Supplementary Information (SI) for Dalton Transactions.

Supplementary Information for

Alkylzinc-Mediated Transmetallation of a Calcium Hydride

Kyle G. Pearce,* Mary F. Mahon and Michael S. Hill

Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY

Synthetic Details

NMR Spectra

Synthetic Details

General Considerations

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of argon. NMR experiments were conducted in J-Young's NMR tubes and prepared in a glovebox. NMR spectra were recorded on a Bruker BioSpin GmbH spectrometer operating at 400.13 MHz (^{1}H) and 100.62 MHz (^{13}C). Elemental analyses were performed at Elemental Microanalysis Ltd., Okehampton, Devon, UK or by the Elemental Analysis Services Team at London Metropolitan University. Solvents were dried by passage through a commercially available solvent purification system and stored under argon in ampoules over 4 Å molecular sieves. C_6D_6 and C_7D_8 were purchased from Merck, dried over potassium, distilled and stored over molecular sieves. ZnR_2 (R = Me, Et) were purchased from Merck as a standard solution, transferred to a J-Young's ampoule and used without further purification. $[(BDI)CaH]_2$ (BDI = HC{(Me)CN-2,6-*i*-$Pr_2C_6H_3$}$_2$),[1] [(BDI)Ca(H)3,5-$^tBu_2$PhCa(BDI)],[2] and Zn^{i}Pr$_2$ were synthesised according to literature procedures.[3]

Note: Although these compounds circumvent the use of toxic organomercurial compounds, they are still air-sensitive and require manipulation under an inert atmosphere, though they are not pyrophoric.

Reaction Between $[(BDI)CaH]_2$ and $ZnEt_2$

$ZnEt_2$ (1.0 M in heptane, 32.6 µl, 0.033 mmol) was added to a J. Young's NMR tube containing a C_7D_8 (ca. 0.6 cm^3) solution of $[(BDI)CaH]_2$ (15 mg, 0.016 mmol). The reaction was monitored over 16 hours, observing the formation and consumption of **$[(BDI)Ca(\mu\text{-}CH_2CH_3)_2Zn(\mu\text{-}H)]_2$ (6)** and $[(BDI)CaEt]_2$. After 16 hours [(BDI)ZnEt] was exclusively formed spectroscopically, alongside a small amount of precipitate in the NMR tube, assumed to be $[Ca(H)Et]_\infty$. The reaction mixture was decanted away from the precipitate and concentrated under reduced pressure to afford [(BDI)ZnEt] as a colourless solid. Yield: 13.7 mg, 86%.

This reaction can alternatively be performed from an isolated sample of **$[(BDI)Ca(\mu\text{-}CH_2CH_3)_2Zn(\mu\text{-}H)]_2$**, though this leads to a much slower reaction, taking a week to complete (**Figure S1**). The formation of $[(BDI)CaEt]_2$ is easily observed, though again, ultimately results in the exclusive formation of (BDI)ZnEt (**Figure S2**).

The spectroscopic signatures of $[(BDI)CaEt]_2$ and [(BDI)ZnEt] are consistent with the literature.[1,4]

Synthesis of $[(BDI)Ca(\mu\text{-}CH_2CH_3)_2Zn(\mu\text{-}H)]_2$ (6)

$[(BDI)CaH]_2$ (30 mg, 0.033 mmol) and $ZnEt_2$ (1.0 M in hexane, 63.2 µl, 0.065 mmol) were introduced into a vial and dissolved in toluene (ca. 1 cm^3). Once all solids were dissolved, the reaction vial was placed in the freezer (–35 °C), affording colourless crystals after 16 hours. The supernatant was decanted, and the colourless crystals were washed with cold hexane (1 cm^3). The crystals were crushed and dried *in vacuo*. Yield: 35 mg, 92 %.

^{1}H NMR (C_7D_8): δ = 7.13 (s, Ar-H, 3H), 4.79 (s, $\underline{H}$CCN, 1H), 3.26 (hept, $\underline{H}C(CH_3)_2$, $^3J_{HH}$ = 6.97 Hz, 4H), 3.06 (s, Zn-H, 1H), 1.66 (s, NCC$\underline{H}_3$, 6H), 1.25 (d, HC(C$\underline{H}_3$)$_2$, $^3J_{HH}$ = 6.80 Hz, 12 H), 1.21 (d, HC(C$\underline{H}_3$)$_2$, $^3J_{HH}$ = 6.80 Hz, 12 H), 1.06 (t, Zn(μ-CH$_2$C$\underline{H}_3$), $^3J_{HH}$ = 7.97 Hz, 6H), –0.11 (q, Zn(μ-C$\underline{H}_2$CH$_3$), $^3J_{HH}$ = 7.97 Hz, 4H).

