An NHC-Stabilized Disilavinylidene: Synthesis, Structure and Reactivity

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Introduction

The behavior of silicon in multiply bonded compounds differs markedly from that of its lighter homologue carbon. This is exemplified by the presence of four energetically minimum structures A – D for SiH3 (Chart 1) on the potential energy hypersurface (PES), in contrast to only two minimum structures (HCCH and H2C=C:) for CH3.[1] The bridged (A) and monobridged (B) SiH3 molecules were identified by spectroscopic studies,[2] and trans-bent disilenes Si2R2 of type D with bulky substituents were isolated in the condensed phase.[3] However, no experimental evidence for disilavinylidenes (C) has been reported to date. Using N-heterocyclic carbenes (NHCs), we herein present an efficient two-step synthesis and some initial reactivity studies of the first NHC-stabilized disilavinylidene.[4]

Results

NHCl-Stabilized Bromo(silyl)silylenes

The entry into this chemistry was provided by the NHC-stabilized Si(II) dibromide SiBr2(Sldipp), which upon reaction with (E)-Br(η5-C3H5)=Si(η5-C3H5)Tbb or LiTbb afforded the first NHC-stabilized bromo(silyl)silylene SiBr(SiBr2Tbb)(Sldipp) (1) (Scheme 1). Compound 1 was isolated as an extremely air-sensitive, yellow solid in 50 – 61 % yield.

NHC-Stabilized Disilavinylidenes

The reduction of 1 with two equivalents of K2C8 in benzene leads to the first NHC-stabilized disilavinylidene (Z)-SiBr(SiBr2Tbb)(Sldipp) (2) (Scheme 2), which after work-up was isolated as an extremely air-sensitive, bright-red solid in 60 % yield.

Reactivity of the NHC-Stabilized Disilavinylidene 2

The NHC-stabilized disilavinylidene 2 contains multiple reactive sites, such as the Si – Br and Si – Si bonds, the Si lone pair or the displaceable NHC group, which opens up many potential reaction pathways. Some initial results of the exploration of the fascinating reactivity of 2 are presented in Scheme 3 and Figure 5.

Summary

The first NHC-stabilized bromo(silyl)silylenes and disilavinylidenes (1, 2) were isolated and fully characterized by X-ray diffraction analysis, NMR spectroscopy and quantum chemical calculations. Both compounds feature many reactive sites, which facilitated the isolation of many novel and exciting low-valent Si compounds.

References