

A Singly Bonded Amido-Distannyne: H₂ Activation and Isocyanide Coordination

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SUPPLEMENTARY INFORMATION

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1. Syntheses

General considerations. All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Diethyl ether was distilled over Na/K alloy (25:75), while THF, hexane and toluene were distilled over molten potassium. ¹H, ¹³C{¹H}, ²⁹Si{¹H} and ¹¹⁹Sn{¹H} NMR spectra were recorded on a Bruker AvanceIII spectrometer and were referenced to the resonances of the solvent used, external SiMe₄, or external SnMe₄. IR spectra were recorded for solid samples using an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. Microanalyses were carried out at the Science Centre, London Metropolitan University. A reproducible microanalysis could not be obtained for L[†]SnBr as the recrystallised product contained toluene of crystallization which could not be completely removed by placing the sample under reduced pressure for several hours. L[†]H¹ and {(^{Mes}Nacnac)Mg}₂² were prepared by literature procedures. All other reagents were used as received.

Synthesis of L[†]SnBr. L[†]H (3.00 g, 4.81 mmol) was dissolved in THF (60 cm³) and the solution cooled to -80 °C. To this was added BuⁿLi (3.16 cm³ of a 1.6 M solution in hexane), whereupon, the reaction mixture was warmed to ambient temperature and stirred for 2 h. The resultant solution was added to a suspension of SnBr₂ (1.47 g, 5.29 mmol) in THF (10 cm³) held at -80 °C. After 1 h, the reaction mixture was warmed to ambient temperature, and all volatiles subsequently removed *in vacuo*. The residue was extracted into hot toluene, the extract filtered, and volatiles removed from the filtrate *in vacuo*. Washing of the residue with hexane afforded L[†]SnBr as an off-white powder (3.28 g, 83 %). N.B. Crystals of the compound suitable for an X-ray diffraction experiment were grown from a toluene solution. M.p.: 220-225 °C (decomp.); ¹H NMR (C₆D₆, 400 MHz, 298 K), δ = 0.95 (d, ³J_{HH} = 6.8 Hz, 6H, Ar[†]-Prⁱ-CH₃), 1.43 (d, ³J_{HH} = 6.8 Hz, 18H, SiPrⁱ₃-CH₃), 2.23 (sept, ³J_{HH} = 6.8 Hz, 3H, SiPrⁱ₃-CH), 2.48 (sept, ³J_{HH} = 6.8 Hz, 1H, Ar[†]-*p*-Prⁱ-CH), 6.43 (s, 2H,

Ph_2CH), 6.76 (m, 2H, $\text{Ar}^\dagger\text{-}m\text{-ArH}$), 6.90-7.31 (m, 20H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75.5 MHz, 298 K), $\delta = 16.1$ ($\text{SiPr}^i_3\text{-CH}$), 20.0 ($\text{SiPr}^i_3\text{-CH}_3$), 24.1 ($\text{Ar}^\dagger\text{-Pr}^i\text{-CH}_3$), 33.7 ($\text{Ar}^\dagger\text{-Pr}^i\text{-CH}$), 52.3 (Ph_2CH), 126.8, 127.4, 128.5, 128.8, 129.8, 130.5, 131.3, 140.7, 143.8, 144.2, 145.3, 145.7 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 80 MHz, 298 K), $\delta = 9.30$; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_6D_6 , 149.2 MHz, 298 K): $\delta = 290.6$; IR, ν/cm^{-1} (ATR): 3058 (w), 3025 (w), 1945 (w), 1873 (w), 1804 (w), 1598 (w), 1378 (m), 1325 (w), 1222 (m), 1195 (m), 1115 (m), 1074 (m), 1031 (m), 878 (s), 831 (s), 760 (m).

