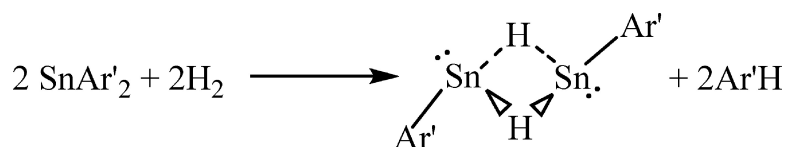


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J. Am. Chem. Soc., **2008**, 130 (37), 12268-12269 • DOI: 10.1021/ja805358u • Publication Date (Web): 21 August 2008

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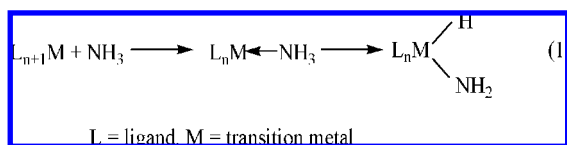
Diarylstannylene Activation of Hydrogen or Ammonia with Arene Elimination

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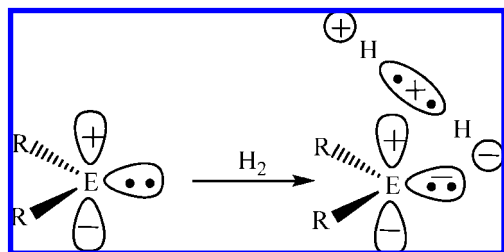
Received July 21, 2008; E-mail: pppower@ucdavis.edu

Activation of H₂ by transition metal complexes has been known and studied for many years.^{1–5} Since 1983 the synthesis and characterization of stable H₂ complexes, of which the first was Mo(CO)₃(PPR₃)₂(η²-H₂),⁶ has permitted the mechanism of the activation process to be studied in great detail. This generally occurs by either a homolytic or heterolytic pathway. The former involves side-on σ-donation by the H–H σ-bond and back-donation by the metal into the H–H σ* orbital.^{6–13} For heterolytic cleavage, the η²-H₂ unit becomes polarized as in H^{δ-}–H^{δ+} to afford hydride transfer to the metal with inter- or intramolecular H⁺ migration to a Lewis base. Surprisingly the related activation of N–H bonds via transition metal complexes is relatively rare,¹⁴ and the first example of NH₃ addition to afford a product that contained both terminal M–NH₂ and M–H groups as in eq 1 was only recently reported.¹⁵



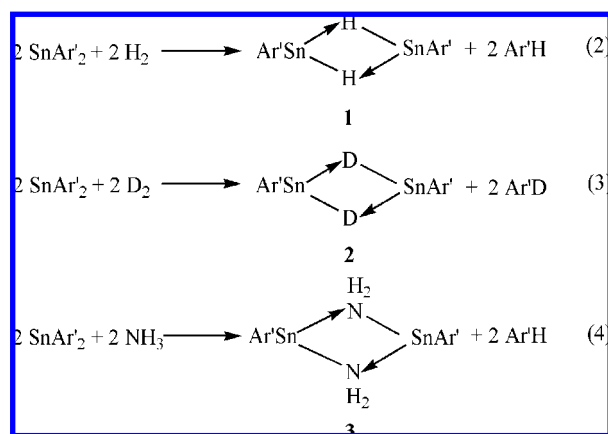
In contrast to these studies the corresponding chemistry for stable main group molecular compounds is virtually nonexistent. In 2005, the first example, which involved the activation of H–H bonds by the germanium species Ar'GeGeAr' (Ar' = C₆H₃-2,6-(C₆H₃-2,6-Prⁱ₂)₂ or C₆H₃-2,6-Dipp₂), was reported.¹⁶ In 2006, the reversible activation of H–H bonds by phosphine-boranes was described by Stephan and co-workers,¹⁷ and facile splitting of hydrogen and ammonia by stable carbenes was published by Bertrand and co-workers in 2007.¹⁸ In the latter case the reactivities of several carbenes with H₂ and NH₃ were investigated and it was found that mono(amino) carbenes readily activate both H₂ and NH₃. The hypothesis that activation of H₂ occurred via the route described in Scheme 1 was supported by the calculations of Schoeller.¹⁸ We now report the activation of H₂ and NH₃ by the heavier group 14 element carbene analogue SnAr'₂ (Ar' = C₆H₃-2,6-(C₆H₃-2,6-Prⁱ₂)₂) which occurs under mild conditions with arene elimination. We also show that the reactivity of stannylenes toward H₂ is dependent on the tin substituents.

