

From this experiment we gained conclusive evidence to the electronic interpretation of the first Si(II)-hydride by integrating all symmetry independent atomic basins (Figure 2). The atomic charges display prominent positive values for silicon (+1.68 e), boron (+1.21 e), and even for C1 (+0.60 e), and were counterbalanced by N1 (-1.31 e), N2 (-1.21 e) and the hydrogen atoms bound to silicon (-0.53 e) and boron (av.: -0.53 e). Even more meaningful are the group charges, displayed in Figure 2, which show an obvious intra-molecular charge transfer. Notably, even the BH₃ group bears a negative charge with the positive charge at the boron atom itself overcompensated by the negative hydrogen atoms. As expected, we found a neutral phenyl ring and the whole negative charge of the ligand is concentrated in the C(NtBu)₂-backbone. Surprisingly, the negative charge is exclusively accumulated in the nitrogen basins while the C1-basin gains positive charge, because the electronegative nitrogen atoms polarize the C–N bonding density. In addition, the hydride atom H100 counterbalances partially the positive charge at Si1, but the SiH-core remains positively charged.

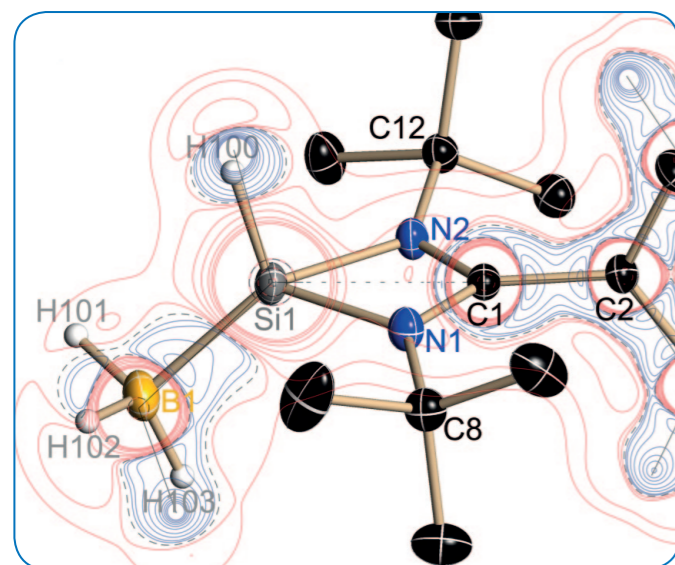


Figure 1: Anisotropic displacement parameters of [(PhC(NtBu)₂)SiH(BH₃)] superimposed on the Laplacian $L(r)$.

APEX II ULTRA for high data quality

This charge density investigation provides another example of the high data quality achievable with Bruker's APEX II ULTRA and also shows the importance of rotating anode based systems in chemical crystallography. Although microfocus X-ray sources can take over a larger amount of the workload which required a rotating anode in the past, the development of modern X-ray optics for rotating anodes, like the HELIOS optic for our TXS, has facilitated investigations previously impossible with an in-house instrument.

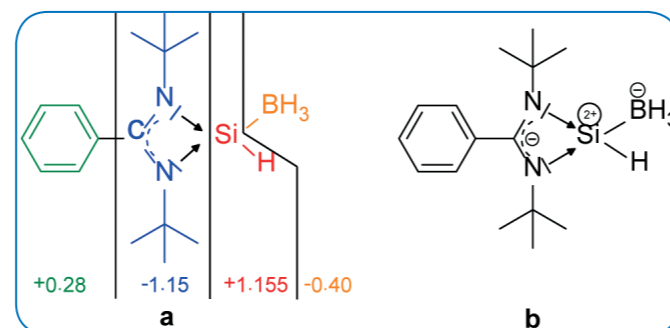


Figure 2: **a)** Group charges in [(PhC(NtBu)₂)SiH(BH₃)] gained from the integration of atomic basins as a sum over the integrated atomic charges and **b)** Canonical formula that contributes most to the bonding.

References

- [1] D. Stalke *Chem. Eur. J.* 2011, 17, 9264.
- [2] A. Jana, D. Leusser, I. Objartel, H. W. Roesky, D. Stalke *Dalton Trans. (Hot Article)* 2011, 40, 5458 and inside front cover, high lighted by A. Schnepf in *Nachr. Chem.* 2011, 59, 698.

