Supplementary Information for

Calcium Formamidinate Derivatives by Hydride Insertion of Carbodiimides

Joshua Dyall, Michael S. Hill,* Mary F. Mahon, Luke Teh and Andrew S. S. Wilson Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK

- Figures S1 S11: ¹H and ¹³C{¹H} NMR spectra for compounds 3 7.
- Details of the single crystal X-ray diffraction analysis of compounds 3, 4, 6 and 7.



Figure S1: ¹H (500 MHz, 298 K) NMR spectrum of [(BDI)Ca({N(Dipp)}₂CH)] (3)





Figure S2: ¹³C{¹H} (126 MHz, 298 K) NMR spectrum of [(BDI)Ca({N(Dipp)}₂CH)] (3).



Figure S3: ¹H (500 MHz, 298 K) NMR spectrum of [(BDI)Ca({N(*t*Bu)}₂CH)] (4).



Figure S4: ${}^{13}C{}^{1}H{}$ (126 MHz, 298 K) NMR spectrum of [(BDI)Ca({N(tBu)}_2CH)] (4).







Figure S7: ¹H (500 MHz, 298 K) NMR spectrum of $[(BDI)Ca(\{N(iPr)\}_2CH)(iPrN=C=NiPr)]$ (6).





(7).



Figure S11: Stacked plot of (a) ¹H NMR spectrum after addition of *i*-PrN=C=N*i*Pr to compound **7**; (b) is compound **7**; (c) compound **6** ¹H (500 MHz, 298 K, C₆D₆).

Single Crystal X-ray Diffraction analysis: Single Crystal X-ray diffraction data for compounds **3**, **4**, **6** and **7** were collected using Cu*K* α ($\lambda = 1.54184$ Å) on a SuperNova, Dual Cu at zero, EosS2 diffractometer. The crystals were kept at 150(2) K during data collections. The structures were solved using the charge-flipping routine available in Olex2³ and refined (via Olex2) with the ShelXL⁴ refinement programme. C34 and C35 exhibited 50:50 disorder in the structure of compound **3**. This lent itself to being modelled and subsequent refinement proceeded without event, subject to restraining the distances from the fractional occupancy carbon atoms to being equidistant from C33. The hydrogen atoms attached to C10 and C22 were readily located also, and refined subject to being at a distance of 0.98Å from the relevant parent atoms.

In addition to one molecule of the calcium complex, the asymmetric unit of compound **4** contains one half of a molecule of hexane. The latter is proximate to a crystallographic inversion centre which serves to generate the remainder of the solvent. The methyl groups attached to C30 were modelled to take account of 70:30 disorder.

N6, C40, C41 and C42 were disordered over 2 sites in a 70:30 ratio in the structure of compound **6**. Comparative C-N and C-C distances were restrained to being similar in both of the disordered components, and ADP restraints were also included for fractional occupancy atoms.

The asymmetric unit in compound **7** comprises 2 calcium dimers, 2 molecules of hexane and 1 molecule of benzene. The bridging hydrides in the former were located and refined without restraints. Substantial smearing of the electron density in the solvent region ultimately resulted in abandoning heavily restrained disorder models in favour of using the solvent mask algorithm available in Olex2. Allowance for the solvent has, however, been made in the formula as presented.

Compound	3	4	6	7
Empirical formula	$C_{54}H_{76}CaN_4$	$C_{41}H_{67}CaN_4$	$C_{43}H_{70}CaN_6$	$C_{164}H_{230}Ca_4N_{12}$
Formula weight	821.26	656.06	711.13	2529.91
Temperature/K	150.01(10)	150.01(10)	150.00(10)	150.01(10)
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_{1}/c$	P-1	$P2_1$	P-1
a/Å	13.41197(8)	11.5170(2)	12.6228(2)	16.8032(2)
b/Å	18.53678(12)	11.5899(3)	12.7912(1)	19.8606(2)
c/Å	20.14152(12)	17.8355(4)	13.6488(2)	23.8983(3)
$\alpha/^{\circ}$	90	79.330(2)	90	78.865(1)
$\beta/^{\circ}$	94.0491(6)	77.278(2)	98.842(1)	85.508(1)
<i>γ</i> /°	90	61.374(2)	90	89.736(1)
Volume/Å ³	4994.98(5)	2029.56(9)	2177.56(5)	7800.76(16)
Ζ	4	2	2	2
$\rho_{\rm calc}{\rm g/cm^3}$	1.092	1.074	1.085	1.077
μ/mm^{-1}	1.353	1.549	1.492	1.594
F(000)	1792.0	722.0	780.0	2756.0
Crystal size/mm ³	$0.325 \times 0.301 \times 0.18$	$0.249\times0.161\times0.075$	$0.293\times0.195\times0.126$	$0.356 \times 0.306 \times 0.269$
20 range for data collection/°	6.488 to 146.922	8.73 to 146.596	6.554 to 146.936	5.276 to 146.63
Reflections collected	74331	23385	25390	111594
Independent reflections, $R_{\rm int}$	10042, 0.0343	8100, 0.0344	6816, 0.0463	30981, 0.0516
Data/restraints/parameters	10042/12/596	8100/0/462	6816/9/483	30981/0/1510
Goodness-of-fit on F^2	1.023	1.021	1.022	1.031
Final R1, wR2 indexes $[I \ge 2\sigma(I)]$	0.0382, 0.0975	0.0436, 0.1155	0.0350, 0.0869	0.0441, 0.1162
Final R1, wR2 indexes [all data]	0.0415, 0.1000	0.0485, 0.1198	0.0372, 0.0887	0.0488, 0.1218
Largest diff. peak/hole / e Å ⁻³	0.31/-0.34	0.68/-0.31	0.21/-0.21	0.27/-0.34

Table S1: Single Crystal X-ray Data Parameters for compounds 3, 4, 6 and 7.

References

- A. P. Dove, V. C. Gibson, P. Hormnirun, E. L. Marshall, J. A. Segal, A. J. P. White, D. J. Williams, *Dalton. Trans.* 2003, 3088.
- 2 S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem.-Eur. J.*, 2010, **16**, 938.
- 3 L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard, H. Puschmann, *Acta Cryst. A* 2015, **71**, 59-75.
- 4 G. M. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3-8.