

# SUPPORTING INFORMATION

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## Azametallacyclopropane $\text{Ca}(\eta^2\text{-Ph}_2\text{CNPh})(\text{hmpa})_3$ : a Calcium-Alternative to a Versatile Ytterbium(II) Catalyst

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## Experimental Section

**General comments.** All experiments were carried out under argon using predried solvents and Schlenk techniques. Following compounds were prepared according to literature: diphenylmethyl-*N*-phenylimine,<sup>1</sup> (2-Me<sub>2</sub>N- $\alpha$ -Me<sub>3</sub>Si-benzyl)<sub>2</sub>Ca (**3**).<sup>2</sup> All other starting reactants were commercially available and rigorously dried over freshly ground calcium hydride prior to use. NMR spectra have been recorded on Bruker DPX300 and DRX500 machines. Crystals were measured on a Siemens Smart diffractometer with APEXII area detector system at -70 °C with Mo K $\alpha$  radiation (0.71073 Å).

**Synthesis of 2-Ca.** The synthesis was performed analogue to that published for **2-Yb** with the difference that longer reaction times were used. To a mixture of metallic calcium pieces (99 % purity, circa 10-20 mesh, 160 mg, 4.0 mmol, activated by 8  $\mu$ L of Br<sub>2</sub>C<sub>2</sub>H<sub>4</sub>), THF (16 mL) and HMPA (4 mL) in a Schlenk tube was added diphenylmethylen-*N*-phenylimine (1028 mg, 4.0 mmol). Stirring this mixture at room temperature for 16 hours gave a very dark-red suspension. Heating this suspension gave a dark solution which could be decanted from unreacted metal. Slow cooling of this solution gave precipitation of **2-Ca** as a uniform crop of large, shiny black (very dark-red) needles. These were washed with pentane and dried *in vacuo*: 1604 mg, 1.92 mmol, 48 %.

Crystals of **2-Ca** are rather insoluble in non-protic solvents like benzene, THF and toluene. In contrast to **2-Yb**,<sup>3</sup> NMR spectra of **2-Ca** in THF-*d*<sub>8</sub> show (also at 60 °C) extremely broad signals indicating slow exchange. However, as observed for **2-Yb**,<sup>3</sup> quenching crystals of **2-Ca** with CD<sub>3</sub>OD, gave a mixture of Ph<sub>2</sub>DCNDPh (42 %), Ph<sub>2</sub>CD<sub>2</sub> (29 %) and PhND<sub>2</sub> (29 %).

Elemental analysis calcd (%) for C<sub>37</sub>H<sub>69</sub>Ca<sub>1</sub>N<sub>10</sub>O<sub>3</sub>P<sub>3</sub> + 1 cocrystallized THF (M = 907.14): C 54.29, H 8.56, N 15.44; found: C 54.39, H 8.36, N 15.73. Mp: 116 °C (dec.). IR (Nujol): 2926 (s), 2853 (s), 1460 (s), 1298 (m), 1195 (m), 987 (s), 798 (m), 745 (m).

**General procedure for dehydrogenative silylation of amines.** For a comparison of the catalytic activity of the calcium catalysts **2-Ca** and **3** with results reported for **2-Yb**,<sup>4</sup> similar procedures and reaction conditions were chosen. The appropriate amount of azametallacyclopropane complex **2-Ca** or the dibenzylcalcium complex **3** (3-10 mol%; 0.0144-0.0480 mmol) was added to a solution of the hydrosilane (0.48 mmol) and the amine (0.48 mmol) dissolved in THF (0.5 mL) at room temperature. Generally immediate evolution of gas could be observed. The conversion was followed by taken samples at regular time intervals and subsequent analysis by <sup>1</sup>H NMR-spectroscopy and GC-MS. All products could be positively assigned by comparison of the <sup>1</sup>H NMR signals with literature data<sup>4</sup> and yields were estimated by integration of substrate and product peaks.

*N*-Triphenylsilylamylamine: <sup>1</sup>H NMR (THF-*d*<sub>8</sub>) δ 0.90 (3H, t, *J* = 7.0 Hz), 1.29-1.36 (4H, m), 1.52 (2H, quin, *J* = 7.0 Hz), 1.93 (1H, br t, *J* = 7.0 Hz), 2.96 (2H, q, *J* = 7.0 Hz), 7.35-7.39 (9H, m), 7.67-7.70 (6H, m).

*N*-Triphenylsilyl-1,1-dimethylpropylamine: <sup>1</sup>H NMR (THF-*d*<sub>8</sub>) δ 0.85 (3H, t, *J* = 7.4 Hz), 1.08 (6H, s), 1.38 (2H, q, *J* = 7.4 Hz), 1.73 (1H, br s), 7.28-7.33 (9H, m), 7.69-7.72 (6H, m).

*N*-Triphenylsilylaniline: <sup>1</sup>H NMR (THF-*d*<sub>8</sub>) δ 4.97 (1H, br s), 6.56 (1H, t, *J* = 7.2 Hz), 6.76 (2H, d, *J* = 7.8 Hz), 6.92 (2H, t, *J* = 7.6 Hz), 7.27-7.32 (9H, m), 7.71 (6H, d, *J* = 6.2 Hz).

