J|A|C|S
COMMUNICATIONS

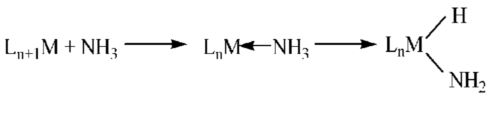
Diarylstannylene Activation of Hydrogen or Ammonia with Arene Elimination

Yang Peng, Bobby D. Ellis, Xinping Wang, and Philip P. Power*

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

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

Activation of H_2 by transition metal complexes has been known and studied for many years.[1−5] Since 1983 the synthesis and characterization of stable H_2 complexes, of which the first was $Mo(CO)_3(PPr^i_3)(\eta^2\text{-}H_2)$,[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 η^2-H_2 unit becomes polarized as in $H^{\delta-}-H^{\delta+}$ 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 NH_3 addition to afford a product that contained both terminal M−NH_2 and M−H groups as in eq 1 was only recently reported.[15]

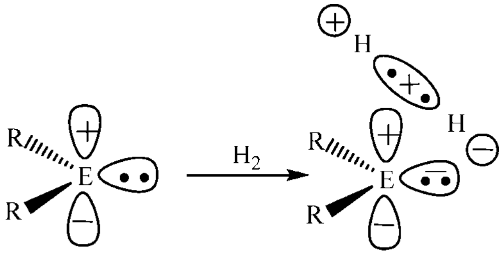


$$L_{n+1}M + NH_3 \longrightarrow L_nM\leftarrow NH_3 \longrightarrow L_nM\begin{smallmatrix}H\\ NH_2\end{smallmatrix} \quad (1)$$

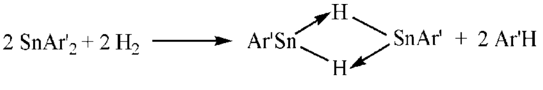
L = ligand, M = transition metal

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′ = C_6H_3-2,6(C_6H_3-2,6-$Pr^i_2)_2$ or C_6H_3-2,6-$Dipp_2$), 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 H_2 and NH_3 were investigated and it was found that mono(amino) carbenes readily activate both H_2 and NH_3. The hypothesis that activation of H_2 occurred via the route described in Scheme 1 was supported by the calculations of Schoeller.[18] We now report the activation of H_2 and NH_3 by the heavier group 14 element carbene analogue $SnAr'_2$ (Ar′ = C_6H_3-2,6(C_6H_3-2,6-$Pr^i_2)_2$) which occurs under mild conditions with arene elimination. We also show that the reactivity of stannylenes toward H_2 is dependent on the tin substituents.

Scheme 1. Schematic Representation of the Activation of by a Divalent Group 14 Molecule, *E* = C [18]

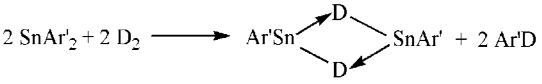


Reaction of a dark blue solution of $SnAr'_2$[19] with H_2 gas at 60−70° for 1 h (eq 2) resulted in a color change to dark green from which orange crystals of **1** were obtained.[20a] X-ray crystallographic examination of the product **1** showed that it had an identical Sn(II) bridging hydride structure 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.



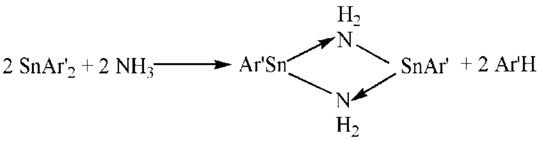
(2)

1



(3)

2



(4)

3

The same procedure as that employed for **1**, using D_2 instead of H_2 (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 $[Ar^*Sn(\mu\text{-}D)]_2$.[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 H_2 or D_2 (as in Scheme 1, E = Sn) to afford Ar'_2SnH_2 or Ar'_2SnD_2 which eliminates Ar′H or Ar′D due to the steric pressure in the molecule (eq 5).[20f,g]

$$SnAr'_2 + X\text{-}Y \longrightarrow \text{"}Ar'_2SnXY\text{"} \xrightarrow{-\ Ar'X} 0.5\,\{Ar'Sn(\mu\text{-}Y)\}_2 \qquad (5)$$

$$X\text{-}Y = H_2,\ D_2,\ H\text{-}NH_2$$

Similar experiments involving the reaction of $SnAr^{\#}_2$[23] ($Ar^{\#}$ = C_6H_3-2,6(C_6H_2-2,4,6-$Me_3)_2$) or $Sn\{N(SiMe_3)_2\}_2$[24] with H_2 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 $Sn\{N(SiMe_3)_2\}_2$ (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)°).

