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# s-Block metal complexes of a bulky, donor-functionalized allyl ligand

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**Electronic supplementary information – experimental, spectroscopic and analytical details**

**General considerations.** All syntheses were carried out using conventional Schlenk techniques. Solvents were pre-dried over sodium wire before being rigorously dried by refluxing over sodium (hexane) or molten potassium (thf). 1,3-*Bis*(trimethylsilyl)propene was prepared according to a literature procedure[1] and all other reagents were obtained from commercial suppliers. NMR spectra were recorded on a Bruker DRX 400 NMR spectrometer. Crystallographic studies were carried out using an Oxford Diffraction XCaliber 2 instrument (compounds **1** and **3**) and a Bruker AXS Diffractometer (compound **2**). Bruker AXS Diffractometer (compound **2**).

**Synthesis of (*E*)-(4-(tetrahydrofuran-2-yl)but-1-ene-1,3-diyl)bis(trimethylsilane) ($L^1H$).** A solution of tetrahydrofurfuryl tosylate (5.63 g, 22.0 mmol) in thf (30 ml) was added to a freshly prepared solution of 1,3-*bis*(trimethylsilyl)allyl lithium (20.0 mmol) in thf (30 ml) at to -78°C. Warming the reaction to room-temperature and stirring for 48 hours afforded a colourless solution and a white precipitate. The thf solvent was evaporated, replaced with an equal volume of hexane and the mixture filtered (Celite, P3) and the hexane removed in vacuo to afford a pale yellow oil. Distillation under reduced pressure (68-72°C, 12 mmHg) afforded $L^1H$ (3.41 g, 63%) as a colourless oil. Anal. calcd. for $C_{14}H_{30}OSi_2$, C 62.15, H 11.18; found C 61.98, H 11.25 %. $^1$**H NMR** (δ/ppm, 500.13 MHz, $CDCl_3$, 294.3 K, *J*/Hz): 5.98, 0.1H, dt, $^3J$ = 7.7 and 18.4, CH–C<u>H</u>=CHSi minor diastereomer; 0.9H, $^3J$ = 7.7 and 18.4, CH–C<u>H</u>=CHSi major diastereomer; 5.42 (major diastereomer) and 5.40 (minor diastereomer), 2 × dd, 1H, $^3J$ = 18.4 and 18.4, $^4J$ = 0.9 and 0.9; 3.85-3.74, 2 × m, 2H, tetrahydrofurfuryl C<u>H</u>O and C<u>H</u>HO; 3.70-3.63, m, 1H, tetrahydrofurfuryl CH<u>H</u>O; 1.95, m, 1H, tetrahydrofurfuryl C<u>H</u>HCHO; 1.82, m, 2H, tetrahydrofurfuryl C<u>H</u>$_2$CH$_2$O; 1.59, 1H, m, C<u>H</u>–CH=CH; 1.36, m, 1H, tetrahydrofurfuryl CH<u>H</u>CHO. $^{13}$**C NMR** (δ/ppm, 125.76 MHz, $CDCl_3$, 295.8 K): 149.23 and 148.68, <u>C</u>H=CHSi; 127.83 and 127.74, CH=<u>C</u>HSi; 79.71 and 79.63, tetrahydrofurfuryl CHO; 68.64, 68.17 tetrahydrofurfuryl CH$_2$O; 36.16 and 36.07, <u>C</u>H–CH=CHSi; 35.51 and 35.07; tetrahydrofurfuryl <u>C</u>H$_2$CHO; 32.86 and 31.39, <u>C</u>H$_2$CH–CH=; 26.83 and 26.58, tetrahydrofurfuryl <u>C</u>H$_2$CH$_2$O; 0.02, 0.01,

2.42 and -2.47, $Si(CH_3)_3$.

