

Supplementary Material

A homoleptic tetravalent cerium silylamide

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Experimental Details

General Procedures. All manipulations were performed with rigorous exclusion of air and water in an argon-filled glovebox (*MBraun MB150B-G*; <1 ppm O₂, <1 ppm H₂O). Hexane, toluene, and tetrahydrofuran were purified by using Grubbs columns (*MBraun SPS-800*, solvent purification system) and stored in a glovebox. Benzene-[D]₆ was obtained from *Aldrich*, degassed, dried over Na for 24 h, and filtered. Complex **1**^{2b} and PhICl₂¹⁸ were synthesised according to modified literature procedures. Complex **1a**¹⁹ was synthesised from Ce[N(SiMe₃)₂]₃ with excess tetramethyldisilazane (*ABCR*) in hexane. Trityl chloride (≥97%), hexachloroethane (99%) and hexamethylbenzene (99%) were purchased from *Sigma-Aldrich* and used as received. NMR spectra were recorded on a *Bruker-AVANCE-DMX400* spectrometer (5 mm BB, ¹H: 400.13 MHz) in [D]₆-benzene at 25 °C. ¹H, ¹³C and ²⁹Si shifts are referenced to internal solvent resonances and reported relative to TMS. IR spectra were recorded on either a *NICOLET Impact 410 FTIR* or a *NICOLET 6700 FTIR* spectrometer using a DRIFT chamber with dry KBr/sample mixtures and KBr windows, collected data were converted using the Kubelka-Munk refinement. CHN elemental analysis was performed on an *Elementar Vario MICRO cube*.

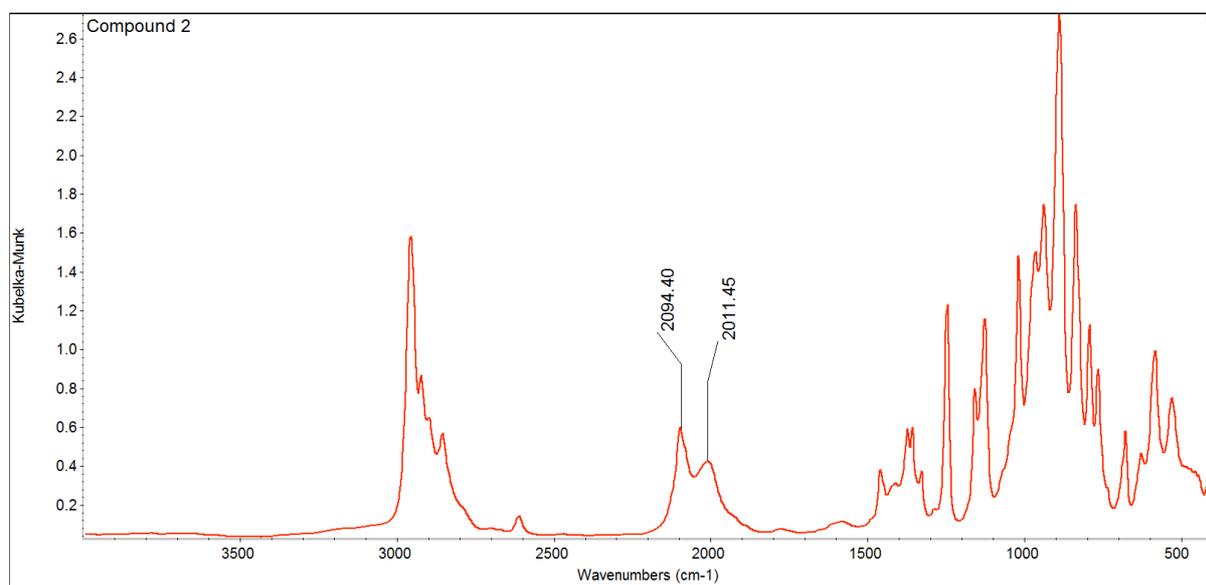


Figure S1 DRIFT spectrum of compound 2.