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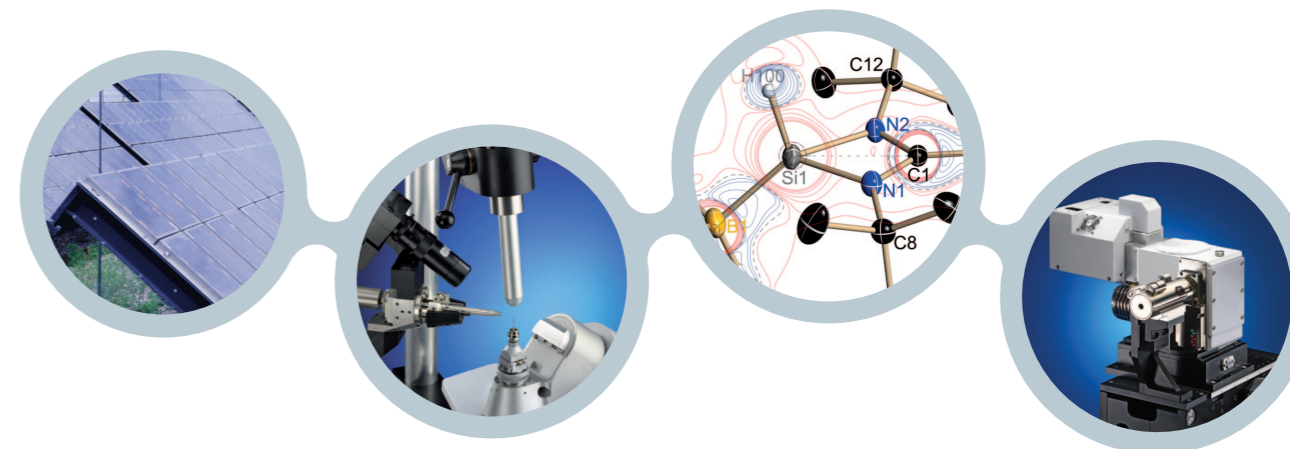
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Application Note SC-XRD #393

Charge density investigation of Stable Silicon(II) Monohydride

Lewis acid-base stabilized silicon

Group 14 hydrides are of steadily growing practical interest since they are widely used in synthetic chemistry, as alloys for electronic devices, and as precursors for high purity elements. Silicon can be envisaged as the sister element of carbon and several silicon hydrides derived from Si(IV) are known. Although GeH₂ and PbH₂ are readily available, the corresponding stable Si(II) compound of oxidation state II is elusive to date. Unstable species have been studied at high or at very low temperatures, the later stabilized in a matrix. However, Si(II) hydrides have not been stabilized at room temperature, so far. Recently, we reported the synthesis of the stable Lewis acid-base stabilized silicon(II) monohydride [(PhC(NtBu)₂)SiH(BH₃)] in good yield. The target hydride was obtained from the reaction of the corresponding silicon(II) chloride [(PhC(NtBu)₂)SiCl(BH₃)] with potassium tris(secondary butyl)borohydride [K{BH(sBu)₃}].

First silicon(II) monohydride

Based on charge density investigations from a high-resolution, low-temperature diffraction experiment [1] it looks like there is only one consistent interpretation of the electronic structure of [(PhC(NtBu)₂)SiH(BH₃)]. It should be pointed out that LiSiH(BH₃) is the first silicon(II) monohydride, contain-

ing a central silicon atom. A covalent, shared interaction to a sp³-hybridized boron atom stabilizes the hydride. The positively charged H–Si–BH₃ moiety is coordinated by the lone-pairs of the benzamidinate ligand. These non-shared interactions allow a highly flexible coordination geometry at the silicon atom [2] compared to covalently bound ligands.

Details from X-ray analysis

The structure determination of such unprecedented species is far from routine. A combination of advanced hardware and powerful software is essential to get the high quality data needed for a successful multipole refinement that is essential to the experimental charge density investigation. Here Bruker's TURBO X-RAY SOURCE equipped with HELIOS X-ray optics and the sensitive APEX II detector were combined with the flexible integration engine SAINT - part of the APEX2 software suite. We collected data up to 2θ = 100° with an impressive completeness of 92.4 %. Based on all data the multipole-refined model gave us excellent final *R*-values of *R*₁ = 0.0320 and *wR*₂ = 0.0376.