N.B. from one preparation of $\text{L}^\dagger\text{SnBr}$, a few crystals of the previously reported aniline, $\text{Ar}^\dagger\text{NH}_2$,¹ and the C-H activated N-heterocyclic stannylene dimer, $\{\text{Sn}\{\kappa^2\text{-N,C-N(H)}\{\text{C}_6\text{H}_2[\text{CPh}_2][\text{C(H)Ph}_2]\text{Pr}^i\text{-}2,6,4\}\}_2$, were obtained. The mechanism of formation of the latter is unknown, though this may involve elimination of BrSiMe_3 from $\text{L}^\dagger\text{SnBr}$, subsequent benzhydryl C-H activation by the low-valent tin centre of the intermediate, and hydrogen migration from that tin centre to the adjacent nitrogen site. That said, attempts to prepare the compound by heating solutions of $\text{L}^\dagger\text{SnBr}$ were not successful. Given the low yield of the compound, no spectroscopic data could be obtained for it, though its X-ray crystal structure was obtained (see below).

Synthesis of $\text{L}^\dagger\text{SnSnL}^\dagger$, 1. $\text{L}^\dagger\text{SnBr}$ (1.00 g, 1.22 mmol) was dissolved in a toluene/diethyl ether mix (5 cm^3 / 20 cm^3), and the solution cooled to -80°C . To this was added a solution of $\{(\text{MesNacnac})\text{Mg}\}_2$ (435 mg, 0.61 mmol) in diethyl ether (20 cm^3). The reaction mixture was slowly warmed to -20°C during which time it took on a deep green colour. Volatiles were removed from the mixture *in vacuo* at -20°C , and the residue was then extracted into pre-cooled (-20°C) hexane (20 cm^3), before the extract was filtered. The deep green filtrate was concentrated *in vacuo* and stored at -30°C for 24 h to afford large orange/green crystals of **1** (410 mg, 45 %). N.B. Crystals of the compound suitable for the X-ray diffraction experiment were grown from a toluene/hexane solution. M.p.: $96\text{-}100^\circ\text{C}$ (melts and decomp.); ^1H NMR (C_6D_6 , 400 MHz, 298 K), $\delta = 1.01$ (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H, $\text{Ar}^\dagger\text{-Pr}^i\text{-CH}_3$), 1.22 (d, $^3J_{\text{HH}} = 6.8$ Hz, 18H, $\text{SiPr}^i_3\text{-CH}_3$), 1.42 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 3H, $\text{SiPr}^i_3\text{-CH}$), 2.59 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 1H, $\text{Ar}^\dagger\text{-}p\text{-Pr}^i\text{-CH}$), 6.40 (s, 2H, Ph_2CH), 6.97 (m, 2H, $\text{Ar}^\dagger\text{-}m\text{-CH}$), 7.00-7.48 (m, 20H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75.5 MHz, 298 K), $\delta = 17.3$ ($\text{SiPr}^i_3\text{-CH}$), 20.0 ($\text{SiPr}^i_3\text{-CH}_3$), 24.3 ($p\text{-Pr}^i\text{-CH}_3$), 33.5 ($p\text{-Pr}^i\text{-CH}$), 51.9 (Ph_2CH), 126.6, 127.1, 128.5, 128.7, 129.3, 130.1, 130.4, 140.9, 142.4, 144.9, 146.5, 152.5 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 80 MHz, 298 K), $\delta = 6.00$; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_6D_6 , 149.2 MHz, 298 K): no signal observed; UV/vis, λ_{max} , nm (ϵ , $\text{Lcm}^{-1}\text{mol}^{-1}$): 409 (6500); IR, ν/cm^{-1} (ATR): 3058 (w), 3025 (w), 1943 (w), 1870 (w), 1802 (w), 1599 (w), 1388 (m), 1365 (m), 1223 (m), 1116 (w), 1074 (w), 1031 (w), 881 (m), 759 (s), 657 (s); anal. calc. for $\text{C}_{88}\text{H}_{104}\text{Sn}_2\text{N}_2\text{Si}_2$: C, 71.25 %; H, 7.07 %; N, 1.89 %; found: C, 71.18 %; H, 7.17 %; N, 1.88 %.