**Synthesis of $[1]_2$.** A mixture of $L^1H$ (0.54 g, 2.0 mmol) and hexane (20 ml) was cooled to -78°C and $^nBuLi$ in hexanes (1.6M, 1.25 ml, 2.0 mmol) was added dropwise. Slowly warming the reaction to room-temperature and stirring for 16 hours afforded a yellow solution and a precipitate. Gently heating the precipitate afforded a yellow solution which, on storage at room-temperature overnight, resulted in the formation of large colourless blocks of $[L^1H]_2$, $[\mathbf{1}]_2$, (0.70 g, 63% based on Li). Anal. calcd. for $C_{14}H_{29}LiOSi_2$, C 60.81, H 10.57; found C 60.27, H 10.25 %. $^{13}$**C NMR** (δ/ppm, 100.65 MHz, benzene-$d_6$, 295.8 K): 151.20, central allyl CH; 139.45, central allyl CH; 134.80, allyl C; 89.27, tetrahydrofufuryl CH; 82.33, allyl C; 80.36, tetrahydrofufuryl CH; 68.64, tetrahydrofurfuryl $CH_2O$; 57.90, terminal allyl CH; 37.69, 35.73, 31.87, 31.45, 26.97, 26.05, 21.61, tetrahydrofurfuryl $CH_2$; 3.23, 1.70, 0.03, -1.25, Si(CH3)3. $^1$**H NMR** (δ/ppm, 400.23 MHz, benzene-$d_6$, 294.3 K, *J*/Hz, non-integer integrals are due to presence of two diastereomers): 7.18, d, integration not possible due to overlap with solvent peak, central allyl CH; 6.00, br m, 1.3H, central allyl CH; 4.10, br m, 0.7H, tetrahydrofufuryl CH; 3.97, br quintet, 1.3H, tetrahydrofurfuryl CH; 3.79, br q, 1.3H, tetrahydrofurfuryl $CH_2O$; 3.59, br m, 2H, tetrahydrofurfuryl $CH_2O$; 3.38, br m, 0.7H, tetrahydrofurfuryl $CH_2O$; 3.15, br d, 0.7H, $^3J$ = 16, terminal allyl CH; 2.64, br m, 1H, tetrahydrofurfuryl SiC–C$\underline{H}_2$–CH; 2.49, br m, 3H, tetrahydrofurfuryl SiC–C$\underline{H}_2$–CH; 2.27, br dd, 0.7H, $^3J$ = 14.6, $^nJ$ = 2.3, 0.7H, terminal allyl CH; 1.55, v br m, 8H, tetrahydrofurfuryl $(C\underline{H}_2)_2$–$CH_2$–O; 0.43, 0.33, 0.16, 0.00, 4 × s, 36H, $Si(CH_3)_3$.

**Synthesis of $[\{2(thf)\}_2]_\infty$.** A solution of $[\mathbf{1}]_2$ was freshly prepared from $L^1H$ (0.55 g, 2.02 mmol) and $^nBuLi$ (1.6 M, 1.27 ml, 2.03 mmol) and was added drop-wise to a stirred suspension of $KO^tBu$ (0.27 g, 2.02 mmol) in hexane (20 ml) at room-temperature. A viscous red-brown solution was obtained on stirring for 8 hours and evaporation of the hexane solvent afforded a powder, which upon dissolution in thf (2 ml) and storage at +5°C for 2 days afforded amber crystals of $[\{\mathbf{2}(thf)\}_2]_\infty$ (0.26 g, 34% isolated

yield). Anal. calcd. for $C_{18}H_{37}KO_2Si_2$, C 56.78, H 9.79; found C, 55.90, H 9.59 %. $^{13}$**C NMR** (δ/ppm, 100.65 MHz, benzene-$d_6$, 295.8 K): 139.75, allyl C: 138.69, central allyl CH; 136.78, central allyl CH; 135.48, allyl C; 79.94, 79.79, tetrahydrofurfuryl CH; 68.18, thf $CH_2O$; 67.93, 67.89, tetrahydrofurfuryl $CH_2O$; 38.82, terminal allyl CH; 36.08, 35.96, C<u>C</u>$H_2$CHO; 32.07, 32.02, tetrahydrofurfuryl CH<u>C</u>$H_2CH_2CH_2O$; 26.27, 26.12, CH$CH_2$<u>C</u>$H_2CH_2O$; 21.40, thf <u>C</u>$H_2CH_2O$; 15.36, terminal allyl CH; 3.21, 1.88, 0.03, -1.26, $Si(CH_3)_3$. $^1$**H NMR** (δ/ppm, 400.23 MHz, benzene-$d_6$, 294.3 K, *J*/Hz, non-integer integrals are due to presence of two diastereomers): 6.83, br d, 0.3H, $^3J$ = 16.1, central allyl CH; 6.01, m, 1.3H, central allyl CH; 3.84, br m, 3H, tetrahydrofurfuryl CH and $CH_2O$; 3.56, br m, 4H, thf $CH_2O$; 2.78, br d, 0.3H, $^3J$ = 16.1, terminal allyl CH; 2.56, br m, 2H, tetrahydrofurfuryl SiC–C<u>H</u>$_2$–CH; 2.48 and 2.45, 2 × overlapping d, 2H, terminal allyl CH; 1.77-1.15, very br m, accurate integration not possible, tetrahydrofurfuryl CHC<u>H</u>$_2$C<u>H</u>$_2$; 1.41, br m, 4H, thf C<u>H</u>$_2$$CH_2O$; 0.33, 0.29, 0.20, 0.00, 4 × s, 36H, $Si(CH_3)_3$.

