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 LiAlH\(_4\). All solvents for vacuum line manipulations were stored in vacuo over LiAlH\(_4\) in resealable flasks. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft mbH (all \(\geq 99\) 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 (\(^{31}\)P NMR), respectively. Elemental analyses were carried out with an Elementar vario EL. LaCl\(_3\),\(^1\) and \(\{\text{CH}_3(\text{PPh}_2\text{NSiMe}_3)_2\}\),\(^2\) 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. C\(_6\)D\(_6\) (~ 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

\[ \text{Ph} \quad \text{SiH}_2\text{Ph} \]

2-Benzyl-1-(phenylsilyl)pyrrolidine, \(^1\)H NMR (C\(_6\)D\(_6\), 400 MHz, 25°C) \( \delta \) 7.55 – 6.92 (m, 10H, 2Ph), 5.05 (dd, \( J^{(1\text{H},1\text{H})} = 10 \text{ Hz}, 2 \text{ H} \)), 3.51 (m, 1H), 2.92 (m, 2H); 2.72 (dd, \( J^{(1\text{H},1\text{H})} = 5.4 \text{ Hz}, 1\text{ H} \)); 2.32 (dd, \( J^{(1\text{H},1\text{H})} = 8.6 \text{ Hz}, 1\text{ H} \)); 1.47 – 1.34 (m, 4H); \(^{13}\)C\(^{1}\)H-NMR (C\(_6\)D\(_6\), 100 MHz, 25°C): \( \delta \) 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

\[ \text{Ph} \quad \text{SiH}_2\text{Ph} \]

2-Benzyl-1-(phenylsilyl)piperidine, \(^1\)H-NMR (C\(_6\)D\(_6\), 400 MHz, 25°C) \( \delta \) 7.30 – 6.76 (m, 10H, 2Ph), 4.70 (dd, \( J^{(1\text{H},1\text{H})} = 10 \text{ Hz}, 2 \text{ H} \)), 3.05 (m, 1H), 2.76 – 2.70 (m, 2H); 2.55 (dd, \( J^{(1\text{H},1\text{H})} = 5.6 \text{ Hz}, 1\text{ H} \)); 2.37 (dd, \( J^{(1\text{H},1\text{H})} = 7.5 \text{ Hz}, 1\text{ H} \)); 1.25 – 1.07 (m, 6H); \(^{13}\)C\(^{1}\)H-NMR (C\(_6\)D\(_6\), 100 MHz, 25°C): \( \delta \) 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