N.B. The conversion of **1** to $L^{\dagger}Sn(\mu-H)_2SnL^{\dagger}$ **2** was achieved by placing C_6D_6 solutions of **1** under an atmosphere of dihydrogen in a 5mm J. Young's nmr tube at 25 °C. The tube was shaken at regular intervals and the progress of the reaction monitored by 1H NMR spectroscopy. That is, the ratio of the integrals of the methine protons of the flanking Ph_2CH groups of both compounds was used to determine reaction completeness.

Synthesis of $L^{\dagger}(Bu^tNC)SnSn(CNBu^t)L^{\dagger}$, **3.** The procedure for the synthesis of **1** was followed, using $L^{\dagger}SnBr$ (250 mg, 0.30 mmol) and $\{(^{Mes}Nacnac)Mg\}_2$ (109 mg, 0.15 mmol) in a toluene/diethyl ether mixture ($5\text{ cm}^3/10\text{ cm}^3$), followed by the addition of neat Bu^tNC (38 μ L, 0.33 mmol) to the solution of *in situ* generated **1**. After stirring the reaction mixture for 1h at -20 °C, volatiles were removed *in vacuo* and the residue was extracted in hexane. The extract was filtered and concentrated to incipient crystallisation, then placed at -30 °C for 1 week to afford large dark orange/green crystals of **3** (90 mg, 36 %). M.p.: 101-108 °C (melt and decomp.); 1H NMR (C_6D_6 , 400 MHz, 298 K), δ = 0.86 (s, 9H, $CNC(CH_3)_3$), 1.02 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $Ar^{\dagger}-Pr^i-CH_3$), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 18H, $SiPr^i_3-CH_3$), 1.40 (sept, $^3J_{HH}$ = 6.8 Hz, 3H, $SiPr^i_3-CH$), 2.60 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, $Ar^{\dagger}-p-Pr^i-CH$), 6.43 (s, 2H, Ph_2CH), 6.93 (m, 2H, $Ar^{\dagger}-m-CH$), 6.96-7.46 (m, 20H, ArH); $^{13}C\{^1H\}$ NMR (C_6D_6 , 75.5 MHz, 298 K), δ = 17.0 ($SiPr^i_3-CH$), 20.0 ($SiPr^i_3-CH_3$), 24.2 ($p-Pr^i-CH_3$), 30.3 ($CNC(CH_3)_3$), 33.5 ($p-Pr^i-CH$), 51.8 (Ph_2CH), 53.7 ($CNC(CH_3)_3$); 125.7, 126.5, 127.0, 128.4, 128.6, 130.4, 137.8, 141.0, 142.0, 145.0, 146.9, 152.6 ($Ar-C$), $CNC(CH_3)_3$ resonance not observed; $^{29}Si\{^1H\}$ NMR (C_6D_6 , 80 MHz, 298 K), δ = 5.42; ^{119}Sn NMR (C_6D_6 , 149.2 MHz, 298K): δ = 241 (p.w. at 1/2 peak height: 90Hz), $^{117/119}Sn$ satellites not observed; UV/vis, λ_{max} , nm (ϵ , $Lcm^{-1}mol^{-1}$): 420 (5200); IR, ν/cm^{-1} (ATR): 3060 (w), 3026 (w), 2786 (w), 2138 (s, CN) 1944 (w), 1890 (w), 1802 (w), 1599 (m), 1426 (m), 1210 (s), 1192 (m), 1120 (m), 1031 (m), 896 (s), 786 (s), 761 (s), 716 (s), 679 (s); anal. calc. for $C_{98}H_{122}Sn_2N_4Si_2$: C, 71.35 %; H, 7.45 %; N, 3.40; found: C, 71.12 %; H, 7.40 %; N, 3.51 %.

