Synthesis and Derivatization of Homoleptic Dinuclear Lanthanide Siloxide Complexes

Andreas Fischbach[a], Georg Eickerling[b], Wolfgang Scherer[b], Eberhardt Herdtweck[a], and Reiner Anwander[a]

[a] Department Chemie, Lehrstuhl für Anorganische Chemie, Technische Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany
[b] Institut für Physik, Universität Augsburg, Universitätsstraße 1, D-86159 Augsburg, Germany

Reprint requests to Dr. R. Anwander. Fax: +49 (0)89 289 13473. E-mail: reiner.anwander@ch.tum.de

Z. Naturforsch. **59b,** 1353 – 1364 (2004); received August 13, 2004

Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Homoleptic dinuclear lanthanide siloxide complexes $[Ln(OSi\textit{t}BuPh_2)_2(\mu\text{-}OSi\textit{t}BuPh_2)]_2$ (Ln = Y (**1a**), La (**1b**)), $[Ln(OSiH\textit{t}Bu_2)_2(\mu\text{-}OSiH\textit{t}Bu_2)]_2$ (Ln = Y (**2a**), La (**2b**), Nd (**2c**), Lu (**2d**)), and $\{Ln[OSi(O\textit{t}Bu)_3]_2[\mu\text{-}OSi(O\textit{t}Bu)_3]\}_2$ (Ln = Y (**3a**), La (**3b**)) were synthesized according to the silylamide route in yields between 67 and 92%. Their bis(siloxide)-bridged molecular arrangement was proven by variable temperature ^{1}H NMR spectroscopy as well as by an X-ray structure analysis of **2c**. The IR spectra of complexes **2** feature low-energy Si–H stretching vibrations (1965 – 1915 cm^{-1}) indicative of β(Si–H)···Ln agostic interactions. Complexes **2** and **3** readily form monomeric bis(donor) adducts with tetrahydrofurane, triphenylphosphine oxide, and *N*-methylimidazol as shown for fully characterized $Ln(OSiH\textit{t}Bu_2)_3(thf)_2$ (Ln = Y (**4a**), La (**4b**)), $Y(OSiH\textit{t}Bu_2)_3(OPPh_3)_2$ (**5**), $Ln(OSiH\textit{t}Bu_2)_3(\textit{N}\text{-MeIm})_2$ (Ln = Y (**6a**), La (**6b**)), and $Y[OSi(O\textit{t}Bu)_3]_3(thf)_2$ (**7**). Treatment of complexes **1** – **3** with excess of trimethylaluminum (TMA) generated several alkylated rare-earth metal species including homoleptic $Ln(AlMe_4)_3$ as indicated by ^{1}H NMR spectroscopy. $La[OSi(O\textit{t}Bu)_3](AlMe_4)_2(AlMe_3)$ (**8b**) was isolated by crystallization and analyzed by X-ray diffraction.

Key words: Lanthanides, Siloxide Ligands, Metallosiloxanes, Adduct Formation, Tetramethylaluminate