*N*-Triphenylsilyl-*N*-methylbutylamine: <sup>1</sup>H NMR (THF-*d*<sub>8</sub>) δ 0.73 (3H, t, *J* = 7.4 Hz), 1.12 (2H, sextet, *J* = 7.5 Hz) 1.47 (2H, quin, *J* = 7.6 Hz), 2.66 (3H, s), 2.86 (2H, t, *J* = 7.5 Hz), 7.27-7.32 (9H, m), 7.58-7.61 (6H, m).

**General procedure for dehydrogenative silylation of 1-hexyne.** For a comparison of the catalytic activity of the calcium catalysts **2-Ca** and **3** with results reported for **2-Yb**,<sup>5</sup> similar procedures and reaction conditions were chosen. It was found, however, that lower catalyst concentrations of **2-Ca** could be used. The calcium catalyst **2-Ca** or **3** (0.024 mmol) was dissolved in THF (0.5 mL) and the silane (0.48 mmol) and appropriate amount of 1-hexyne (0.24, 0.48 or 0.96 mmol) were added to this solution at room temperature. Generally

immediate evolution of gas could be observed. After 17 hours the reaction was quenched with water and 2 M HCl and the resulting mixture was extracted with diethyl ether. All combined organic layers were dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The yields were determined by <sup>1</sup>H NMR spectroscopy and GC-MS. The products could be positively assigned by comparison of the <sup>1</sup>H NMR-spectra and mass spectra with literature data.

1-Triphenylsilyl-1-hexyne: <sup>1</sup>H NMR (THF-*d*<sub>8</sub>) δ 0.72 (3H, t, *J* = 7.1 Hz), 1.21-1.37 (4H, m), 2.07 (2H, t, *J* = 6.8 Hz), 7.13-7.19 (9H, m), 7.86-7.89 (6H, m); MS *m/z* 340 (M<sup>+</sup>), 263 (M<sup>+</sup>-Ph), 105 (SiPh<sup>+</sup>).

1-Methylphenylsilyl-1-hexyne: <sup>1</sup>H NMR (THF-*d*<sub>8</sub>) δ 0.35 (3H, d, *J* = 3.8 Hz), 0.86 (3H, t, *J* = 7.1 Hz), 1.34-1.49 (4H, m), 2.22 (2H, t, *J* = 6.6 Hz), 4.55 (1H, q, *J* = 3.8 Hz) 7.26-7.30 (3H, m), 7.55-7.57 (2H, m); MS *m/z* 202 (M<sup>+</sup>) 187 (M<sup>+</sup>-Me), 105 (SiPh<sup>+</sup>).

Di(1-hexynyl)methylphenylsilane: <sup>1</sup>H NMR (THF-*d*<sub>8</sub>) δ 0.37 (3H, s), 0.85 (6H, t, *J* = 6.9 Hz), 1.34-1.47 (8H, m), 2.20 (4H, t, *J* = 6.8 Hz), 4.55 (1H, q, *J* = 3.8 Hz) 7.26-7.28 (3H, m), 7.62-7.65 (2H, m); MS *m/z* 282 (M<sup>+</sup>), 267 (M<sup>+</sup>-Me), 105 (SiPh<sup>+</sup>).

### **Catalytic isomerization of 1-hexyne.**

For a comparison of the results for catalyst **2-Ca**, catalytic experiments were carried out exactly analogue to those described for the earlier reported **2-Yb** catalyst.<sup>6</sup> As the Yb/hmpa ratio influenced the yields, we have chose equal Ca/hmpa ratios. Catalytic experiments with 10 mol% **2-Ca** +1 hmpa or 5 mol% **2-Ca** + 5 hmpa have been carried out.

To the azametallacyclopropane complex **2-Ca** (5 or 10 mol%; 0.024 or 0.048 mmol) was added the appropriate amount of HMPA (0.120 or 0.048 mmol, respectively). Then 1-hexyne (0.48 mmol) was added to the mixture at room temperature. After 17 hours samples were taken and subsequent analysed by <sup>1</sup>H NMR-spectroscopy and GC-MS. The yields were determined by <sup>1</sup>H NMR spectroscopy and GC-MS. The product could be positively assigned by comparison of the <sup>1</sup>H NMR signals and mass spectra with literature data (Table 1).<sup>6</sup>

**2-Hexyne:**  $^1\text{H}$  NMR (THF- $d_8$ )  $\delta$  0.95 (3H, t,  $J = 7.3$  Hz), 1.45 (2H, sextet,  $J = 7.2$  Hz), 1.71 (3H, t,  $J = 2.5$  Hz), 2.05 (2H, tq,  $J = 7.2, 2.5$  Hz); MS  $m/z$  82 ( $\text{M}^+$ ).

Table 1. Comparison between **2-Ca** and **2-Yb** catalysts.

Entry	catalyst	t(h)	Conversion (%)
BuC $\equiv$ CH $\rightarrow$ PrC $\equiv$ C-CH $_3$			
1	<b>2-Ca</b> 10 mol % + 1 hmpa	17	>98
2 <sup>6</sup>	<b>2-Yb</b> 10 mol % + 1 hmpa	17	89
3	<b>2-Ca</b> 5 mol % + 4 hmpa	17	>98
4 <sup>6</sup>	<b>2-Yb</b> 5 mol % + 4 hmpa	17	95

## References

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