10.1021/ja805358u CCC: $40.75 © 2008 American Chemical Society

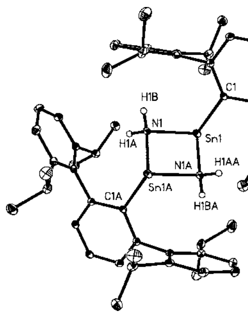


Figure 1. Thermal ellipsoid (30%) drawing of **3**. Hydrogen atoms, except those at nitrogen, are not shown for clarity.

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 crystallography[25] 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 NSnN = 76.38(5)° and SnNSn = 103.62(5)°. 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 Sn−N bridging distances (2.1913(13) and 2.1918(13) Å) are in good agreement with the reported Sn−N distance 2.21 Å in $\{Ar^*Sn(\mu\text{-}NH_2)\}_2$ ($Ar^* = C_6H_3\text{-}2,6(C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3)_2$)[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 N−H stretching modes of the $-NH_2$ groups. These frequencies are close to those at 3370 and 3290 cm^{-1} observed for $[Ar^*Sn(\mu\text{-}NH_2)]_2$.[26] The reaction probably proceeds in the same manner as that described in eq 5 to generate an $Ar'_2Sn(H)NH_2$ intermediate which eliminates Ar′H to afford **3**.

In summary we have shown that the stannylenene $SnAr'_2$[19] 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 $Sn\{N(SiMe_3)_2\}_2$ 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 (E = 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.