^{13}C{^{1}H} NMR (C_7D_8): δ = 166.4 (N$\underline{C}$CH$_3$), 145.7 (*i*-Ar-C), 141.63 (Ar-C), 123.9 (Ar-C), 94.5 (H$\underline{C}$CN), 28.6 (H$\underline{C}$(CH$_3$)$_2$), 24.9 (HC($\underline{C}$H$_3$)$_2$), 24.8 (HC($\underline{C}$H$_3$)$_2$), 24.6 (NC$\underline{C}$H$_3$), 13.6 (Zn(μ-CH$_2$$\underline{C}H_3$), 7.6 (Zn(μ-$\underline{C}H_2CH_3$).

Synthesis of [(BDI)Ca(μ-CH$_2$(CH$_3$)$_2$)$_2$Zn(μ-H)]$_2$ (7)

[(BDI)CaH]$_2$ (62.8 mg, 0.07 mmol) and Zn^{i}Pr$_2$ (20.7 mg, 0.14 mmol) were introduced into a vial and dissolved in toluene (ca. 1 cm^3). Immediately after all reagents were dissolved colourless crystals of **7** formed. Yield: 77.7 mg, 91 %.

The identification of **7** was confirmed by unit cell screening multiple crystals, only ever identifying **7**. Spectroscopic analysis was impeded by the insoluble nature of **7**, which would not redissolve, even at 40 °C.

Anal. Calc. for $C_{70}H_{112}N_4Zn_2Ca_2$: C, 68.88; H, 9.25; N, 4.59. Found: C, 66.02; H, 8.44; N, 4.04.

Synthesis of [(BDI)Ca(3,5-^{t}Bu$_2$Ph)MeCa(BDI)] (9)

ZnMe$_2$ (1.0 M in heptane, 16.3 μl, 0.016 mmol) was added to a J. Young's NMR tube containing a C_7D_8 (*ca.* 0.6 cm^3) solution of [(BDI)Ca(H)3,5-^{t}Bu$_2$PhCa(BDI)], (0.033 mmol), resulting in a pale yellow colouration. The reaction mixture was filtered into a vial and placed in the freezer (–35 °C), affording colourless crystals after 16 hours. Yield: 26 mg, 71%.

The crystals were predominantly found to be **9** through multiple screening experiments, however, much like precedent coordinatively unsaturated calcium aryl species, **9** is relatively unstable upon dissolution, observing [LCaMe]$_2$ as the predominant product.

^{1}H NMR (C_7D_8): δ = 4.77 (s, $\underline{H}$CCN, 1H), 3.24 (br s, $\underline{H}$C(CH$_3$)$_2$, 4H), 1.61 (s, NCC$\underline{H}_3$, 6H), 1.44 (s, Ar-C$\underline{H}_3$, 9H), 1.29 (s, Ar-C$\underline{H}_3$, 9H), 1.21 (overlapping, HC(C$\underline{H}_3$)$_2$, 24 H), –1.63 (s, μ-C$\underline{H}_3$, 3H).

