Supplementary Material

All reactions were carried out with careful exclusion of water and oxygen with the aid of a Braun Labmaster 100 drybox and/or modified Schlenk line techniques. Toluene and hexane were dried over Vac. Atm. Co. dri-solv solvent purifier system and degassed just prior to use. N',N',N",N"-tetramethyletheylenediamine was refluxed over calcium hydride and vacuum distilled. The starting materials $Ca[N(SiMe_3)_2]_2(thf)_2$,[5] $Ca(CH_2Ph)_2(thf)_4$[10] and $Li(CH_2Ph)tmeda$[11] were prepared according to literature methods. ^1H NMR and ^{13}C NMR spectra were collected on a Bruker DPX-300 spectrometer and referenced to $[D_6]$benzene or $[(CD_3)_4Si]_{external}$. Melting points were obtained in a sealed capillary tube under inert gas, and are uncorrected. IR spectra were obtained as a Nujol mull on a Nicolet IR200 spectrometer. The high reactivity of the compound prevented elemental analysis as decomposition in less than twenty four hours inside a freshly regenerated dry box is observed upon removal of mother liquor.

1: a) Freshly prepared $Li(CH_2Ph)tmeda$ (4 mmol, 0.86 g in 20 mL toluene) was added to $Ca(CH_2Ph)_2(thf)_4$ (2 mmol, 0.44 g in 10 mL toluene) at room temperature. The reaction mixture was stirred overnight and filtered the next day. X-ray quality yellow crystals were obtained after two weeks at -23°C. Yield: 0.59 g (45%).

b) $Ca[N(SiMe_3)]_2]_2(thf)_2$ (5 mmol, 2.50 g) was dissolved in 20 mL toluene and added to the freshly prepared $Li(CH_2Ph)tmeda$ (10 mmol, 2.14 g in 20 mL toluene) at room temperature. The bright orange solution turned dark orange as the reaction progressed overnight. The supernatant was decanted from the oil and placed in -23°C freezer, upon which yellow blocks suited for crystallographic studies were obtained after 2 weeks. Yield: (<10%).

Analytical and crystallographic data obtained from the yellow block crystals obtained from routes a) and b) are identical. M.p. 100 – 103°C (sealed capillary); ^1H NMR (300 MHz, 25°C, C_6D_6; $(CD_3)_4Si$): δ_H = 1.47 (s, 24H, N', N', N", N" – C*H*$_3$), 1.66 (s, 8H, N', N', N", N" – C*H*$_2$), 2.01 (s, 4H, C*H*$_2$Ph 6.14 (m, 4H, *p*-C*H*), 6.58 – 6.60 (m, 8H, *o*-C*H*), 7.01–7.05 (m, 8H, *m*-C*H*). ^{13}C NMR (75 MHz, 25ºC, C_6D_6): δ_C = 39.95 (*C*H$_2$Ph), 45.61 (N', N', N", N" – C*H*$_3$), 56.77 (N', N', N", N" – C*H*$_3$), 109.09 (*p*-*C*H), 117.92 (*o*-*C*H), 130.51 (*m*-*C*H), 157.21 (C_{ipso}). IR (Nujol): ν = 2917 (w), 2843 (w) 2586 (m), 24443 (m), 2386 (m), 2353 (w), 2316 (w), 2263 (w), 2165 (m), 2018 (w), 1952 (w), 1936 (w), 1907 (s), 1793 (s), 1695 (m), 1605 (s), 1454 (s), 1376 (m), 1245 (w), 1094 (w), 1025 (w), 923 (m), 845 (m), 730 (s), 694 (s).

Crystal structure analyses: **1**:$CaLi_2N_4C_{47}H_{68}$, M_r = 743.02 g/mol, tetragonal, a = b = 13.6240(7), c = 28.4840(1) Å, α = β = γ = 90°, V = 5287.0(5) Å^3, T = 100(2) K, space group I-42d (no. 122), Z = 4, μ = 0.142 mm^{-1} ($Mo_{K\alpha}$ radiation); yellow blocks 0.50 x 0.50 x 0.50 mm^3; 1738 independent reflections ($5.10 \leq 2\theta \geq 44.98°$); R_1 = 0.0656 ($I > 2\sigma(I)$), wR_2 = 0.1837 (all data).

The crystal data were collected using a Bruker SMART system with 3-circle goniometer and APEX-CCD detector. The extreme air sensitivity of the crystals required rapid mounting, even with submerging the crystals in highly viscous hydrocarbon oil

(Infinium). Crystal data were collected at 100K. The crystal structure was solved using Direct methods and the refinement by full-matrix least-squares method on F^2.[19] All non-hydrogen atoms were refined anisotropically. Highly disordered toluene solvent was removed from the refinement using "squeeze" as available in the Platon program suite.[20] Crystallographic data (excluding structure factors) for **1** has been deposited with Cambridge Crystallographic Data Center as supplementary publication no. listed as 663415. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax:(+44)1223-336-033; email: deposit@ccdc.cam.ca.uk).

References

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