2. X-Ray Crystallography

Crystals of $L^{\dagger}SnBr \cdot (toluene)_{0.5}$, **1** $\cdot (toluene)/(hexane)_{0.5}$, **3** $\cdot (hexane)_3$, $Ar^{\dagger}NH_2$ **1S**, and $\{Sn\{\kappa^2-N,C-N(H)\{C_6H_2[CPh_2][C(H)Ph_2]Pr^i-2,6,4\}\}_2 \cdot (toluene)_2$ **2S** $\cdot (toluene)_2$ suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were carried out with a Bruker Apex X8 diffractometer using a graphite monochromator with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). All structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97)³ using all unique data. All non-hydrogen atoms are anisotropic with hydrogen atoms included in calculated positions (riding model), except for the amino protons of **1S**, the positional and displacement parameters of which were freely refined. Crystal data, details of data

collections and refinements for all structures can be found in their CIF files and are summarized in Table S1.

Table S1. Summary of Crystallographic Data for Compounds $L^{\dagger}SnBr \cdot (toluene)_{0.5}$, $1 \cdot (toluene)/(hexane)_{0.5}$, $3 \cdot (hexane)_3$, $Ar^{\dagger}NH_2$ **1S**, and $\{Sn\{\kappa^2-N,C-N(H)\{C_6H_2[CPh_2][C(H)Ph_2]Pr^i-2,6,4\}\}_2 \cdot (toluene)_2$ **2S** $\cdot (toluene)_2$

	$L^{\dagger}SnBr \cdot (toluene)_{0.5}$	$1 \cdot (toluene)/(hexane)_{0.5}$	$3 \cdot (hexane)_3$	1S	2S $\cdot (toluene)_2$
empirical formula	$C_{47.5}H_{56}BrNSiSn$	$C_{98}H_{119}N_2Si_2Sn_2$	$C_{116}H_{164}N_4Si_2Sn_2$	$C_{35}H_{33}N$	$C_{84}H_{78}N_2Sn_2$
formula weight	867.62	1618.51	1908.07	467.62	1352.86
crystal system	triclinic	triclinic	monoclinic	monoclinic	triclinic
space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> ₂ / <i>n</i>	<i>P</i> ₂ / <i>n</i>	<i>P</i> -1
<i>a</i> (Å)	9.9346(4)	15.2590(7)	17.5664(8)	5.7642(3)	10.8594(7)
<i>b</i> (Å)	13.1778(5)	15.4261(8)	13.8316(5)	18.6519(9)	12.3800(7)
<i>c</i> (Å)	17.8089(8)	20.5749(9)	21.8305(12)	24.6623(13)	12.8382(7)
α (deg.)	72.260(2)	88.697(2)	90	90	103.735(3)
β (deg.)	74.655(2)	83.069(2)	91.274(5)	91.236(5)	101.423(3)
γ (deg.)	71.450(2)	64.915(2)	90	90	94.545(3)
vol (Å ³)	2068.62(15)	4352.0(4)	5302.9(4)	2650.9(2)	1628.88(17)
<i>Z</i>	2	2	2	4	1
ρ (calcd) (g.cm ⁻³)	1.393	1.235	1.195	1.172	1.379
μ (mm ⁻¹)	1.646	1.235	0.541	0.067	0.815
<i>F</i> (000)	894	1698	2032	1000	696
<i>T</i> (K)	123(2)	123(2)	123(2)	123(2)	123(2)
reflections collected	28260	40836	72060	11908	10506
unique reflections	8954	15466	12152	4914	5282
<i>R</i> _{int}	0.0182	0.0489	0.0961	0.0325	0.0473
R1 indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0409	0.0737	0.0598	0.0502	0.0687
wR2 indices (all data)	0.1082	0.1609	0.1709	0.1129	0.1660
CCDC No.	977197	977194	977196	977193	977195