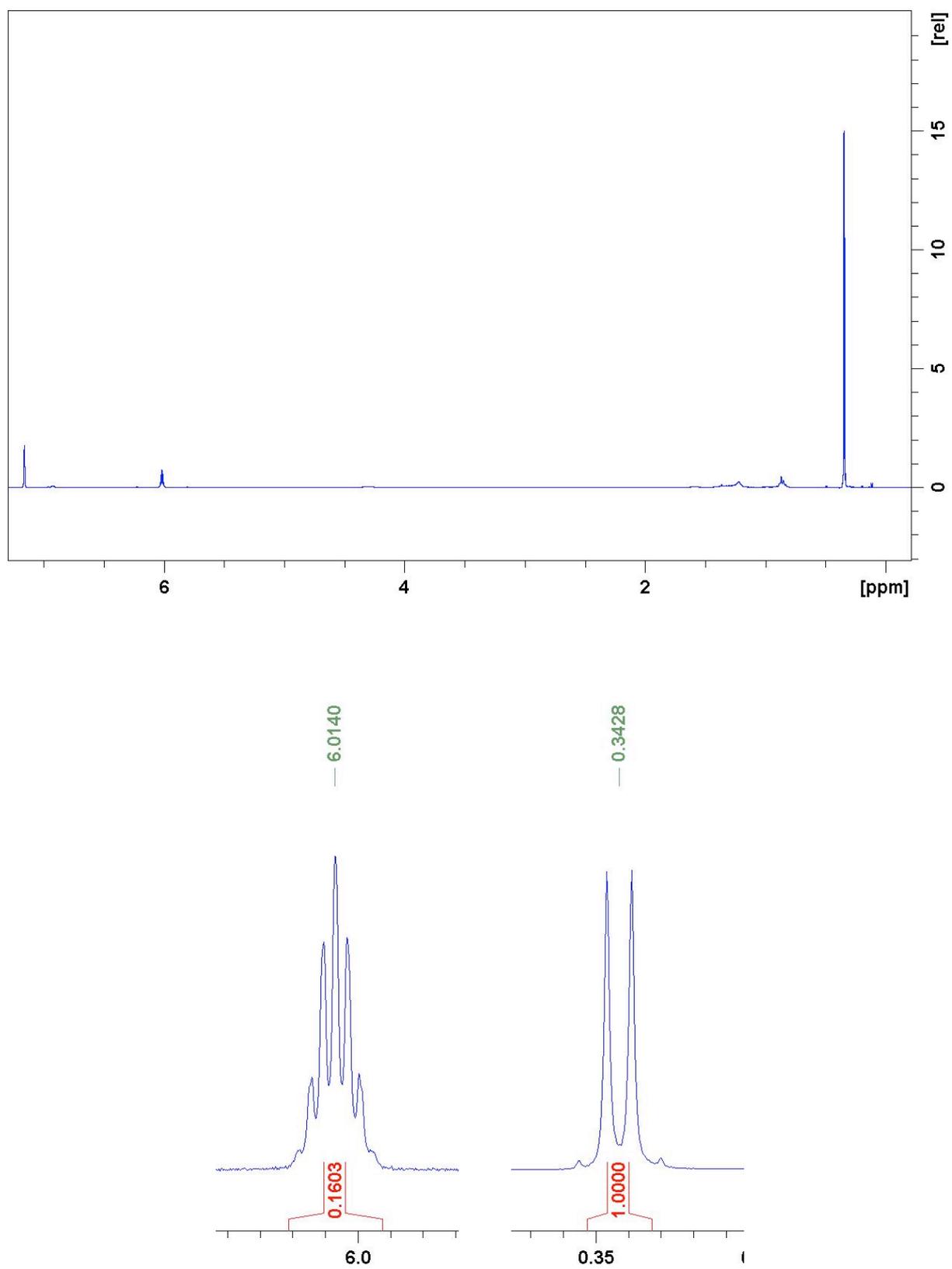


Figure S2 ^1H NMR (400 MHz) spectrum of compound **2** in $[\text{D}_6]$ benzene.

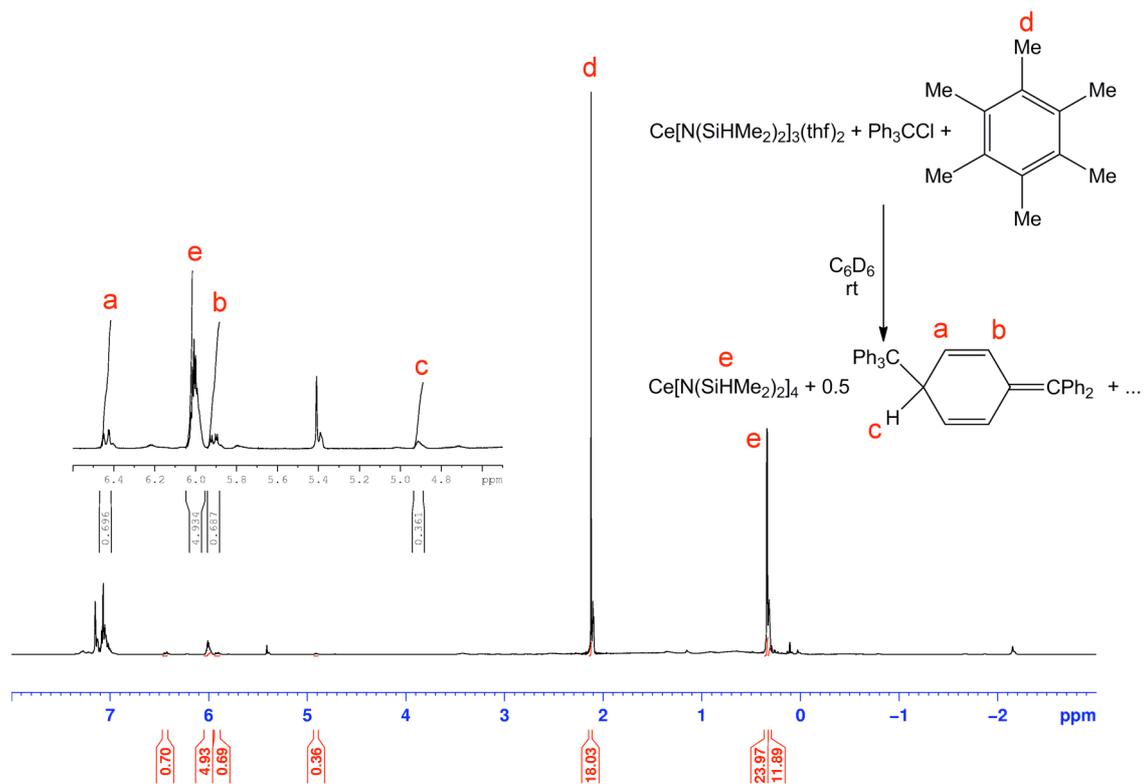


Figure S3. ^1H NMR (400 MHz) spectrum of $\text{Ce}[\text{N}(\text{SiHMe}_2)_2]_3(\text{thf})_2$ oxidation by Ph_3CCl in $[\text{D}_6]$ benzene.