Scheme 1. Schematic Representation of the Activation of by a Divalent Group 14 Molecule, E = C¹⁸

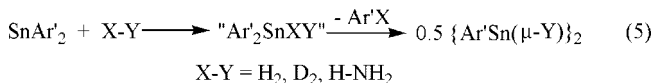


Reaction of a dark blue solution of SnAr'₂¹⁹ with H₂ gas at 60–70° for 1 h (eq 2) resulted in a color change to dark green

from which orange crystals of **1** were obtained.^{20a} X-ray crystallographic examination of the product **1** showed that it had an identical Sn(II) bridging hydride structure to those recently reported.²¹ Examination of the ¹H NMR spectrum also revealed a significantly deshielded signal at *ca.* 9.13 ppm which matched the Sn–H chemical shifts in Sn(II) hydrides synthesized by reduction using boron or aluminum hydrides. The ¹H NMR spectrum of the reaction mixture also displayed signals due to Ar'H.^{20f} Subsequent workup of the solution gave crystals of the arene which were shown to be identical to those of an authentic sample.



The same procedure as that employed for **1**, using D₂ instead of H₂ (eq 3), afforded the deuteride **2**.^{20b} X-ray crystallography showed that the orange crystalline product had almost the same unit cell parameters in which the length and volume are within 3 standard deviations of those measured for **1**. The ¹H NMR spectrum of **2** revealed no trace of the Sn–H signal at 9.13 ppm seen for **1**. The deuterium (²H) NMR spectrum of **2** displayed a broad signal at 8.95 ppm, which is consistent with the formation of [Ar'*Sn(μ-D)]₂.²² Further workup of the mother liquor afforded Ar'D examined by ¹H and ²H spectroscopy which suggests that the reaction proceeds by the initial addition of H₂ or D₂ (as in Scheme 1, E = Sn) to afford Ar'₂SnH₂ or Ar'₂SnD₂ which eliminates Ar'H or Ar'D due to the steric pressure in the molecule (eq 5).^{20f,g}



Similar experiments involving the reaction of SnAr'[#]₂ (Ar'[#] = C₆H₃-2,6-(C₆H₂-2,4,6-Me₃)₂) or Sn{N(SiMe₃)₂}₂²⁴ with H₂ under identical conditions yielded no evidence of hydrogenation after several days.^{20d,e} The electronic spectra of SnAr'₂ (λ_{max} = 600 nm),¹⁹ SnAr'[#]₂ (λ_{max} = 553 nm),²³ and Sn{N(SiMe₃)₂}₂ (λ_{max} = 487 nm) suggest an inverse correlation between the HOMO–LUMO gap and reactivity.¹⁹ This supports the view that the reactivity of SnAr'₂ may involve enhanced triplet character corresponding to its wide C–Sn–C angle (117.6(8)°).

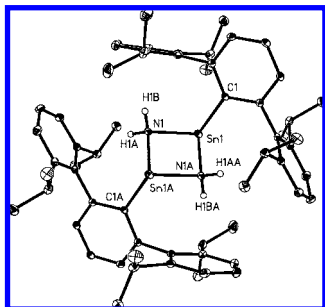


Figure 1. Thermal ellipsoid (30%) drawing of **3**. Hydrogen atoms, except those at nitrogen, are not shown for clarity.

