

Supplementary Information for

Calcium-Centred Phosphine Oxide Reactivity: Sequential P-C Metathesis,

Reduction and P-P Dehydrocoupling

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General Experimental Procedures

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of either nitrogen or argon. NMR experiments were conducted in Youngs tap NMR tubes made up and sealed in a glovebox, NMR were collected on a Bruker AV-300 spectrometer at 75 MHz (^{13}C), 121.5 MHz (^{31}P). The spectra were referenced relative to residual solvent resonances. Elemental analyses were performed by Mr. Stephen Boyer at SACS, London Metropolitan University.

Solvents (Toluene, THF, hexane) were dried by passage through a commercial (MBraun) solvent purification system. C_6D_6 and d_8 -toluene were purchased from Goss Scientific Instruments Ltd. and dried over molten potassium before distillation under nitrogen and storage over molecular sieves. The BDI ligand precursor,¹ β -diketiminate derivative, $[(\text{BDI})\text{CaN}(\text{SiMe}_3)_2(\text{THF})]$,² $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$,³ and $[\text{Ca}\{\text{CH}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$ ⁴ and compound **1**⁵ were prepared by literature procedures. Other reagents were purchased from Sigma-Aldrich and used as received.

Synthesis of $[\text{Ca}\{\text{CH}(\text{SiMe}_3)_2\}_2(\text{OPPh}_3)_2]$, **2**

Ph_3PO (0.23 g, 0.81 mmol) was added to a stirred solution of $[\text{Ca}\{\text{CH}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$ (0.20 g, 0.40 mmol) in toluene (10 mL). The solution was stirred until all the reagents had dissolved at which point a dark red/orange color had developed. Volatiles were removed until incipient crystallisation occurred before storage at $-30\text{ }^\circ\text{C}$ produced compound **2** as pale yellow crystals (0.26 g, 70 %). M.p. decomposes $> 50\text{ }^\circ\text{C}$. Crystals suitable for an X-ray diffraction analysis were obtained

by slow diffusion of hexane into a benzene solution of **2**. Anal. Calc. for $C_{50}H_{68}CaO_2P_2Si_4$: C, 65.60; H, 6.49. Found: C, 65.45; H, 6.37. 1H NMR (300 MHz, 298K, C_6D_6) δ = -1.32 (s, 2H, $CH(SiMe_3)_2$) 0.42 (s, 36H, $SiCH_3$), 7.00 – 7.05 (m, 18H, *o,p*- C_6H_5), 7.05 – 7.57 (s, 12H, *m*- C_6H_5); ^{13}C NMR (75 MHz, 298K, C_6D_6) δ = 6.8 ($SiCH_3$), 128.8 (d, J = 12.6 Hz), 130.5 (d, J = 108.1 Hz), 132.7 (d, J = 2.0 Hz), 132.9 (d, J = 10.6 Hz); ^{31}P NMR (121.5 MHz, 298K, C_6D_6) +33.8.