NMR Spectra

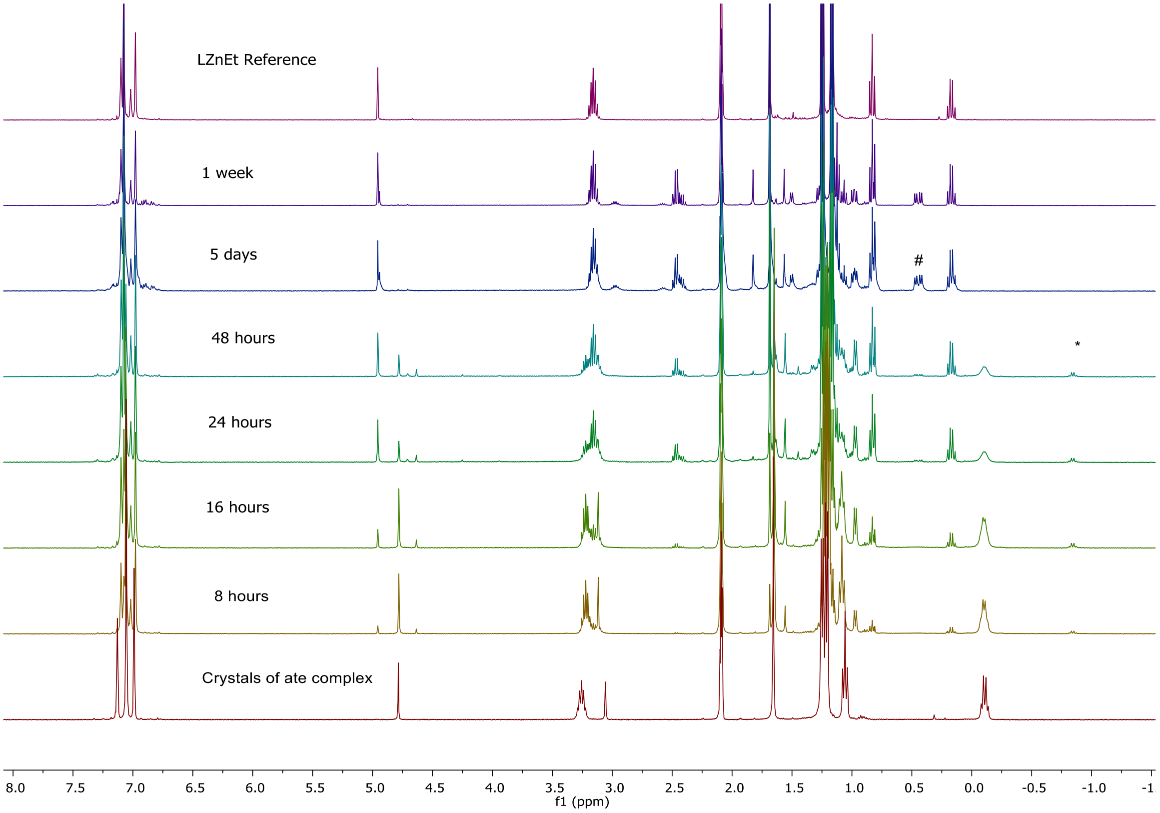

Figure S1. *Overlayed ^{1}H NMR Spectrum (C_7D_8, 298 K, 400.13 MHz) from adding $ZnEt_2$ to $[(BDI)CaH]_2$, demonstrating the formation of $[(BDI)CaEt]_2$ (*) and (BDI)ZnEt.# = Homoleptic $[(BDI)_2Ca]$.*

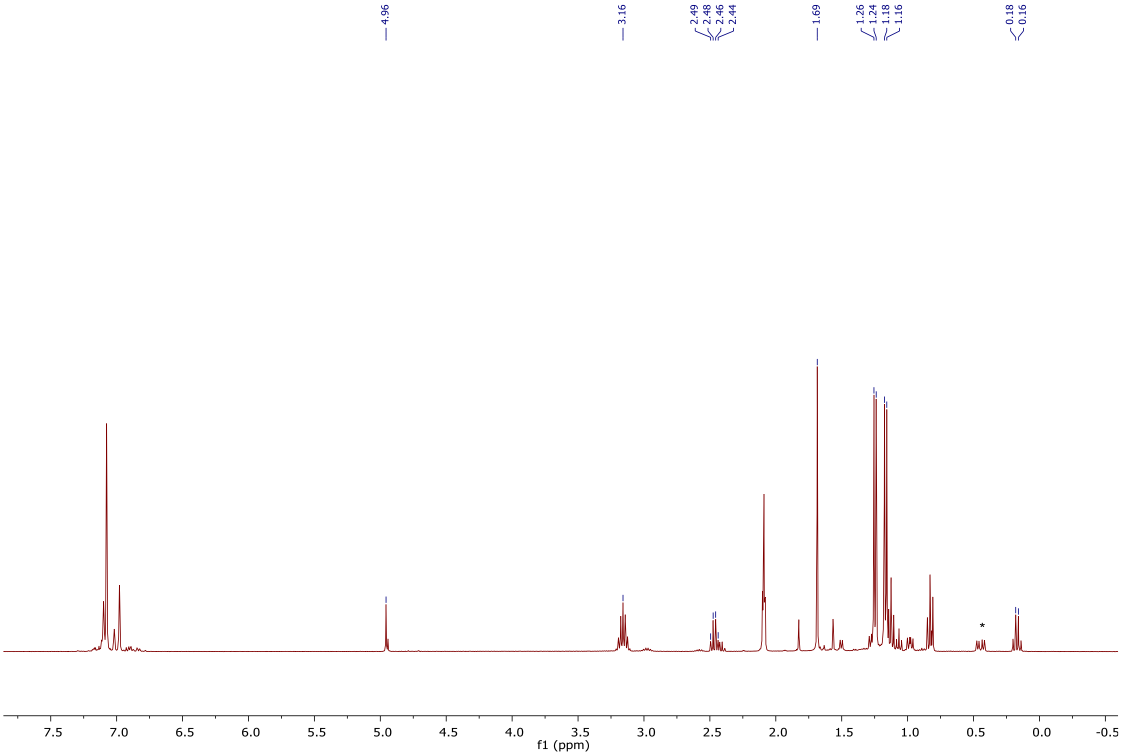

Figure S2. *^{1}H NMR Spectrum (C_7D_8, 298 K, 400.13 MHz) for **[(BDI)ZnEt]** in reaction mixture, formed after 1 week.*