References

(1) Halpern, J. *Adv. Inorg. Chem.* **1956**, *11*, 301.
(2) Brothers, P. J. *Prog. Inorg. Chem.* **1981**, *28*, 1.
(3) James, B. R. *Homogenous Hydrogenation*, Wiley, New York, 1973.
(4) Kubas, G. J. *Adv. Inorg. Chem.* **2001**, *56*, 127.
(5) Osborn, J.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711.
(6) Kubas, G. J.; Ryan, R. R.; Swanson, B. L.; Vergamini, P. J.; Wasserman, H. *J. Am. Chem. Soc.* **1984**, *106*, 451.
(7) Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes*; Kluwer: New York, 2001.
(8) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95.
(9) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1982**, *121*, 155.
(10) Heinekey, D. M.; Oldham, W. J. *Chem. Rev.* **1993**, *93*, 913.
(11) Crabtree, R. H. In *Modern Coordination Chemistry: The Legacy of Joseph Chatt*; Leigh, G. J., Winterton, N., Eds.; Royal Society of Chemistry: Cambridge, 2002; p 31.
(12) Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201.
(13) Heinekey, D. M.; Lledas, A.; Lluch, J. M. *Chem. Soc. Rev.* **2004**, *33*, 175.
(14) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 971.
(15) Zhao, J.; Goldman, A. S.; Hartwig, J. S. *Science* **2005**, *307*, 1080.
(16) Spikes, G. H.; Fettinger, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232.
(17) Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124.
(18) Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439.
(19) Spikes, G. H.; Peng, Y.; Fettinger, J. C.; Power, P. P. *Z. Anorg. Allg. Chem.* **2006**, *632*, 1005.
(20) All manipulations were carried out under anaerobic and anhydrous conditions. (a) **1**. $[Ar'Sn(\mu\text{-}H)]_2$: A solution of $SnAr'_2$ (1.15 g, 1.26 mmol) in toluene (50 mL) was stirred at 65° 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°C. Yield: 39%. ^1H NMR (C_6D_6): 0.93 (d, 6H, $^3J_{HH} = 6.6$ Hz, $CH(CH_3)_2$, 1.02 (d, 6H, $^3J_{HH} = 6.6$ Hz, $CH(CH_3)_2$, 1.04 (d, 6H, $^3J_{HH} = 6.6$ Hz, $CH(CH_3)_2$, 1.11 (d, 6H, $^3J_{HH} = 6.6$ Hz, $CH(CH_3)_2$), 3.00 (overlap septets, 4H, $CH(CH_3)_2$), 7.03 (d, 4H,^{3} $J_{HH} = 7.5$ Hz, *m-DippH*), 7.10 (m, overlap ArH), 7.30 (t, 2H, $^3J_{HH} = 7.5$ Hz, *p-DippH*), 9.13 (s, 1H, $^1J_{Sn\text{-}H}$ = ca. 89 Hz, Sn-*H*). $^{119}Sn\{^1H\}$ NMR: δ 657. (b) **2**. $[Ar'Sn(\mu\text{-}D)]_2$: 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 °C. Yield: 45%. ^1H NMR (C_6D_6): 0.93 (d, 6H, $^3J_{HH} = 6.6$ Hz, $CH(CH_3)_2$, 1.02 (d, 6H, $^3J_{HH} = 6.6$ Hz, $CH(CH_3)_2$), 1.04 (d, 6H, $^3J_{HH} = 6.6$ Hz, $CH(CH_3)_2$), 1.11 (d, 6H, $^3J_{HH} = 6.6$ Hz, $CH(CH_3)_2$), 3.00 (overlap septets, 4H, $CH(CH_3)_2$), 7.03 (d, 4H, $^3J_{HH} = 7.5$ Hz, *m-DippH* 7.10−7.28 (m, overlap ArH),) ^2H NMR (C_7H_8): 8.98 (s, 1*D*). $^{119}Sn\{^1H\}$ NMR (C_7D_8): δ 610. (c) **3**. $[Ar'Sn(\mu\text{-}NH_2)]_2$: To a deep blue solution of $SnAr'_2$ (0.45g, 0.5 mmol) in toluene (50 mL) at−78° 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: 120−125°. ^1H NMR (C_7D_8): δ 0.72 (s, 2H, NH_2), 1.48 (d, 12H, $^3J_{HH} = 6.6$ Hz, $CH(CH_3)_2$), 1.63 (d, 12H, $^3J_{HH} = 6.6$ Hz, $CH(CH_3)_2$), 3.42 (septets, 4H, $CH(CH_3)_2$), 7.48 (t, 2H, $^3J_{HH} = 6.6$ Hz, *p-DippH*), 7.58 (t, 1H, $^3J_{HH} = 6.6$ Hz, $p\text{-}C_6H_3$), 7.65 (d, 4H, $^3J_{HH} = 