Supplementary information for:

Catalytic 2,3,4-Hexatriene Formation by Terminal Alkyne Coupling at Calcium

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General Experimental

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of either dinitrogen or argon. NMR experiments were conducted in Youngs tap NMR tubes made up and sealed in a Glovebox. NMR spectra were collected on a Bruker AV-300 spectrometer (^{13}C NMR 75 MHz). ESI-MS were recorded on a Bruker MicroOTOF-Q instrument operating in positive ion mode. Solvents (toluene, benzene, THF, hexane) were dried by distillation from standard drying reagents and stored in ampoules over molecular sieves. C_6D_6 was purchased from Goss Scientific Instruments Ltd. and dried over molten potassium

before distillation under nitrogen and storage over molecular sieves. Compound **1**, **3** and **5** were prepared by literature procedures.[1-3] Ar = 2,6-di-iso-propylphenyl.

*Synthesis of [{ArNC(Me)CHC(Me)NAr}Ca(C≡CCH$_2$OCH$_3$)]$_2$ (**4**):* To a solution of **3** (0.25 g, 0.37 mmol) in toluene (20 mL), under N_2, was added $CH_3OCH_2C{\equiv}CH$ (0.026 g, 30 μL, 0.37 mmol). The reaction mixture was stirred for 2 hours at room temperature and the solvent volume reduced to incipient crystallisation (*ca* 5 mL). Warming to redissolve the solid and storage at 5^{o}C for 2 hours gave pale yellow crystals of compound **4** suitable for X-ray diffraction analysis (0.13 g, 67%) M.p. >250^{o}C (d). Elemental analysis calc. for $C_{66}H_{92}Ca_2N_4O_2$: C,75.24; H, 8.80; N, 5.32. Found C, 75.20; H, 8.86; N, 5.27 . ^{1}H NMR (C_6D_6, 300 MHz, 298K) 1.14 (d, 12H, CH(C*H*$_3$), *J* = 6.5 Hz), 1.21 (d, 12H, CH(C*H*$_3$), *J* = 6.7 Hz), 1.59 (s, 6H, C(C*H*$_3$)), 2.94 (s, 3H, OC*H*$_3$), 3.02 (br. m, 4H, C*H*(CH$_3$)), 3.05 (s, 2H, C*H*$_2$OCH$_3$), 4.61 (s, 1H, C*H*), 7.12-7.16 (m, 6H); ^{13}C NMR (C_6D_6, 75.5 MHz, 298 K) 23.4 (CH(*C*H$_3$)), 24.5 (CH(*C*H$_3$)), 28.4 (*C*H(CH$_3$)), 28.6 (NC(*C*H$_3$)), 57.1 (*C*H$_2$OCH$_3$), 91.0 (*C*H), 94.3 (OC*H*$_3$), 123.4 (*m*-*C*$_6$H$_3$), 123.6 (*p*-*C*$_6$H$_3$), 136.4 (*C*≡CCa), 141.3 (*o*-*C*$_6$H$_3$), 142.8 (C≡*C*Ca), 146.8 (*i*-*C*$_6$H$_3$), 167.6 (*C*N).

*Catalytic synthesis of (E/Z) [(CH$_3$OCH$_2$)HC=C=C=CH(CH$_2$OCH$_3$)], (**2**);* $CH_3C{\equiv}CH$ (0.10g, 1.43 mmol) and [{(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$N$_3$Ca{N(SiMe$_3$)$_2$}(THF)$_2$], compound **5** (0.06g, 0.008 mmol) were dissolved in C_6D_6 and heated to 75^{o}C. Reaction monitoring by ^{1}H NMR spectroscopy indicated *ca.* 91% conversion to compound **2** after 48 hours. Compound **2** was isolated by vaccum transfer from the NMR tube. ^{1}H NMR (C_6D_6, 300 MHz, 298K) 3.21 (s, 3H, OC*H*$_3$), 5.24 (d, 2H, C*H*$_2$OCH$_3$, $^3J_{HH}$ = 5.7 Hz), 6.71 (t, 1H, C*H*, $^3J_{HH}$ = 5.7 Hz); ^{13}C NMR (C_6D_6, 75.5 MHz, 298 K) 55.0

(CH_2OCH_3), 90.9 (OCH_3), 123.4 (=*C*H), 201.8 (=*C*=). ESI-MS (MeOH, 200ºC)**:** positive ion: *m/z*, 141.091 ($[M]^+$ + H) (calc. 141.09).