The addition of an excess of dry ammonia to a dark blue solution of SnAr'_2 in toluene rapidly discharged the color. Concentration of the solution produced colorless crystals of the new species **3** (eq 4).^{20c} X-ray crystallography²⁵ afforded a dimeric structure as illustrated in Figure 1. The tin centers were symmetrically bridged by the NH_2 ligands in which the two hydrogens were located in the electron density map. The rhombohedral Sn_2N_2 core is planar with the angles $\text{NSnN} = 76.38(5)^\circ$ and $\text{SnNSn} = 103.62(5)^\circ$. The tins have terminally bound Ar' ligands which yield trigonal pyramidal coordination as shown by the sum of the angles at tin of 266.16° . The $\text{Sn}-\text{N}$ bridging distances (2.1913(13) and 2.1918(13) Å) are in good agreement with the reported $\text{Sn}-\text{N}$ distance 2.21 Å in $\{\text{Ar}^*\text{Sn}(\mu\text{-NH}_2)\}_2$ ($\text{Ar}^* = \text{C}_6\text{H}_3-2,6(\text{C}_6\text{H}_2-2,4,6\text{-Pr}'_3)_2$)²⁶ which differs from **3** in that it has a bulkier terphenyl ligand. The IR spectrum displayed two weak sharp bands at 3357 and 3260 cm^{-1} that are due to the two $\text{N}-\text{H}$ stretching modes of the $-\text{NH}_2$ groups. These frequencies are close to those at 3370 and 3290 cm^{-1} observed for $[\text{Ar}^*\text{Sn}(\mu\text{-NH}_2)]_2$.²⁶ The reaction probably proceeds in the same manner as that described in eq 5 to generate an $\text{Ar}'_2\text{Sn}(\text{H})\text{NH}_2$ intermediate which eliminates $\text{Ar}'\text{H}$ to afford **3**.

In summary we have shown that the stannylene SnAr'_2 reacts with H_2 or NH_3 to afford the products **1** or **3**. The corresponding lack of reactivity of H_2 toward SnAr'_2 or $\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$ suggests that the ability of SnAr'_2 to activate H_2 may be associated with increased triplet character in its ground state. The reaction differs from that of carbenes in that an arene is eliminated. However the initial step probably proceeds according to Scheme 1 ($\text{E} = \text{Sn}$).

Acknowledgment. We thank the U.S. Department of Energy Office of Basic Energy Sciences DE-FG02-07ER46475 for financial support. B.D.E. thanks the NSERC of Canada for a postdoctoral fellowship. We thank Dr. Jeff De Ropp and Prof. R. A. Andersen for helpful discussions.