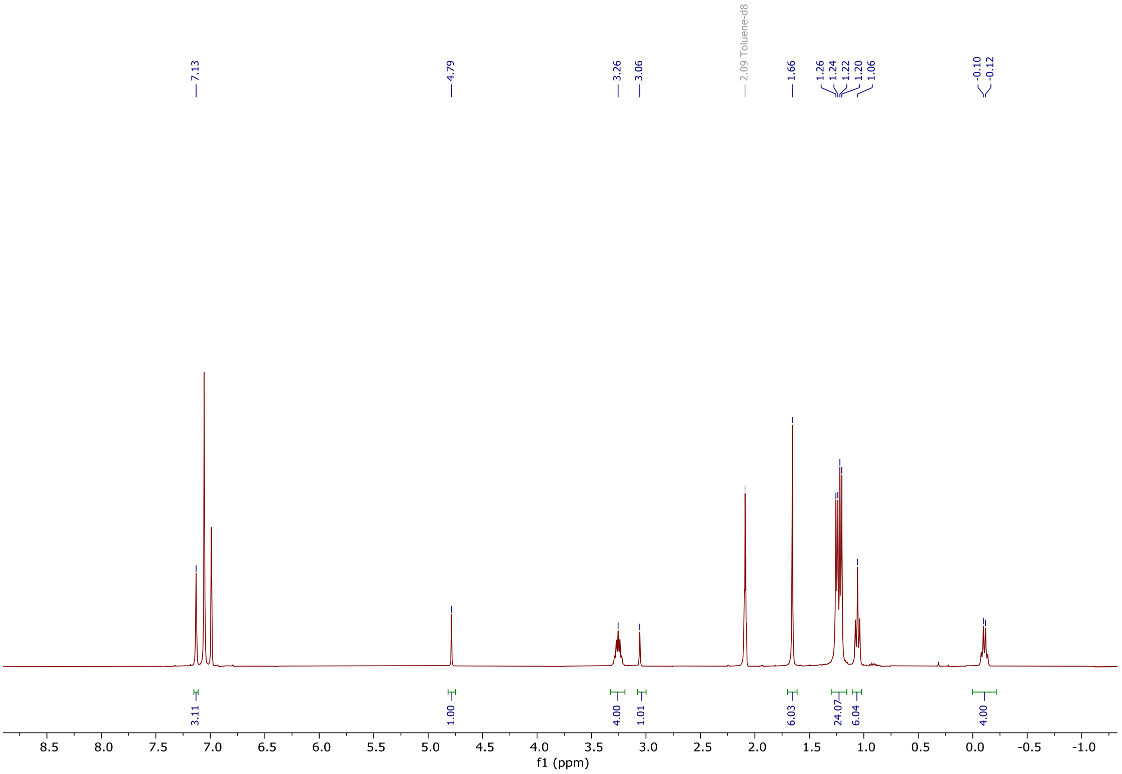

Figure S3. *^{1}H NMR Spectrum (C_7D_8, 253 K, 400.13 MHz) for* ***[(BDI)Ca(μ-CH_2CH_3)$_2$Zn(μ-H)]$_2$ (6)***.

