

**A Bis(phosphinimino)methanide Lanthanum Amide as Catalyst for the
Hydroamination / Cyclisation, Hydrosilylation and Sequential Hydroamination /
Hydrosilylation Catalysis.**

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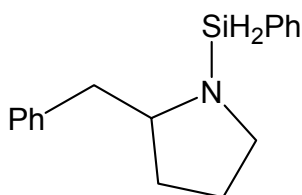
Supporting Information

Experimental Section.

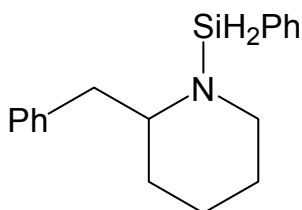
General: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-4} torr) line, or in an argon-filled M. Braun glove box. Ether solvents (THF and ethyl ether) were predried over Na wire and distilled under nitrogen from K (THF) or Na wire (ethyl ether) as well as benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from LiAlH₄. All solvents for vacuum line manipulations were stored *in vacuo* over LiAlH₄ in resealable flasks. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft mbH (all ≥ 99 atom % D) and were degassed, dried, and stored *in vacuo* over Na/K alloy in resealable flasks. NMR spectra were recorded on JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane and 85 % phosphoric acid (³¹P NMR), respectively. Elemental analyses were carried out with an Elementar vario EL. LaCl₃,¹ and {CH₂(PPh₂NSiMe₃)₂},² were prepared according to literature procedures.

General for the Hydroamination and Hydrosilylation Reaction (NMR scale reaction): Compound **1** was weighed under argon gas into an NMR tube. C₆D₆ (~ 0.7 mL) was condensed into the NMR tube, and the mixture was frozen to -196 °C. The reactant was injected onto the solid mixture, and the whole sample was melted and mixed just before the insertion into the core of the NMR machine (*t*₀). The ratio between the reactant and the product was exactly calculated by comparison of the integrations of the corresponding signals.

NMR data for the Hydrosilylation/Hydroamination



2-Benzyl-1-(phenylsilyl)pyrrolidine, ^1H NMR (C_6D_6 , 400 MHz, 25°C) δ 7.55 – 6.92 (m, 10H, 2Ph), 5.05 (dd, $J(^1\text{H}, ^1\text{H}) = 10$ Hz, 2 H), 3.51 (m, 1H), 2.92 (m, 2H); 2.72 (dd, $J(^1\text{H}, ^1\text{H}) = 5.4$ Hz, 1H); 2.32 (dd, $J(^1\text{H}, ^1\text{H}) = 8.6$ Hz, 1H); 1.47 – 1.34 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6 , 100 MHz, 25°C): δ 140.2, 136.0, 135.1, 129.7, 128.5, 128.4, 128.3, 126.2, 62.4, 48.9, 44.1, 32.1, 26.0



2-benzyl-1-(phenylsilyl)piperidine, ^1H -NMR (C_6D_6 , 400 MHz, 25°C) δ 7.30 – 6.76 (m, 10H, 2Ph), 4.70 (dd, $J(^1\text{H}, ^1\text{H}) = 10$ Hz, 2 H), 3.05 (m, 1H), 2.76 – 2.70 (m, 2H); 2.55 (dd, $J(^1\text{H}, ^1\text{H}) = 5.6$ Hz, 1H); 2.37 (dd, $J(^1\text{H}, ^1\text{H}) = 7.5$ Hz, 1H); 1.25 – 1.07 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6 , 100 MHz, 25°C): δ 140.7, 136.1, 135.1, 130.2, 129.6, 128.5, 128.3, 126.2, 56.8, 43.3, 38.3, 30.0, 27.5, 20.8

[1] M. D. Taylor and C. P. Carter *J. Inorg. Nucl. Chem.* 1962, **24**, 387-391.

[2] R. Appel and I. Ruppert *Z. Anorg. Allg. Chem.* 1974, **406**, 131-144.