Synthesis of [(BDI)CaN(SiMe₃)₂(OPPh₃)], **3**

In a glovebox, [(BDI)CaN(SiMe₃)₂(THF)] (200 mg, 0.29 mmol) and Ph₃PO (81 mg, 0.29 mmol) were weighed into a Schlenk tube and toluene (10 cm³) was added via cannula transfer. The solution was stirred until all solid material had dissolved giving a yellow solution. The solvent was then slowly removed under vacuum until precipitation occurred. The solution was warmed slightly to dissolve the precipitate and was stored at -20°C for 24 hours. This resulted in the formation of compound **3** as pale yellow crystals (0.17 g, 64%). M.p. (toluene) 180 °C with decomposition. Anal. Calc. for $C_{53}H_{74}CaN_3OPSi_2$: C, 71.01; H, 8.32; N, 4.69. Found: C, 70.92; H, 8.19; N, 4.67. 1H NMR (300 MHz, 298 K, C_6D_6): δ = 0.15 (s, 18H, $SiCH_3$), 1.32 (d, 12H, $CH(CH_3)_2$), 1.41 (d, 12H, $CH(CH_3)_2$) 1.67 (s, 6H, CH_3); 3.15 (m, 2H, $CH(CH_3)_2$), 3.54 (m, 2H, $CH(CH_3)_2$), 4.73 (s, 1H, $H-C_\gamma$), 6.95 – 7.30 (m, 21H, aryl). ^{13}C NMR (75 MHz, 298K, C_6D_6) δ = 7.0 ($SiCH_3$), 24.9, 26.2, 29.0, 124.5, 133.3, 137.8, 141.7, 142.4, 148.7, 166.5. $^{31}P\{^1H\}$ NMR (12.5 MHz, 298 K, C_6D_6): δ = +34.8 (s).

Synthesis of [(BDI)CaN(SiMe₃)₂(OPPh₂)]₂, **4**

In a glovebox, [(BDI)CaN(SiMe₃)₂(THF)] (200 mg, 0.296 mmol) and Ph₂P(O)H (60 mg, 0.29 mmol) were weighed into a Schlenk tube and toluene (10 cm³) was added via cannula transfer. The solution was stirred until all solid material had dissolved giving a yellow solution. The solvent was then slowly removed under vacuum until precipitation occurred. The solution was warmed slightly to dissolve the precipitate and was then stored at -20°C for 1 week. The product **4** was isolated as colourless crystals (68 mg, 35%). M.p. (toluene) 190 °C with decomposition. Anal. Calc. for $C_{82}H_{102}Ca_2N_4O_2P_2$: C, 74.74; H, 7.80; N, 4.25. Found: C, 74.85; H, 7.81; N, 4.18. 1H NMR (300 MHz, 298 K, *d*₈-toluene): δ = 0.76 (d, 12H, $CH(CH_3)_2$, J = 6 Hz), 0.97 (d, 12H, J = 6 Hz, $CH(CH_3)_2$); 1.56 (s, 6H, CH_3); 3.02 (m, J = 6 Hz, 4H, $CH(CH_3)_2$); δ =

4.93 (s, 1H, *H*-C_γ); δ = 6.94 – 7.08 (m, 18H, aryl). ³¹P{¹H} NMR (121.5 MHz, 298 K, *d*₈-toluene): δ = +89.5 (s).

Reaction between Ph₃PO, Ph₃SiH₃ and [Ca{CH(SiMe₃)₂}(THF)₂]

In a glove box, PhSiH₃ (9.76 μl, 0.079 mmol) was added to a mixture of [Ca{CH(SiMe₃)₂}(THF)₂] (20 mg, 0.040 mmol) and Ph₃PO (22 mg, 0.079 mmol) dissolved in *d*₈-toluene (1 ml). The red/orange solution was added to a Youngs tap NMR tube which, upon removal from the glove box, was monitored by ¹H and ³¹P{¹H} NMR spectroscopy. A ¹H NMR spectrum recorded immediately after addition of the reagents is shown in Figure S1 and illustrates the production of PhH₂Si-CH(SiMe₃)₂, indicative of Ca-H formation as well as C₆H₆ derived from P-phenyl cleavage. A small quantity of Ph₂SiH₂ is also visible due to redistribution of PhSiH₃.

A background reaction performed under the same conditions but without addition of the calcium alkyl provided < 2% conversion of Ph₃PO to Ph₃P over a period of 7 days.

