York, 1997. (b) Pereyre, M.; Quintand, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: London, 1987.

(2) (a) Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 2130. (b) Balasubramanian, K. *J. Chem. Phys.* **1988**, *89*, 5731.

(3) For recent reviews of low-coordinate group 14 compounds, see: (a) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71. (b) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 232. (c) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275. (d) Rappaport, Z.; Apeloig, Y., Eds. *The Chemistry of Organic Silicon Compounds*; John Wiley and Sons: Chichester, 1998; Vol. 2. (e) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373. (f) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463.

(4) Twamley, B.; Haubrich, S. T.; Power, P. P. *Adv. Organomet. Chem.* **1999**, *44*, 1.

(5) Synthesis of **4**: Under anaerobic and anhydrous conditions, (i-Bu)$_2$AlH (2.52 mL, 2.52 mmol, 1.0 M in hexanes) was syringed dropwise into a pale yellow solution of **3**[6] (1.60 g, 2.52 mmol) in diethyl ether (30 mL) at ca. −78 °C, to afford a light green solution. The solution was stirred at ca. −78 °C for 1 h and when it was warmed to ca. −45 °C where it became dark blue. A turquoise precipitate formed at approximately 0 °C and the solution was stirred at room temperature for 30 min. The solvent was removed under reduced pressure, the blue solid was extracted with benzene (15 mL) and recrystallized from hot benzene overnight, giving large orange crystals of **4**·4C$_6$H$_6$. Yield: 0.92 g, 0.61 mmol, 48.4%; mp 174−7 °C. Anal. Calcd for C$_{36}$H$_{50}$Sn, **4**: C, 71.89; H, 8.38. Found: C, 71.41; H, 8.63. IR (Nujol, cm^{-1}): 1828, 1771 (Sn−H stretches); 610, 560 (Sn−H bends). UV−vis (hexanes) λ_{max}, ϵ (mol^{-1} cm^{-1}): 395 nm, 360; 608 nm, 160. ^{1}H NMR (C$_6$D$_6$, 399.77 MHz, 25 °C): δ 1.09 (d, 12 H, ^3J = 6.8 Hz, *o*-CH(C*H*$_3$)$_2$), 1.17 (d, 12 H, ^3J = 6.8 Hz, *o*-CH(C*H*$_3$)$_2$), 1.32 (d, 12 H, ^3J = 6.8 Hz, *p*-CH(C*H*$_3$)$_2$), 2.86 (sept., 2 H, ^3J = 6.8 Hz, *p*-C*H*(CH$_3$)$_2$), 3.04 (sept., 4 H, ^3J = 6.8 Hz, *o*-C*H*(CH$_3$)$_2$), 7.10 (s, 4H, *m*-Trip), 7.15 (s, 24 H, 4 benzenes), 7.16−7.19 (m, 3H, *m*-C$_6$H$_3$ and *p*-C$_6$H$_3$), 7.87 (s, 1H, ^1J(Sn−H) = 592 Hz, Sn-*H*). ^{13}C {^{1}H} NMR (C$_6$D$_6$, 100.53 MHz, 25 °C): δ 24.25 (*o*-CH(*C*H$_3$)$_2$), 24.29 (*p*-CH(*C*H$_3$)$_2$), 26.20 (*o*-CH(*C*H$_3$)$_2$), 30.85 (*o*-*C*H(CH$_3$)$_2$), 34.57 (*p*-*C*H(CH$_3$)$_2$), 121.74 (*m*-Trip), 126.87 (*p*-C$_6$H$_3$), 129.89 (*m*-C$_6$H$_3$), 130.47 (*i*-Trip), 137.92 (*p*-Trip), 146.82 (o-Trip), 148.52 (*o*-C$_6$H$_3$), 167.98 (*i*-C$_6$H$_3$). ^{119}Sn {^{1}H} NMR (C$_6$D$_6$, 149.16 MHz, 25 °C): δ 698.7.

(6) Olmstead, M. M.; Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 11705

(7) Crystal data for **4** at 90 K with Mo Kα (λ = 0.71073 Å) radiation: a = 13.1343(6) Å, b = 13.2288(6) Å, c = 13.3728(6) Å, α = 93.676(1)°, β = 97.678(1)°, γ = 115.380(1)°, triclinic, space group $P1$, Z = 1, $R1$ = 0.0434 for 12 981 ($I > 2\sigma(I)$) data, $wR2$ = 0.0985 for all (29 682) data.

(8) Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, *16*, 1920.

(9) Wells, A. F. *Structural Inorganic Chemistry*; Oxford University Press: New York, 1984.