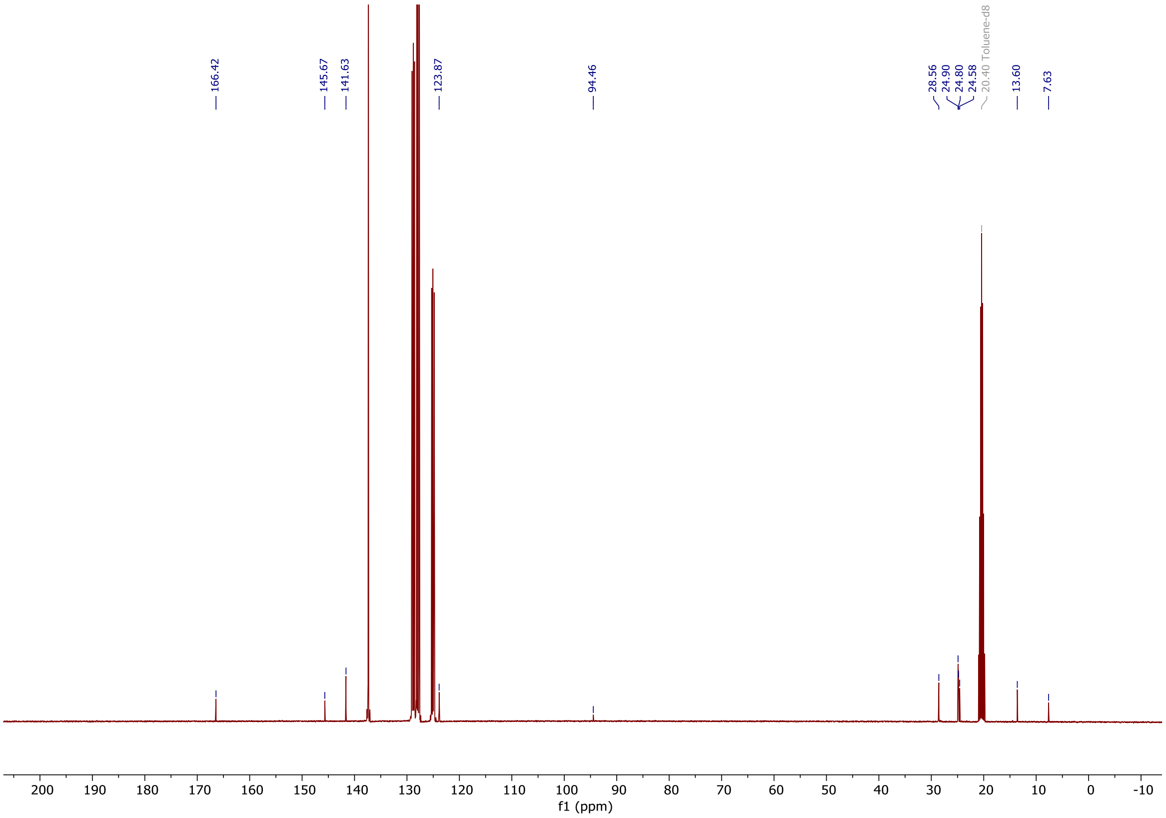

Figure S4. *^{13}C{^{1}H} NMR Spectrum (C_7D_8, 253 K, 100.62 MHz) for* ***[(BDI)Ca(μ-CH_2CH_3)$_2$Zn(μ-H)]$_2$ (6)***.