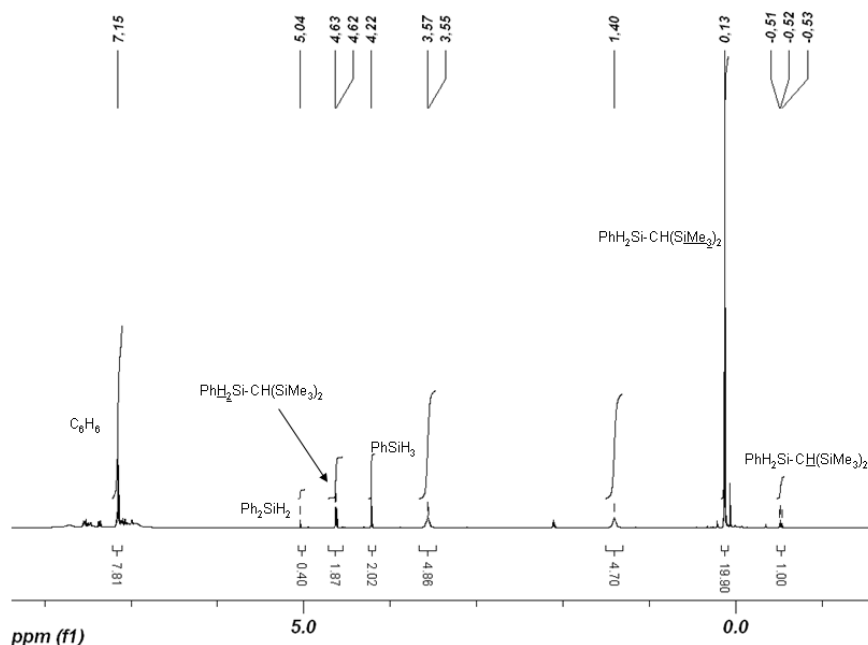


Figure S1: ¹H NMR spectrum recorded immediately after addition of PhSiH₃ to a solution of [Ca{CH(SiMe₃)₂}(THF)₂] and Ph₃PO.

Reaction between PhSiH₃ and compound 3

In a glove box, PhSiH₃ (5.51 µl, 0.05 mmol) were dissolved in *d*₈-toluene (1 ml) and 2 (40 mg, 0.05 mmol) was added to the solution which turned orange. The solution was added to a Youngs tap NMR tube which, upon removal from the glovebox, was monitored by ¹H and ³¹P{¹H} NMR spectroscopy. A representative and annotated ³¹P{¹H} NMR spectrum is illustrated in Figure S2.

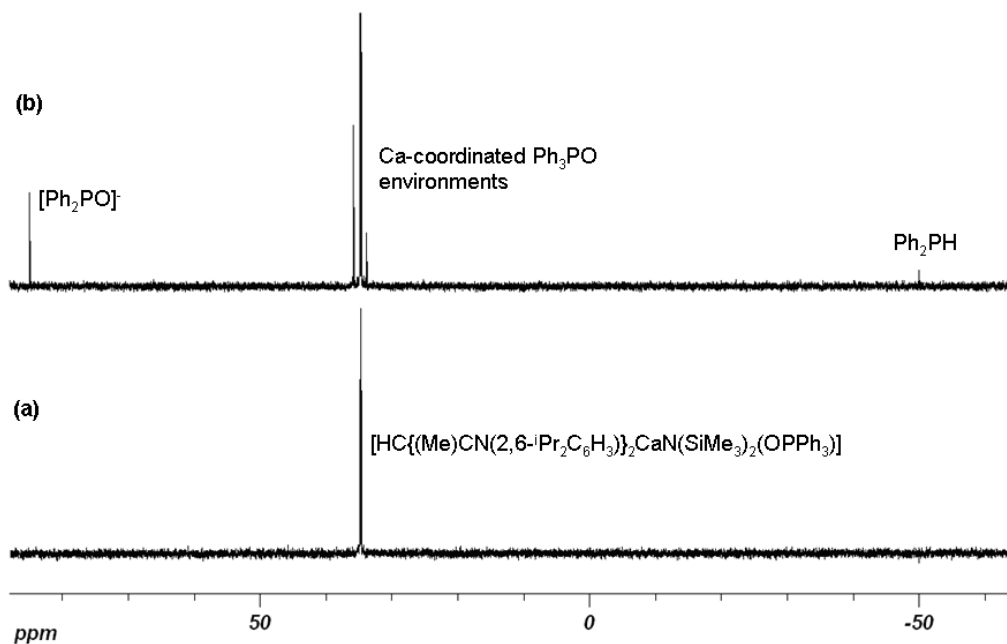


Figure S2: ³¹P{¹H} NMR spectrum of compound 3 recorded (a) before and (b) immediately after addition of PhSiH₃.

