

***Ansa-tris(allyl) complexes of alkali metals: tripodal analogues of
cyclopentadienyl and *ansa*-metallocene ligands***

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Electronic supplementary information – experimental and analytical details

General considerations. All syntheses were carried out using conventional Schlenk-type techniques involving rigorous exclusion of air and moisture. Solvents were pre-dried over sodium wire before being rigorously dried by refluxing over sodium/potassium alloy (hexane) or sodium benzophenone (thf). Anhydrous SnCl₂ was purchased from Lancaster and used as supplied, and 1,3-*bis*(trimethylsilyl)allyl potassium was prepared according to a literature procedure.¹ NMR spectra were recorded on a Bruker DRX 500 NMR spectrometer equipped with a CryoProbe. Crystallographic studies were carried out using a Nonius Kappa CCD diffractometer.

Synthesis of [1·thf]. A solution of 1,3-*bis*(trimethylsilyl)allyl potassium (0.67g, 3.0 mmol) in thf (10 ml) was added dropwise to a solution of SnCl₂ (0.19 g, 1.0 mmol) in thf (10ml) at -78°C. The reaction mixture was slowly warmed to room-temperature and then stirred for 2 hours to result in a bright yellow solution. The thf solvent was removed *in vacuo* to result in a sticky amber solid that was dissolved in hexane (10 ml) and filtered through Celite (P3). The hexane solution was reduced in volume to ca. 2 ml and stored at -15°C for 3 days, affording yellow, very-air sensitive crystals suitable for X-ray diffraction. Removal of the supernatant hexane solvent by syringe and drying *in vacuo* for ca. 30 minutes afforded **1**·thf (0.34 g, 43% isolated yield), melts 103-105°C to an amber oil. Anal. Calcd. for C₃₁H₇₁OKSi₆Sn, C 47.36, H 9.10; found C 47.18, H 9.01 %. ¹¹⁹Sn NMR (δ ppm, 186.50 MHz, toluene-*d*₈, 300.0 K, referenced to SnMe₄ in benzene-*d*₆): -132.87 (br s). ¹³C NMR (δ ppm, 125.75 MHz, toluene-*d*₈, 300.0 K, *J*/Hz, atom labels refer to those assigned in Figure 1 of the Communication Main Text): 127.78, C2, ¹*J*(C2-H2) not observed; 112.78, C3, ¹*J*(C3-H3) = 277; 68.00, thf; 39.67, C1, ¹*J*(¹³C-¹¹⁹Sn) = 1549.5, ¹*J*(¹³C-¹¹⁷Sn) = 1481.5, ¹*J*(¹³C-¹H) = 195; 25.67, thf; 0.84, Me₃Si; 0.07, Me₃Si. ¹H NMR (δ ppm, 500.05 MHz, toluene-*d*₈, 300.0 K, *J*/Hz): 6.43, dd, 3H, H2, ³*J*(H2-H3) = 18.0, ³*J*(H2-H1) = 14.1; 4.42, d, 3H, H3; 3.57, m, 4H, thf; 1.43, m, 4H, thf; 1.20 d, 3H, H1; 0.42, 27H, Me₃Si; 0.23, 27H, Me₃Si.