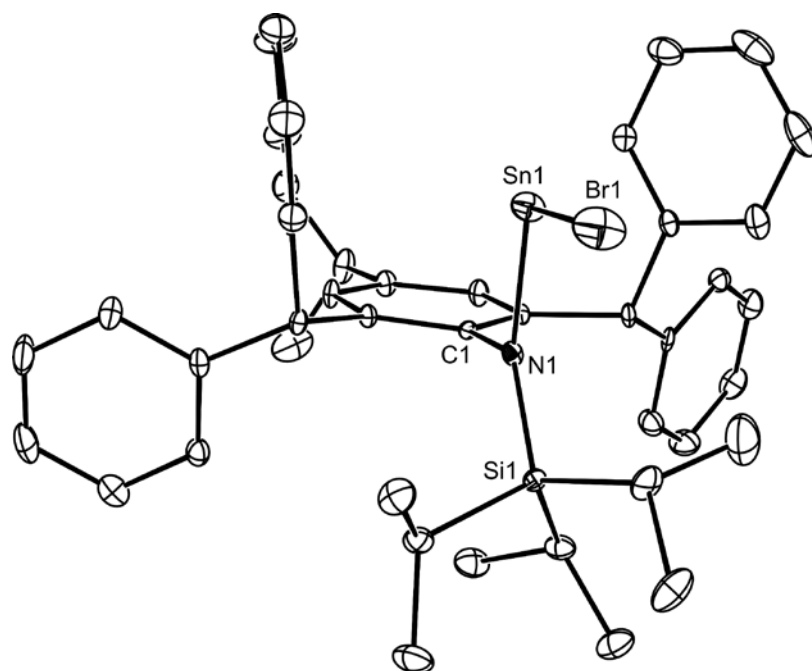


Fig. S1 Molecular structure of L⁺SnBr (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Sn(1)-N(1) 2.116(2), Sn(1)-Br(1) 2.5782(4), N(1)-Sn(1)-Br(1) 104.89(6), C(1)-N(1)-Si(1) 121.34(17), C(1)-N(1)-Sn(1) 100.07(14), Si(1)-N(1)-Sn(1) 138.49(12).

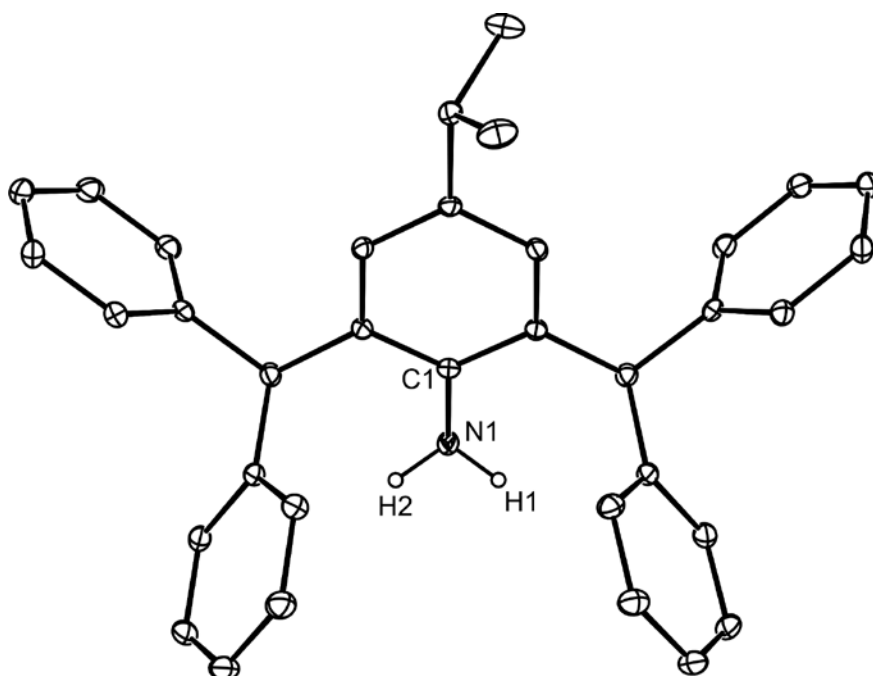


Fig. S2 Molecular structure of Ar⁺NH₂ 1S (25% thermal ellipsoids; hydrogen atoms, except amino protons, omitted).