Reaction between Ph₂P(O)H, PhSiH₃ and [Ca{CH(SiMe₃)₂}(THF)₂]

In a glove box, Ph₂P(O)H (11 mg, 0.06 mmol) and PhSiH₃ (6.84 µl, 0.06 mmol) were dissolved in C₆D₆ (1 ml) and [Ca{CH(SiMe₃)₂}(THF)₂], (12 mg, 0.028 mmol) was added to the solution which turned yellow and evolved a steady stream of gas bubbles. The solution was added to a Youngs tap NMR tube which upon removal from the glove box was monitored by ¹H and ³¹P{¹H} NMR spectroscopy. ³¹P{¹H} NMR spectra from this reaction are illustrated in Figure 3 of the main body of the communication.

Crystallographic data

Data for **2** and **4** were collected at 150 K on a Nonius Kappa CCD diffractometer equipped with a low temperature device, using graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å). Data were processed using the Nonius Software.⁶ Structure solution, followed by full-matrix least squares refinement was performed using the programme suite X-SEED throughout.⁷

Crystallographic data for **2**: (C₆₂H₈₀CaO₂P₂Si₄, $M_r = 1071.64$) crystal dimensions 0.20 x 0.20 x 0.20 mm³: monoclinic, space group C2/c, $a = 26.5254(2)$, $b = 11.7454(2)$, $c = 23.6923(5)$ Å, $\beta = 122.870(1)^\circ$, $V = 6199.6(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.148$ g cm⁻³, $\mu = 0.270$ mm⁻¹. Of 31751 reflections measured ($3.62 < \theta < 25.03^\circ$), 5430 were independent ($R_{\text{int}} = 0.1448$), $R1 = 0.0466$, $wR2 = 0.1092$ [for 4255 reflections with $I > 2\sigma(I)$], $R1 = 0.0677$, $wR2 = 0.1219$ (all data) GOF = 1.050. The asymmetric unit comprises of ½ of a molecule. The central calcium is located on a crystallographic special position (2-fold rotation axis implicit in the space group symmetry). The data were truncated to θ of 25° as diffraction fell off rapidly with higher Bragg angles.

Crystallographic data for **4**: (C₈₉H₁₁₀Ca₂N₄O₂P₂, $M_r = 1409.91$) crystal dimensions 0.30 x 0.25 x 0.08 mm³: triclinic, space group P-1, $a = 13.4254(2)$, $b = 15.0443(3)$, $c = 19.9224(4)$ Å, $\alpha = 86.844(1)$, $\beta = 82.166(1)$, $\gamma = 85.912(1)^\circ$, $V = 3971.96(13)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.179$ g cm⁻³, $\mu = 0.233$ mm⁻¹. Of 68872 reflections measured ($4.13 < \theta < 26.40^\circ$), 16164 were independent ($R_{\text{int}} = 0.0898$), $R1 = 0.0627$, $wR2 = 0.1555$ [for 10610 reflections with $I > 2\sigma(I)$], $R1 = 0.1054$, $wR2 = 0.1744$ (all data) GOF = 1.053. The asymmetric unit consists of two independent dimer halves, in addition to one molecule of toluene. The latter was split evenly over two voids in the structure, both proximate to inversion centers, and was hopelessly disordered. Ultimately, treatment with SQUEEZE was employed.

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