Synthesis of 2. A mixture of allyltrimethylsilane (43.6 ml, 274 mmol) and thf (100 ml) was cooled to -78°C and n-butyllithium (1.6 M, 171.5 ml, 274 mmol) was added dropwise over 1 hour. The reaction mixture was slowly warmed to room-temperature (approx. 293 K) and stirred for 16 hours. The resulting yellow solution of lithium allyltrimethylsilane was then cooled to -78°C and MeSiCl_3 (13.68 g, 91.5 mmol) added dropwise and the reaction mixture allowed to warm to room-temperature and stirred for 20 hours. Following removal of the thf solvent in vacuo, hexane (80 ml) was added and the resulting solution filtered (Celite, P3). The hexane solvent was then removed in vacuo and the resulting liquid distilled under reduced pressure to afford **2** as a colourless oil (27.3 g, 78%), bp $107\text{-}109^{\circ}\text{C}/0.1$ mm Hg. ^{13}C NMR (δ /ppm, 125.75 MHz, CDCl_3 , 300.0 K) 142.6 $\underline{\text{C}}\text{H}=\text{CH}(\text{SiMe}_3)$; 129.2, $\text{CH}=\underline{\text{C}}\text{H}(\text{SiMe}_3)$; 24.7 $\text{MeSi}-\underline{\text{C}}\text{H}_2$; -1.031, SiMe_3 ; -5.9, $\underline{\text{Me}}\text{Si}$. ^1H NMR (δ /ppm, 500.05 MHz, CDCl_3 , 300.0 K, J/Hz): 5.99, dt, 3H, $\text{CH}_2-\underline{\text{C}}\text{H}=\text{CH}$, $^3J = 18.4$ and 7.8 ; 5.47, dt, 3H, $\text{CH}_2-\underline{\text{C}}\text{H}=\text{CH}(\text{SiMe}_3)$, $^3J = 18.4$, $^4J = 1.3$; 1.66, dd, $\underline{\text{C}}\text{H}_2$; 0.03, s, 27H, SiMe_3 ; -0.03, s, 3H, MeSi . Anal. Calcd. for $\text{C}_{19}\text{H}_{42}\text{Si}_4$, C 59.60, H 11.06; found C 59.45, H 11.05 %.

Synthesis of [3·(tmeda)₃]. A mixture of **2** (0.38 g, 1.0 mmol) and hexane (10 ml) was cooled to -78°C and n-butyllithium (1.6M, 1.88 ml, 3.0 mmol) was added dropwise. The reaction mixture was warmed to room-temperature and stirred for 12 hours followed by the addition of tmeda (0.35 g, 3.0 mmol) and further stirring for 1 hour to afford a pale red solution. The solution was filtered (Celite, P3), reduced in volume to ca. 2 ml and stored at -15°C overnight to afford pink crystals of [3·(tmeda)₃] (0.24 g, 32% isolated yield) mp $125\text{-}128^{\circ}\text{C}$. ^{13}C NMR (δ /ppm, 125.75 MHz, CDCl_3 , 300.0 K, atom labels refer to those assigned in Figure 4 of the Communication Main Text): 128.2, C9; 70.1, C10; 61.5, C8; 46, NMe_2 , broad; 56.5, CH_2N , broad. ^1H NMR (δ /ppm, 500.05 MHz, CDCl_3 , 300.0 K, J/Hz): 7.18, dd, 1H, H9, $^3J(\text{H9-H10}) = 16.8$, $^3J(\text{H9-H8}) = 10.9$; 6.98, t, 1H, H3/3A, $^3J = 15.4$; 6.86, t, 1H, H3/H3A, $^3J = 15.3$; 3.58, d, 1H, $^3J = 16.0$; 3.44, d, 1H, $^3J = 15.6$; 3.35, d, 1H, H10, $^3J = 16.9$; 3.02, d, 1H, $^3J = 14.7$; 2.63, d, 1H, H8, $^3J = 10.9$; 2.52, d, 1H, $^3J = 14.8$; 2.35-2.09,

broad, overlapping multiplets, 48H, $3 \times \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$); 0.54, (s, 3H, MeSi); 0.44, 0.43, 0.41
($3 \times$ s, $3 \times$ 9H, $3 \times$ Me₃Si). Anal. Calcd. for C₃₇H₈₇Li₃N₆Si₄, C 59.31, H 11.70, N 11.22; found C
58.91, H 11.20, N 11.38 %.