6.6$ Hz, *m-Dipp*)), 7.68 (d, 2H,^{3} J_{HH} =7.5 Hz, $m\text{-}C_6H_3$). $^{13}C\{^1H\}$ NMR(C_7D_8): 24.31 ($CH(CH_3)_2$), 26.55 ($CH(CH_3)_2$), 31.22 ($CH(CH_3)_2$), 126.45 ($p\text{-}C_6H_3$), 128.91 (*p-Dipp*), 129.54 (*i-Dipp*), 130.24 ($m\text{-}C_6H_3$), 138.17 (*i-Dipp*), 147.15 ($o\text{-}C_6H_3$), 157.42 ($i\text{-}C_6H_3$). $^{119}Sn\{^1H\}$ 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° 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%. ^1H NMR (C_6D_6): 1.90 (s, 12H, $o\text{-}CH_3$), 2.21 (s, 6H, $p\text{-}CH_3$), 6.77 (s, 4H, *m-Mes*), 6.80 (d, 2H, $J_{HH} = 7.5$ Hz, $m\text{-}C_6H_3$), 7.12 (t, 1H, $J_{HH} = 7.8$ Hz, $p\text{-}C_6H_3$). $^{119}Sn\{^1H\}$ NMR: δ 635.[23.] (e) **5**. $Sn\{N(SiMe_3)_2\}_2$: An orange solution of $Sn\{N(SiMe_3)_2\}_2$ (1.09 g, 2.5 mmol) in toluene (50 mL) was stirred at 70° for 3 days under a H_2 atmosphere. No color change was observed. The solvent was pumped off, and ^1H, ^{119}Sn NMR spectroscopy indicated unchanged $Sn\{N(SiMe_3)_2\}_2$. Recovered yield >85%. ^1H NMR (C_6D_6): 0.28 (s, 18H, $-CH_3$). $^{119}Sn\{^1H\}$ NMR: δ 767.[27a,b](f) Ar′H (from mother liquor): ^1H NMR (C_6D_6): δ 1.11 (d, 6H, $^3J_{HH} = 6.6$ Hz, $CH(CH_3)_2$), 1.14 (d, 6H, $^3J_{HH} = 6.6$ Hz, $CH(CH_3)_2$), 2.90 (septets, 4H, $CH(CH_3)_2$), 6.89 (s, $i\text{-}C_6H_3$), 7.04 (s, *i-Dipp*), 7.09 (d, 4H, $m\text{-}C_6H_3$), 7.10 (d, 4H, $^3J_{HH} = 6.6$ Hz, *m-Dipp*)), 7.22 (t, 1H, $^3J_{HH} = 7.5$ Hz, $p\text{-}C_6H_3$), 7.31 (t, 4H, $^3J_{HH} = 6.6$ Hz, *p-Dipp*). (g) Ar′D (mother liquor): ^1H NMR (C_6D_6): δ 1.11 (d, 6H, $^3J_{HH} = 6.6$ Hz, $CH(CH_3)_2$), 1.14 (d, 6H, $^3J_{HH} = 6.6$ Hz, $CH(CH_3)_2$), 2.89 (septets, 4H, $CH(CH_3)_2$), 7.04 (s, *i-Dipp*), 7.09 (d, 4H, $m\text{-}C_6H_3$), 7.10 (d, 4H, $^3J_{HH} = 6.6$ Hz, *m-Dipp*)), 7.22 (t, 1H, $^3J_{HH} = 7.5$ Hz, $p\text{-}C_6H_3$), 7.31 (t, 4H, $^3J_{HH} = 6.6$ Hz, *p-Dipp*). ^2H NMR (C_6H_{14}): 6.98 (s, $i\text{-}C_6H_3$).
(21) Rivard, E.; Fischer, R. C.; Wolf, R.; Peng, Y.; Merrill, W. A.; Schley, N. D.; Zhu, Z.; Pu, L.; Fettinger, J. C.; Teat, S. J.; Nowik, I.; Herber, R. H.; Takagi, N.; Nagase, S.; Power, P. P. *J. Am. Chem. Soc.* **2007**, *129*, 16197.
(22) Eichler, B. E.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 8785.
(23) Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, *16*, 1920.
(24) Fjelberg, T.; Hope, H.; Lappert, M. F.; Power, P. P.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 639.
(25) Crystal Data for **3·4PhMe** 90(2) K with Mo Kα ($\lambda = 0.710\,73$ Å), fw = 1433.20, triclinic, $P\bar{1}$, colorless block, $a = 12.0051(6)$ Å, $b = 13.3719(7)$ Å, $c = 13.6933(7)$ Å, $\alpha = 110.5722(7)°$, $\beta = 102.3158(7)°$, $\gamma = 103.5991(7)°$, $V = 1891.60(17)$ Å^3, $Z = 1$, 21 146 total reflections, 8667[$I > 2\sigma(I)$] $R1 = 0.0220$, $wR2 = 0.0552$, R indices (all data) $R1 = 0.0268$, $wR2 = 0.0578$.
(26) Stanciu, C.; Hino, S.; Stender, M.; Richards, A. F.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **2005**, *44*, 2774.
(27) (a) Wrackmeyer, B. In *Unkonventionelle Wechselwirkungen in der Chemie metallischer Elemente*; Krebs, B., Ed.; VCH: Weinheim, 1992; pp 111−124. (b) Wrackemeyer, B. *Ann. Rep. NMR Spectrosc.* **1999**, *38*, 20.

JA805358U