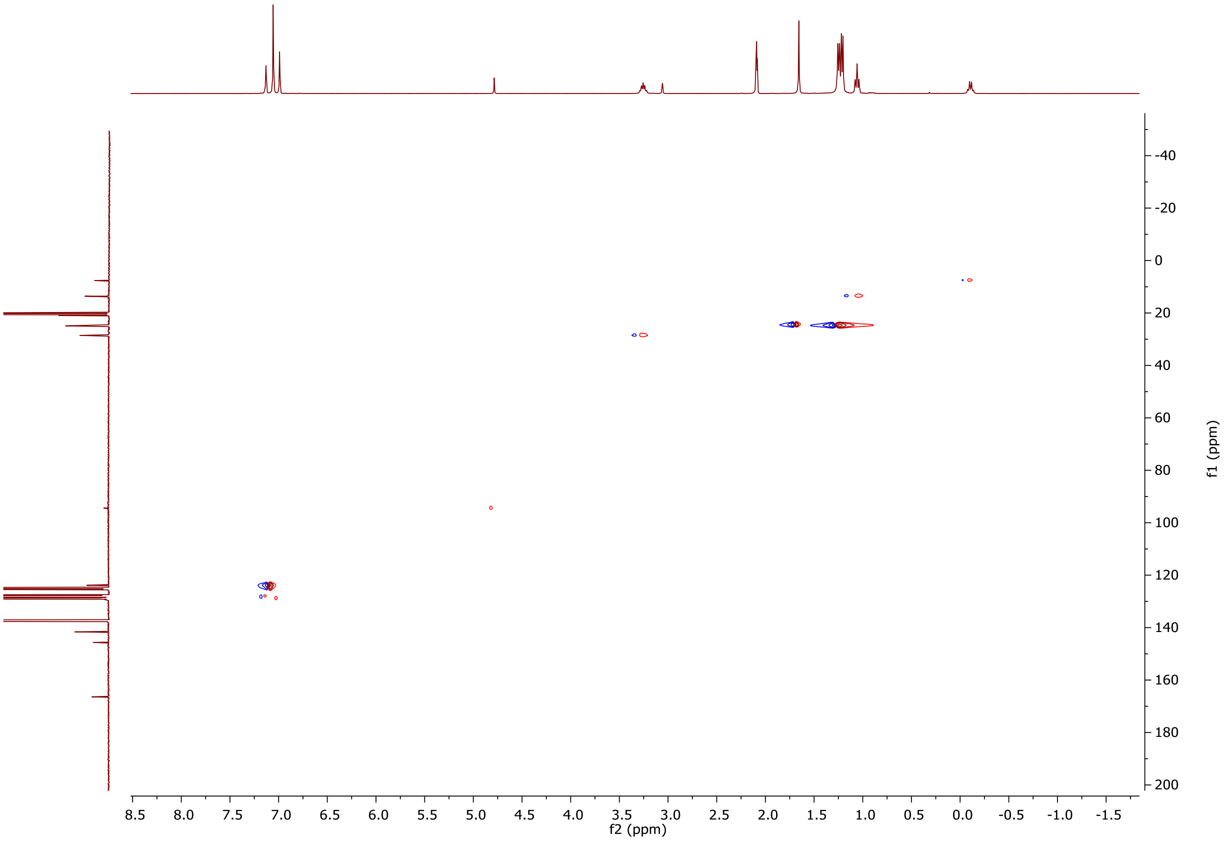

Figure S5. *^{1}H-^{13}C HSQC trace (C_7D_8, 253 K, 400.13, 100.62 MHz) for* ***[(BDI)Ca(μ-CH_2CH_3)$_2$Zn(μ-H)]$_2$ (6)****.*

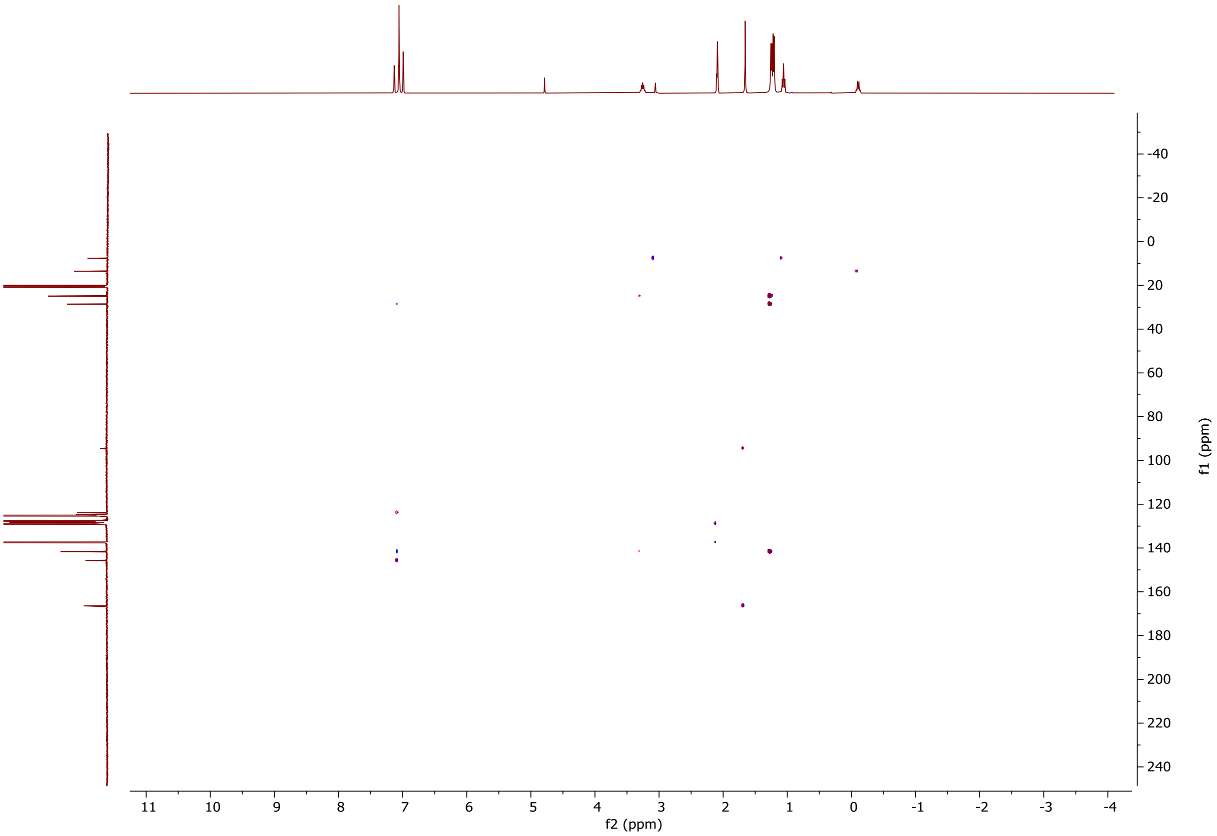

Figure S6. *^{1}H-^{13}C HMBC trace (C_7D_8, 253 K, 400.13, 100.62 MHz) for* ***[(BDI)Ca(μ-CH_2CH_3)$_2$Zn(μ-H)]$_2$ (6)****.*

