From Chlorosilyliumylidene Complexes to Cyclic Silylones with an Electron-Rich Silicon(O) Atom

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Introduction
The investigation of low-valent Group 14 species keeps increasing research interest. By taking advantages of kinetic and thermodynamic stabilization diverse novel silicon and germanium species have been generated during last decades. In this context, we successfully synthesized a series of donor-supported silicon oxygen double bond containing species starting from a zwitterionic N-heterocyclic silylene. Recently, we continued to apply this stabilization concept for the quest of the zero-valent silicon complexes via chlorosilyliumylidene complexes. By employing chelating bis(ylide) ligands and bis-N-heterocyclic carbenes (NHC), several novel chlorosilyliumylidene complexes [L₅(Cl)Si:]:Cl (L₅ = neutral chelating bidentate ligand) as well as their germanium analogues [L₅(Cl)Ge]:Cl have been obtained. Remarkably, the reduction of cyclic bis-NHC supported chlorosilyliumylidene complex and its germanium analogues led to the isolation of the first cyclic silylone and germylon, respectively.

Synthesis and Reactivity

For silylone 3:

Si₁-C₁ 1.864(1) Å
Si₁-C₂ 1.874(1) Å
C₁-Si₁-C₂ 89.1 Å

δ²⁹Si NMR: δ = -80.1 ppm (C₄D₈)

(NHC)Cl₂ or GeCl₂-dioxane
THF, r.t.
- NHC or 
- dioxane

For germylon 4:

Ge₁-C₁ 1.967(2) Å
Ge₁-C₂ 1.962(2) Å
C₁-Ge₁-C₂ 86.6(1) Å

Theoretical Calculations

HOMO of 1 (Si σ-lone pair orbital)  LUMO of 1 (Si π-type orbital)  HOMO of 3 (Si π-lone pair orbital)  HOMO-1 of 3 (Si σ-lone pair orbital)

Proton Affinity (1) of 3: 281.7 kcal·mol⁻¹, Proton Affinity (2) of 3: 189.4 kcal·mol⁻¹

References