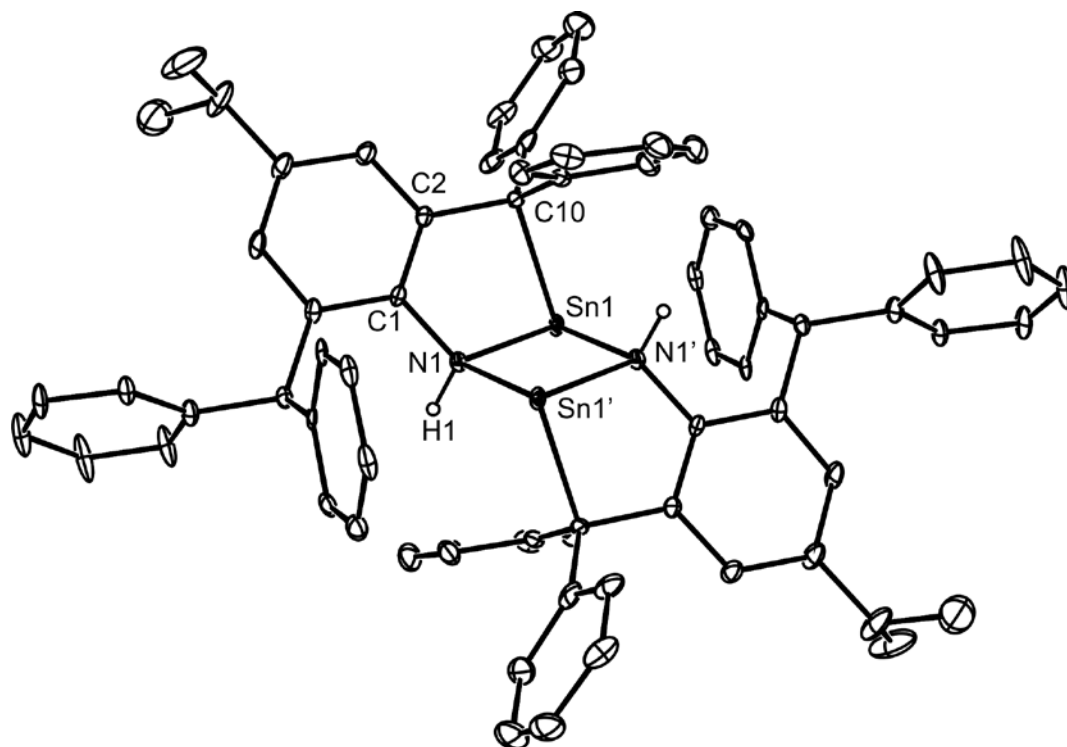


Fig. S3 Molecular structure of $\{\text{Sn}\{\kappa^2\text{-N,C-N(H)}\{\text{C}_6\text{H}_2[\text{CPh}_2][\text{C(H)Ph}_2]\text{Pr}^i\text{-2,6,4}\}\}_2$ **2S** (25% thermal ellipsoids; hydrogen atoms, except amido protons omitted). Selected bond lengths (Å) and angles (°): Sn(1)-N(1)' 2.242(6), Sn(1)-N(1) 2.251(6), Sn(1)-C(10) 2.338(7), N(1)-C(1) 1.444(8), N(1)'-Sn(1)-N(1) 79.8(2), N(1)'-Sn(1)-C(10) 94.5(2), N(1)-Sn(1)-C(10) 77.2(2), C(1)-N(1)-Sn(1) 122.8(4), C(1)-N(1)-Sn(1) 107.6(4), Sn(1)'-N(1)-Sn(1) 100.2(2). Symmetry operation: '-x+1, -y+2, -z+2.

3. References

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