Crystallographic details for compounds **1·thf** and **[3·(tmeda)₃]**

Crystals were mounted on thin glass fibres using perfluoropolyether oil and frozen in situ in a flow of cold nitrogen gas from a Cryostream instrument. Data were collected using an Enraf Nonius Kappa CCD diffractometer using monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Cell refinement and data reduction was performed using the HKL SCALEPACK & DENZO² and COLLECT³ utilities. Absorption corrections were made based on ψ - and ω -scans using the SORTAV⁴ program. Structures were solved using direct methods and refined on F^2 using the program SIR-92⁵ and then refined using SHELXTL-97.⁶ All non-hydrogen atoms were refined anisotropically for all structures. For **[1·thf]** and **[3·(tmeda)₃]**, the allylic hydrogen atoms were located directly in the electron peak difference maps and were allowed to refine freely. All other hydrogen atoms were fixed manually on idealized positions, with values of U_{iso} set to 1.5 times the carrier atom. In **[1·thf]**, the thf solvent molecule was disordered about a 3-fold axis, with the coordinating O-atom located at $[-1/3, +1/3, l]$; hydrogen atoms were not assigned and compensatory alterations were made to the final structural formula, as required for a single C₄H₈O unit. In **[3·(tmeda)₃]** the positions of carbon atoms in the tmeda backbone were found to be disordered over two positions (not shown in Figure 4). Due to the inherent disorder in the tmeda ligand containing C19 and C20, hydrogen atoms on these parent atoms have been removed from the structure and corrected for in the .cif file.

Table S1. Crystal data and structure refinement for 1-thf.

Empirical formula	C ₃₁ H ₇₁ KOSi ₆ Sn	
Formula weight	786.22	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	R3c	
Unit cell dimensions	$a = 17.4815(9)$ Å	$\alpha = 90^\circ$.
	$b = 17.4815(9)$ Å	$\beta = 90^\circ$.
	$c = 27.596(2)$ Å	$\gamma = 120^\circ$.
Volume	7303.5(8) Å ³	
Z	6	
Density (calculated)	1.029 Mg/m ³	
Absorption coefficient	0.774 mm ⁻¹	
$F(000)$	2388	
Crystal size	0.17 x 0.12 x 0.12 mm ³	
Theta range for data collection	3.64 to 20.59°.	
Index ranges	$-17 \leq l \leq 16$, $-17 \leq k \leq 17$, $-27 \leq l \leq 27$	
Reflections collected	7480	
Independent reflections	1622 [$R(\text{int}) = 0.0517$]	
Completeness to theta = 20.59°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.986 and 0.854	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1622 / 1 / 136	
Goodness-of-fit on F^2	1.089	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0312$, $wR2 = 0.0698$	
R indices (all data)	$R1 = 0.0483$, $wR2 = 0.0789$	
Absolute structure parameter	-0.03(4)	
Largest diff. peak and hole	0.204 and -0.143 e.Å ⁻³	

Table S2. Crystal data and structure refinement for 3·(tmeda)₃

Empirical formula	C ₃₇ H ₈₇ Li ₃ N ₆ Si ₄	
Formula weight	749.31	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	<i>P4₂/nmc</i>	
Unit cell dimensions	<i>a</i> = 33.6787(3) Å	$\alpha = 90^\circ$.
	<i>b</i> = 33.6787(3) Å	$\beta = 90^\circ$.
	<i>c</i> = 11.17300(10) Å	$\gamma = 90^\circ$.
Volume	12673.0(2) Å ³	
<i>Z</i>	8	
Density (calculated)	0.798 Mg/m ³	
Absorption coefficient	0.117 mm ⁻¹	
<i>F</i> (000)	3376	
Crystal size	0.37 x 0.14 x 0.14 mm ³	
Theta range for data collection	3.53 to 25.00°.	
Index ranges	-40 ≤ <i>h</i> ≤ 35, -29 ≤ <i>k</i> ≤ 40, -13 ≤ <i>l</i> ≤ 13	
Reflections collected	54441	
Independent reflections	5735 [<i>R</i> (int) = 0.0579]	
Completeness to theta = 25.00°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.977 and 0.855	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	5735 / 0 / 268	
Goodness-of-fit on <i>F</i> ²	1.107	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0890, <i>wR</i> 2 = 0.2242	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1116, <i>wR</i> 2 = 0.2374	
Largest diff. peak and hole	0.528 and -0.287 e.Å ⁻³	

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