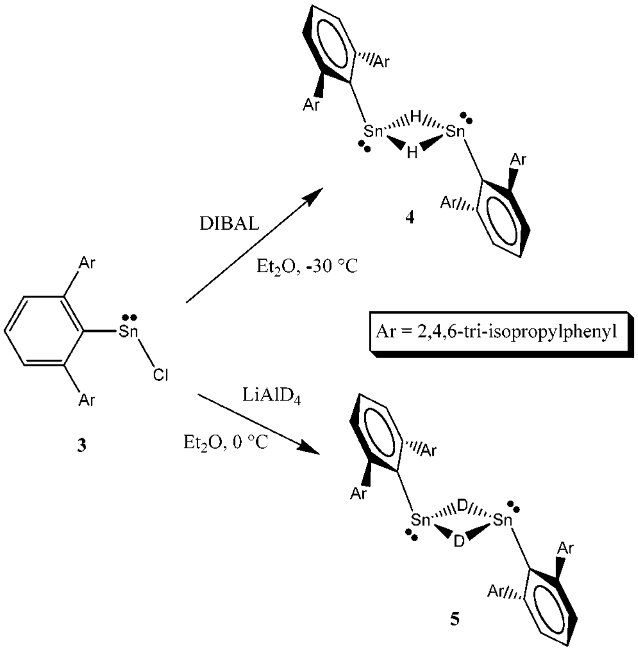
10.1021/ja000180c CCC: $19.00

are slightly different (Sn−H(1) = 1.89(3) Å and Sn−H(1a) = 1.95(3) Å), but the difference is just twice the standard deviation and is of little significance. The C−Sn−H bond angles are C−Sn−H(1) = 91.7(9)° and 93.6(9)°.

The color of **4** in the solid state is orange, but when it is dissolved in hydrocarbon solvent (Et_2O, hexane, benzene, toluene), there is a dramatic color change to dark blue consistent with dissociation to monomers.[10] There is a broad absorption at 608 nm ($\epsilon = 160$ mol^{-1} cm^{-1}) in the UV−visible spectrum of a solution of **4** in hexanes which is consistent with the blue color and may be attributed to an n → p electronic transition.[11]

^1H NMR spectroscopic studies of Sn(IV) hydrides have shown that the hydride chemical shifts are generally in the range of +3 to +7 ppm.[12] Satellite peaks arising from coupling to the ^{117}Sn and ^{119}Sn nuclei with ^1J(Sn−H) values near 1900 Hz are normally observed. For **4** in C_7D_8 solution at 25 °C the hydride absorption was located at +7.87 ppm with satellites featuring an average $^1J(^{117/119}Sn{-}H)$ value of 592 Hz. The $^1J(^{117/119}Sn{-}^1H)$ coupling constant in tin compounds is primarily controlled by the Fermi contact mechanism, which decreases with decreasing s-character in the Sn−X bond.[1a] The orbital used by tin in the Sn−H bond in compound **4** probably has less s-character than Sn−H bonds in Sn(IV) hydrides with the result that the $^1J(^{117/119}Sn{-}H)$ coupling constant in **4** is only about 1/3 (at room temperature) of those seen in Sn(IV) hydrides. Also, the presence of a lone pair at the tin undoubtedly influences the $^1J(^{117/119}Sn{-}H)$ coupling constant.[13] The observation of ^1H NMR was corroborated by the solution ^{119}Sn NMR spectrum which, at 25 °C, displayed a broad absorption (line width at half-height = 675 Hz) at +698.7 ppm. The value of the chemical shift is indicative of a Sn(II) compound.[14] However, the absorption is sufficiently wide that coupling to the hydrogens is difficult to observe. In studies of the ^{119}Sn NMR of various two-coordinate Sn(II) compounds,[15] it was found that they display very large chemical shift anistropies (up to ca. 10 000 ppm) which govern the relaxation time T_2 (a reasonable assumption for large heavy molecules far from the extreme narrowing limit). The short T_2 values lead to broadening[16] of the ^{119}Sn NMR signal of the Sn(II) compounds and hydride **4** is no exception. Variable-temperature ^{119}Sn NMR studies in the range −50° to +75 °C displayed no evidence of chemical exchange arising from a monomer−dimer equilibrium. Repeated heating to +75 °C eventually caused the sample to slowly decompose to a mixture of products. Analysis of these products is currently underway.