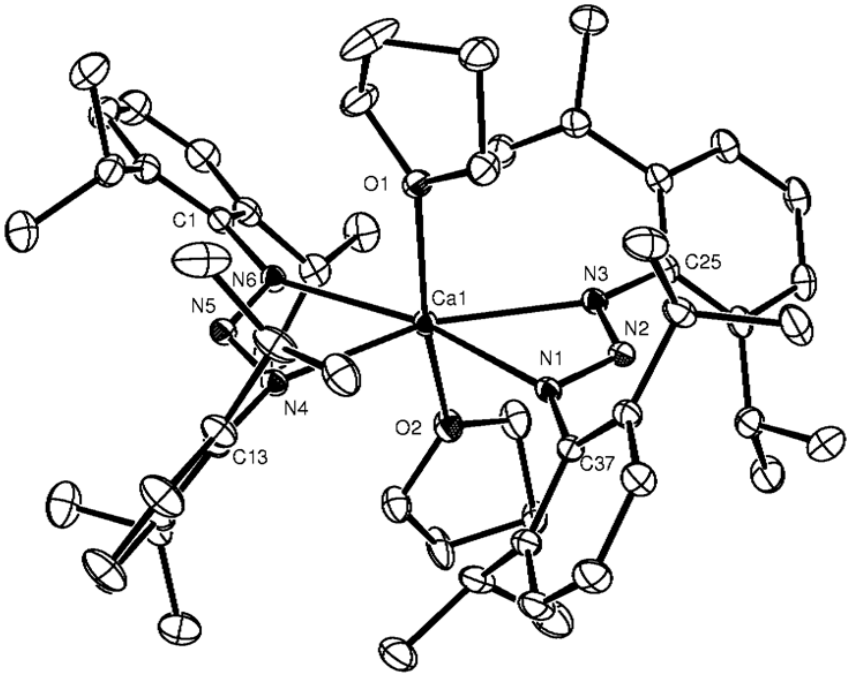
Crystallographic data

Data for **4** were collected at 173(2) K and for **6** at 150(2) K on a Nonius Kappa CCD diffractometer equipped with a low temperature device, using graphite monochromated MoKα radiation (λ = 0.71073 Å). Data were processed using the Nonius Software.[4] Structure solution, the programme suite X-SEED.[5]

Notes on the refinement: For **4** there were two independent molecules of the complex each lying on an inversion centre. The disordered toluene solvate was included with isotropic C atoms and H atoms omitted. For **6** the asymmetric unit contained one molecule of the complex, plus ½ of a hexane molecule (site occupancy = 80%). The solvent was proximate to an inversion centre implicit in the space group. Two carbons in each of the THF ligands exhibited disorder (60:40 ratio for C50-51 and 53:47 for C54-C55).

X-ray diffraction data for **6**. $C_{58.40}H_{89.60}CaN_6O_2$, M = 947.84, monclinic, *C*2/*c*, *a* = 44.3151(3) Å, *b* = 12.43580(10) Å, *c* = 24.4870(2) Å, *β* = 121.189(1)º, *V* = 11544.16(15) Å^3, *Z* = 8, *ρ* = 1.091 g cm^{-3}, R_1 [I > 2σ(I)] = 0.0471, wR_2 [I > 2σ(I)] = 0.1208, R_1 [all data] = 0.0740, wR_2 [all data] = 0.1389, measured reflections = 100189, unique reflections = 13169, R_{int} = 0.0867.

Figure S1. ORTEP representation of **6**. Thermal ellipsoids at 25% probability. H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°) Ca(1)-N(1) 2.4785(13), Ca(1)-N(3) 2.4743(13), Ca(1)-N(4) 2.4149(13), Ca(1)-N(6) 2.4931(13), Ca(1)-O(1) 2.3625(12), Ca(1)-O(2) 2.3840(13), N(1)-Ca(1)-N(3) 51.95(4), N(4)-Ca(1)-N(6) 52.85(4).



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