**Synthesis of [3].** A mixture of $Bu_2Mg$ (1.0 M, 1.02 ml, 1.02 mmol) and $L^1H$ (0.55 g, 2.03 mmol) in hexane (20 ml) was heated under reflux for 16 hours and cooled to room-temperature. The solvent was evaporated *in vacuo* until approximately 2 ml remained, affording a faintly cloudy solution, which was heated briefly to reflux using an oil bath and cooled very slowly to room-temperature in the oil to result in the formation of colourless crystals of [**3**] (0.09 g, 15 % isolated yield). Anal. calcd. for $C_{28}H_{58}MgO_2Si_4$, C 60.81, H 10.57; found C 60.27, H 10.25 %. $^{13}$**C NMR** (δ/ppm, 100.65 MHz, dmso-$d_6$, 295.8 K): 149.33, allyl CH; 148.96, allyl C; 138.49, allyl CH; 134.65, allyl C; 126.34 allyl CH; 79.10 and 78.24, tetrahydrofurfuryl CH; 68.43, 68.03, tetrahydrofurfuryl $CH_2O$; 35.24, allyl CH; 35.37, 34.96, C<u>C</u>$H_2$CHO; 31.98, 31.36, tetrahydrofurfuryl CH<u>C</u>$H_2CH_2CH_2O$; 25.93, 25.69, CH$CH_2$<u>C</u>$H_2CH_2O$; 0.02, -0.25, -1.14, -2.80, $Si(CH_3)_3$. $^1$**H NMR** (δ/ppm, 400.23 MHz, dmso-$d_6$, 294.3 K, *J*/Hz): 3.71, 3.63, 3.53, v br m, 6H, tetrahydrofurfuryl CH and $CH_2O$; 2.23, br d, $^3J$ = 6.7, =CH–C<u>H</u>Si; 1.73, 1.57, 1.35, v br m, 8H, tetrahydrofurfuryl CHC<u>H</u>$_2$C<u>H</u>$_2$$CH_2O$; 0.00, -0.01, -0.05, -0.09, 4 ×

s, 36H, $Si(CH_3)_3$.

## Crystallographic details for compounds $[\mathbf{1}]_2$, $[\{\mathbf{2}(thf)\}_2]_\infty$ and [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 Oxford Diffraction XCaliber 2 instrument (compounds **1** and **3**) or a Bruker AXS Diffractometer (compound **2**) using monochromated Mo Kα radiation (λ = 0.71073 Å). Structures were solved using direct methods and refined on $F^2$ using SHELXTL-97.[2] All non-hydrogen atoms were refined anisotropically for all structures. For $[\mathbf{1}]_2$, $[\{\mathbf{2}(thf)\}_2]_\infty$ and [**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. CCDC reference codes 678934, 678935 and 678936 contain the crystallographic data for for compounds $[\mathbf{1}]_2$, $[\{\mathbf{2}(thf)\}_2]_\infty$ and [**3**], respectively, in .cif format. Data can be obtained free of charge *via* the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html or from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336 033; e-mail deposit@ccdc.cam.ac.uk.

**Table S1 – Crystal data and structure refinement for $[1]_2$**

| | | |
|---|---|---|
| Empirical formula | $C_{28}H_{58}Li_2O_2Si_4$ | |
| Formula weight | 552.98 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | *P*-1 | |
| Unit cell dimensions | $a$ = 10.1331(8) Å | $\alpha$ = 77.614(7)°. |
| | $b$ = 10.8060(9) Å | $\beta$ = 89.490(6)°. |
| | $c$ = 18.5116(14) Å | $\gamma$ = 65.099(8)°. |
| Volume | 1788.2(2) $Å^3$ | |
| *Z* | 2 | |
| Density (calculated) | 1.027 $Mg/m^3$ | |
| Absorption coefficient | 0.187 $mm^{-1}$ | |
| *F*(000) | 608 | |
| Crystal size | 0.70 x 0.70 x 0.50 $mm^3$ | |
| Theta range for data collection | 3.82 to 26.37°. | |
| Index ranges | $-12<=h<=12$, $-13<=k<=13$, $-23<=l<=21$ | |
| Reflections collected | 14428 | |
| Independent reflections | 7253 [*R*(int) = 0.0369] | |
| Completeness to theta = 26.37° | 99.1 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9125 and 0.8805 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 7253 / 12 / 373 | |
| Goodness-of-fit on $F^2$ | 1.040 | |
| Final *R* indices [*I*>2sigma(*I*)] | *R*1 = 0.0539, *wR*2 = 0.1370 | |
| *R* indices (all data) | *R*1 = 0.0887, *wR*2 = 0.1659 | |
| Largest diff. peak and hole | 0.624 and -0.460 $e.Å^{-3}$ | |