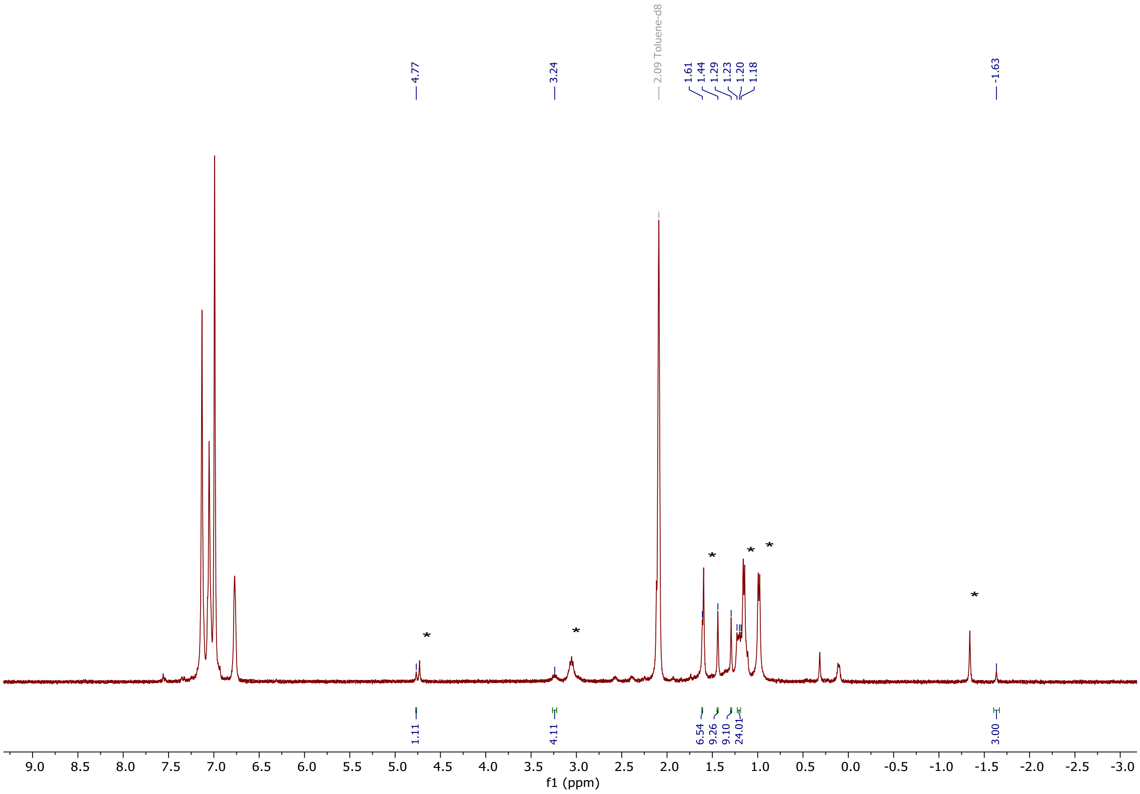

Figure S7. *^{1}H NMR Spectrum (C_7D_8, 253 K, 400.13 MHz) for* ***[(BDI)Ca(3,5-^{t}Bu$_2$Ph)MeCa(BDI)]*** *(**9**).* = [(BDI)CaMe]$_2$*

Crystallographic Data

Single Crystal X-ray diffraction data for compounds **6** and **9** were collected on an Agilent SuperNova EosS2 diffractometer using Cu-Kα (1.54184 Å) radiation, whilst compound **7** was collected on an XtaLAB Synergy, Dualflex, HyPix-Arc 100 diffractometer using Cu-Kα (1.54184 Å) radiation. In each case, the crystals were maintained at 150 K during data collection. Using Olex2,[5] the structures were solved with the olex2.solve[6] structure solution program or ShelXT and refined with the ShelXL[7] refinement package using Least−Squares minimisation.

The asymmetric unit in **6** equates to half of a dimer. The remainder arises by virtue of crystallographic inversion symmetry. H1 was located and refined without restraints. The hydrogens attached to C30, C32 and C33 were also located, and each refined at a distance of 0.98 Å from the relevant parent atom.