Scheme 1. Synthesis of the Hydride (**4**) and Deuteride (**5**)



In the IR spectra of Sn(IV) compounds the stretching frequencies of terminal Sn−H bonds are normally observed in the range 1900 ± 50 cm^{-1} and the bending modes are typically near 675 cm^{-1}.[12d] The Sn−H stretching frequencies for solid **4** may be expected to be shifted to lower wavenumbers since the Sn−H bonds are bridging in the solid. The IR spectrum of **4** (Nujol)[17] displays two strong bands at 1828 and 1771 cm^{-1}. The bending frequencies in **4** are tentatively assigned to bands at 610 and 560 cm^{-1}.

The deuterium analogue of **4** was synthesized to compare physical and spectroscopic data for the two compounds. The tin deuteride **5** was obtained[18] by reacting **3** with $LiAlD_4$ in Et_2O at 0 °C. The ^1H NMR spectrum of a blue solution of **5** shows that the hydride peak at 7.87 disappears. The deuterium (^2H) NMR of **5** shows a broad peak at 7.69 ppm. Infrared spectroscopy of **5** also displays no bands at 1828 or 1771 cm^{-1}. Instead a new band at 1273 cm^{-1} (the other stretch is most likely obscured by the C−C stretches of the ligand) is attributable to the Sn−D stretching frequency. Bending frequencies are tentatively assigned to new bands at 495 and 414 cm^{-1}.[19]

Acknowledgment. We are grateful to the Donors of the Petroleum Research Fund administered by the American Chemical Society for generous financial support. We thank Dr. Brendan Twamley and Prof. Matthew Augustine for helpful discussions regarding NMR spectroscopy.

Supporting Information Available: Tables of data collection parameters, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates (PDF); an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA000180C

---

[10] If the blue solutions are rapidly cooled, however, a blue microcrystalline solid is produced. A blue color is invariably seen with a variety of solvents such as hexane, benzene, toluene, or ether. Slow cooling of these solutions gives an orange solid.

[11] Monomeric, diorgano Sn(II) compounds (e.g. $Sn(C_6H_3\text{-}2,6\text{-}Mes_2)_2$, λ_{max} = 553 nm)display absorptions at similar wavelengths. See ref 8.

[12] (a) Dufermont, J.; Maire, J. C. *J. Organomet. Chem.* **1967**, *7*, 415. (b) Amberger, E.; Fritz, H. P.; Kreiter, C. G.; Kula, M.-R. *Chem. Ber.* **1963**, *96*, 3270. (c) Kula, M.-R.; Amberger, E.; Rupprecht, H. *Chem. Ber.* **1965**, *98*, 629. (d) Harrison, P. G. *Chemistry of Tin*; Chapman and Hall, New York, 1989. (e) Anselme, G.; Declercq, J.-P.; Dubourg, A.; Ranaivonjatovo, H.; Escudié, J.; Couret, C. *J. Organomet. Chem.* **1993**, *458*, 49.

[13] Gil, V. M. S.; Philipsborn, W. v. *Magn. Reson. Chem.* **1989**, *27*, 409.

[14] For a recent review of ^{119}Sn NMR spectroscopy, see: Wrackmeyer, B. *Ann. Reps. NMR Spectrosc.* **1999**, *38*, 203.

[15] Eichler, B. E.; Phillips, B. L.; Power, P. P.; Augustine, M. P. Unpublished work. The large chemical shift anisotropies arise from the very low local symmetry at the tin(II) center in monomeric, two-coordinate compounds.

[16] Poole, C. P.; Farach, H. A. *Relaxation in Magnetic Resonance*; Academic Press: New York, 1971; p 75.

[17] The Nujol mull displays a blue color suggesting the presence of monomer. Since only one Sn−H sketching band would be expected for such a species the two bands may arise from the bridged dimer in the solid.

[18] Synthesis of **5**: $LiAlD_4$ (0.040 g, 0.96 mmol, 3.84 mmol of D$^-$) and **3**^{6} (1.66 g, 2.61 mmol) were placed in a Schlenk flask and Et_2O (cooled to 0 °C) was added to the solids at 0 °C, which afforded a green-blue solution. The flask was warmed to room temperature, and the mixture was stirred for 1 h. The Et_2O was removed under reduced pressure, and the blue solid was extracted with hot benzene (30 mL). Cooling slowly to room temperature gave orange crystals of **5**. Yield: 0.40 g, 0.26 mmol, 20%. Mp 190−3 °C dec to brown. IR (Nujol, cm^{-1}): 1273 (Sn−D stretch); 495, 414 (Sn−D bends). ^2H NMR (C_6H_6, external D_2O reference, 61.37 MHz): δ 7.69.

[19] For terminal tin(IV) deuterides, Sn−D stretching and bending modes usually appear near 1350 and 490 cm^{-1}, respectively.[12d]