**Table S2 – Crystal data and structure refinement for [{2(thf)}$_2$]**

| | | |
|---|---|---|
| Empirical formula | $C_{36}H_{74}K_2O_4Si_4$ | |
| Formula weight | 761.51 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1$ | |
| Unit cell dimensions | $a$ = 10.9205(18) Å | $\alpha$ = 90°. |
| | $b$ = 18.729(3) Å | $\beta$ = 97.988(3)°. |
| | $c$ = 11.2860(18) Å | $\gamma$ = 90°. |
| Volume | 2285.9(6) Å$^3$ | |
| $Z$ | 2 | |
| Density (calculated) | 1.106 Mg/m$^3$ | |
| Absorption coefficient | 0.344 mm$^{-1}$ | |
| $F$(000) | 832 | |
| Crystal size | 1.00 x 0.20 x 0.20 mm$^3$ | |
| Theta range for data collection | 3.00 to 26.37°. | |
| Index ranges | -13<=$h$<=13, -20<=$k$<=23, -14<=$l$<=14 | |
| Reflections collected | 13190 | |
| Independent reflections | 7188 [$R$(int) = 0.0279] | |
| Completeness to theta = 26.37° | 99.1 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9344 and 0.7249 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 7188 / 81 / 471 | |
| Goodness-of-fit on $F^2$ | 1.042 | |
| Final $R$ indices [$I$>2sigma($I$)] | $R$1 = 0.0467, $wR$2 = 0.1135 | |
| $R$ indices (all data) | $R$1 = 0.0557, $wR$2 = 0.1187 | |
| Absolute structure parameter | 0.05(4) | |
| Largest diff. peak and hole | 0.614 and -0.511 e.Å$^{-3}$ | |

**Table S3 – Crystal data and structure refinement for [3]**

| | | |
|---|---|---|
| Empirical formula | $C_{28}H_{58}MgO_2Si_4$ | |
| Formula weight | 563.41 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71069 Å | |
| Crystal system | Orthorhombic | |
| Space group | *Pccn* | |
| Unit cell dimensions | $a$ = 12.0480(10) Å | $\alpha$ = 90°. |
| | $b$ = 15.1550(10) Å | $\beta$ = 90°. |
| | $c$ = 19.4280(10) Å | $\gamma$ = 90°. |
| Volume | 3547.3(4) $Å^3$ | |
| $Z$ | 4 | |
| Density (calculated) | 1.055 $Mg/m^3$ | |
| Absorption coefficient | 0.206 $mm^{-1}$ | |
| $F$(000) | 1240 | |
| Crystal size | 0.8 x 0.1 x 0.1 $mm^3$ | |
| Theta range for data collection | 4.20 to 25.02°. | |
| Index ranges | $-14<=h<=13$, $-17<=k<=17$, $-23<=l<=14$ | |
| Reflections collected | 11765 | |
| Independent reflections | 3120 [$R$(int) = 0.1090] | |
| Completeness to theta = 25.02° | 99.4 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9797 and 0.8524 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3120 / 0 / 171 | |
| Goodness-of-fit on $F^2$ | 0.925 | |
| Final $R$ indices [$I$>2sigma($I$)] | $R1$ = 0.0572, $wR2$ = 0.0859 | |
| $R$ indices (all data) | $R1$ = 0.1348, $wR2$ = 0.1075 | |
| Largest diff. peak and hole | 0.353 and -0.294 $e.Å^{-3}$ | |

## References

1. Fernández-Galán, R.; Hitchcock, P. B.; Lappert, M. F.; Antiñolo, A.; Rodríguez, A. M. *J. Chem. Soc., Dalton Trans.*, 2000, 1743.
2. G. M. Sheldrick, SHELXTL Version 6.10, Bruker AXS Inc, Madison, Wisconsin, 1997.