For compound **7**, the asymmetric unit equates to half of a dimer molecule and one molecule of toluene. The dimer is generated as a result of crystallographic inversion symmetry. H1 was located and refined freely and although all other hydrogens atoms were included at calculated positions, the U_{iso} values for those that interact with Ca1 were refined without restraints.

The asymmetric unit in **9** was noted to contain one molecule of the calcium complex and two regions of solvent. The tertiary-butyl methyl groups, in the main feature and attached to C41, were treated for 50:50 disorder while the hydrogens attached to C30 were located and refined at a distance of 0.98 Å from the parent atom.

The first of the solvent moieties presented as half of a toluene, straddling an inversion centre. This necessarily means that the intrinsic methyl functionality bears 50% site-occupancy. The electron density pertaining to the second solvent region equates to a complete solvent moiety, with half site-occupancy. There was considerable smearing of the associated electron-density and disorder modelling (33:17 ratio) ensued. The phenyl rings in each fractional occupancy component were refined as rigid hexagons. Indeed, distance and ADP restraints were employed, on merit, in disordered regions to assist convergence.

Crystallographic data for all compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 2430071-2430073 for **6**, **7** and **9**, respectively. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033], e-mail: deposit@ccdc.cam.ac.uk.

Table S1. *Crystal Data and Structure Refinement for Compounds* ***6***, ***7*** *and* ***9***.

Identification code	s24msh44 (**6**)	y24msh02 (**7**)	s24msh20 (**9**)
Empirical formula	$C_{66}H_{104}Ca_2N_4Zn_2$	$C_{84}H_{128}Ca_2N_4Zn_2$	$C_{80}H_{114}Ca_2N_4$
Formula weight	1164.43	1404.80	1211.91
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	P-1	$P2_1/n$
a/ Å	12.5967(1)	11.3098(3)	14.7549(1)
b/ Å	16.0732(1)	12.3970(2)	21.8797(2)
c/ Å	17.2203(2)	14.7801(4)	23.3417(2)
α/ °	90	79.833(2)	90
β/ °	109.586(1)	83.380(2)	96.525(1)
γ/ °	90	79.400(2)	90
U/ Å^3	3284.85(5)	1997.58(8)	7486.65(11)
Z	2	1	4
ρ_{calc}/ g cm^{-3}	1.177	1.168	1.075
μ/ mm^{-1}	2.549	2.178	1.633
F(000)	1256.0	760.0	2648.0
Crystal size/ mm^3	0.362 × 0.109 × 0.058	0.276 × 0.072 × 0.052	0.249 × 0.171 × 0.085
2θ range for data collection/°	7.614 to 146.644	6.098 to 162.214	6.758 to 146.758
Index ranges	$-14 \leq h \leq 15$ $-19 \leq k \leq 19$ $-21 \leq l \leq 21$	$-13 \leq h \leq 14$ $-15 \leq k \leq 15$ $-18 \leq l \leq 18$	$-18 \leq h \leq 18$ $-21 \leq k \leq 27$ $-28 \leq l \leq 28$
Reflections collected	41588	23719	64762
Independent reflections, R_{int}	6585, 0.0303	8418, 0.0296	14829, 0.0554,
Data/restraints/parameters	6585/7/377	8418/43/431	14829/264/933
Goodness–of–fit on F^2	1.042	1.087	1.045
Final R1, wR2 [I>=2σ(I)]	0.0259, 0.0696	0.0405, 0.1080	0.0478, 0.1304
Final R1, wR2 [all data]	0.0276, 0.0710	0.0476, 0.1118	0.0521, 0.1355
Largest diff. peak/hole/ e Å^{-3}	0.31/-0.34	0.39/-0.70	0.34/-0.57

References

1. A. S. S. Wilson, M. S. Hill, M. F. Mahon, C. Dinoi, L. Maron, *Science*, 2017, **358**, 1168-1171.
2. K. G. Pearce, C. Dinoi, R. J. Shawmm, L. Maron, M. F. Mahon and M. S. Hill, *Adv. Sci.*, 2023, **10**, 2304765.
3. R. A. Rajagopalan, A. Jayaraman and B. T. Sterenberg, *J. Organomet. Chem.*, 2014, **761**, 84-92.
4. M. R. Crimmin, M. S. Hill, P. B. Hitchcock and M. F. Mahon, *New. J. Chem.*, 2010, **34**, 1572-1578.
5. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339-341.
6. G. M. Sheldrick, *Acta Cryst*. 2015, **A71**, 3-8.
7. G. M. Sheldrick, *Acta Cryst*. 2015, **C71**, 3-8.