Supporting Information Available: Crystallographic data for **3** (CIF), unit cell parameters for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- All manipulations were carried out under anaerobic and anhydrous conditions. (a) **1**. $[\text{Ar}'\text{Sn}(\mu\text{-H})]$: A solution of SnAr'_2 (1.15 g, 1.26 mmol) in toluene (50 mL) was stirred at 65°C for 2 h under a H_2 atmosphere to give a dark green solution. The mixture was concentrated to ca. 10 mL under vacuum which afforded orange crystals of **1** upon cooling to $ca. -16^\circ\text{C}$. Yield: 39%. $^1\text{H NMR}$ (C_6D_6): 0.93 (d, 6H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$, 1.02 (d, 6H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$, 1.04 (d, 6H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$, 1.11 (d, 6H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$, 3.00 (overlap septets, 4H, $\text{CH}(\text{CH}_3)_2$), 7.03 (d, 4H, $^3J_{\text{HH}} = 7.5\text{ Hz}$, *m-DippH*), 7.10 (m, overlap ArH), 7.30 (t, 2H, $^3J_{\text{HH}} = 7.5\text{ Hz}$, *p-DippH*), 9.13 (s, 1H, $^1J_{\text{Sn-H}} = ca. 89\text{ Hz}$, Sn-H). $^{119}\text{Sn}\{^1\text{H}\}$ NMR: δ 657. (b) **2**. $[\text{Ar}'\text{Sn}(\mu\text{-D})]$: A solution of SnAr'_2 (1.05 g, 1.15 mmol) in toluene (50 mL) was stirred at 65°C for 2 h under a D_2 atmosphere to give a dark green solution. The mixture was concentrated to ca. 10 mL under vacuum which afforded orange crystals of **2** upon cooling to $ca. -16^\circ\text{C}$. Yield: 45%. $^1\text{H NMR}$ (C_6D_6): 0.93 (d, 6H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$, 1.02 (d, 6H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$, 1.04 (d, 6H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$, 1.11 (d, 6H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$, 3.00 (overlap septets, 4H, $\text{CH}(\text{CH}_3)_2$), 7.03 (d, 4H, $^3J_{\text{HH}} = 7.5\text{ Hz}$, *m-DippH*), 7.10–7.28 (m, overlap ArH). $^2\text{H NMR}$ (C_7H_8): 8.98 (s, 1D). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_7D_8): δ 610. (c) **3**. $[\text{Ar}'\text{Sn}(\mu\text{-NH}_2)]_2$: To a deep blue solution of SnAr'_2 (0.45 g, 0.5 mmol) in toluene (50 mL) at -78°C was added several drops of liquid ammonia. The solution became light yellow. Warming to room temperature produced a colorless solution, which was concentrated to ca. 30 mL under reduced pressure to give colorless crystals that were identified as **3** on the basis of NMR spectroscopy and X-ray crystallography. Yield: 55%. Mp: $120\text{--}125^\circ\text{C}$. $^1\text{H NMR}$ (C_7D_8): δ 0.72 (s, 2H, NH_2), 1.48 (d, 12H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.63 (d, 12H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 3.42 (septets, 4H, $\text{CH}(\text{CH}_3)_2$), 7.48 (t, 2H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, *p-DippH*), 7.58 (t, 1H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, *p-C}_6\text{H}_3), 7.65 (d, 4H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, *m-DippH*), 7.68 (d, 2H, $^3J_{\text{HH}} = 7.5\text{ Hz}$, *m-C}_6\text{H}_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8): 24.31 ($\text{CH}(\text{CH}_3)_2$), 26.55 ($\text{CH}(\text{CH}_3)_2$), 31.22 ($\text{CH}(\text{CH}_3)_2$), 126.45 (*p-C}_6\text{H}_3), 128.91 (*p-DippH*), 129.54 (*i-DippH*), 130.24 (*m-C}_6\text{H}_3), 138.17 (*i-DippH*), 147.15 (*o-C}_6\text{H}_3), 157.42 (*i-C}_6\text{H}_3). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_7D_8): δ 280.26. IR (Nujol): ν 3357, 3260 cm^{-1} (ν NH_2 , weak). (d) **4**. SnAr'_2 : A purple solution of SnAr'_2 (0.75 g, 1 mmol) in toluene (50 mL) was stirred at 70°C for 6 days under a H_2 atmosphere. No color change was observed. The solvent was pumped off, and ^1H and ^{119}Sn NMR spectroscopy showed that it was the reactant SnAr'_2 . Recovered yield $>80\%$. $^1\text{H NMR}$ (C_6D_6): 1.90 (s, 12H, *o-CH}_3*), 2.21 (s, 6H, *p-CH}_3*), 6.77 (s, 4H, *m-Mes*), 6.80 (d, 2H, $J_{\text{HH}} = 7.5\text{ Hz}$, *m-C}_6\text{H}_3*), 7.12 (t, 1H, $J_{\text{HH}} = 7.8\text{ Hz}$, *p-C}_6\text{H}_3*). $^{119}\text{Sn}\{^1\text{H}\}$ NMR: δ 635. $^{23}\text{Na}\{^1\text{H}\}$ NMR (C_6D_6): δ 767. $^{27}\text{Al}\{^1\text{H}\}$ NMR (from mother liquor): $^1\text{H NMR}$ (C_6D_6): δ 1.11 (d, 6H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.14 (d, 6H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 2.90 (septets, 4H, $\text{CH}(\text{CH}_3)_2$), 6.89 (s, *i-C}_6\text{H}_3*), 7.04 (s, *i-DippH*), 7.09 (d, 4H, *m-C}_6\text{H}_3*), 7.10 (d, 4H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, *m-DippH*), 7.22 (t, 1H, $^3J_{\text{HH}} = 7.5\text{ Hz}$, *p-C}_6\text{H}_3*), 7.31 (t, 4H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, *p-DippH*). (g) $\text{Ar}'\text{D}$ (mother liquor): $^1\text{H NMR}$ (C_6D_6): δ 1.11 (d, 6H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.14 (d, 6H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 2.89 (septets, 4H, $\text{CH}(\text{CH}_3)_2$), 7.04 (s, *i-DippH*), 7.09 (d, 4H, *m-C}_6\text{H}_3*), 7.10 (d, 4H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, *m-DippH*), 7.22 (t, 1H, $^3J_{\text{HH}} = 7.5\text{ Hz}$, *p-C}_6\text{H}_3*), 7.31 (t, 4H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, *p-DippH*). $^2\text{H NMR}$ (C_6H_{14}): 6.98 (s, *i-C}_6\text{H}_3*).******
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JA805358U