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A Facile Route to Functionalized N-Heterocyclic Carbenes (NHCs) with NHC Base-Stabilized Dichlorosilylene

Rajendra S. Ghadwal, Herbert W. Roesky,* Markus Granitzka, and Dietmar Stalke

Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany

Received May 27, 2010; E-mail: hroesky@gwdg.de

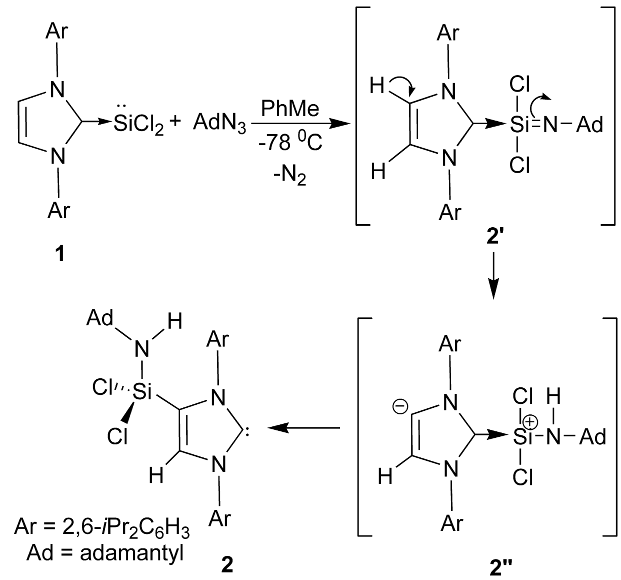
Abstract: Reaction of IPr•$SiCl_2$ (**1**) [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] with 1-azidoadamantane leads to functionalized N-heterocyclic carbene (NHC) **2**. Silyl-substituted NHC **2** reacts easily with 1-azidoadamantane to form triazene **3**, in which the exocyclic C=N bond is slightly shorter than those of regular NHC-derived triazines. **2** could serve as a promising ligand for transition metals.

N-heterocyclic carbenes (NHCs) have been extensively used as versatile ligands in organometallic chemistry[1] and transition-metal catalysis.[2] Moreover, they have found widespread applications as organocatalysts.[3] The extraordinary binding properties of NHCs as strong σ-donating and weak π-accepting ligands have resulted in the isolation of metal complexes in unusual oxidation states.[1,4−6] Further progress in this field is driven by the design and synthesis of new NHCs.[7] The NHCs typically form metal complexes in which the carbene carbon (the C2 position) coordinates to the metal center and the C4 and C5 positions remain unsubstituted. (The numbering of the elements within the imidazole ring of NHCs follows the IUPAC nomenclature). NHCs in which one of these positions is substituted by a metal center are called abnormal NHCs and have been reported for d- and f-block elements.[1,8,9]

Recently, abnormal NHCs have been synthesized by Bertrand and co-workers.[10] The abnormal behavior of NHCs for p-block elements[11−13] is rare and only observed especially when the C2 carbon is not blocked or bound to a metal. Gates and co-workers[12] have reported 4-phosphino-substituted NHCs prepared by the direct reaction of phosphaalkenes with NHCs. Silyl-substituted NHCs have been formed[13] by the reactions of NHCs with transient silylenes. Silylation[13b−d] at the C4 or C5 position of metal-coordinated NHCs has been reported. In order to increase the electronic stabilization effect, functionalization of NHCs at the C4 and C5 positions has attracted attention due to broader applications. In spite of extensive research work in functionalizing NHCs, to date there have been no reports on generating NHCs from stable NHC complexes.

Herein, we report the formation of C4-silyl-substituted NHC **2** by oxidative addition and C−H activation of the NHC-stabilized dichlorosilylene[5] IPr•$SiCl_2$ (**1**) [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] with 1-azidoadamantane (AdN_3). Most silylene reactions with organic azides[14] led to the isolation of silaimines, azidosilanes, or silatetrazolines. In contrast, the formation of **2** shows the unique reactivity of NHC-stabilized dichlorosilylenes and offers a new route to functionalized NHCs. The mechanism[15] is believed to involve the initial formation of the unstable silaimine **2′** under evolution of nitrogen. Silaimine **2′** consists of an easily polarizable Si=N bond and hence abstracts the proton from the C4 position of the coordinated IPr ligand to form **2″**. **2″** rearranges to the stable silyl-substituted NHC **2**, which was isolated as colorless crystals in 87% yield (Scheme 1). It has been shown that substitution of an NHC at the C4 and C5 positions has an influence on the electronic properties of the carbene atom. The C4,C5-dichloro-substituted analogue of IPr is extremely stable[16] and can be handled in air. Therefore, C4 or C5 functionalization of NHCs is extremely important in NHC chemistry.

Scheme 1



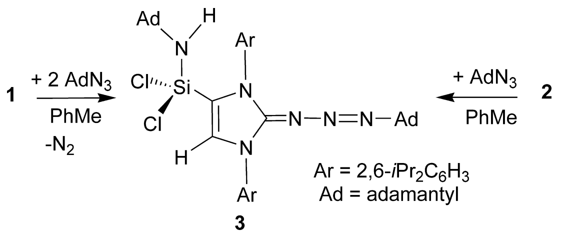
NHC **2** was characterized by elemental analysis and ^1H, ^{13}C, and ^{29}Si NMR spectroscopic studies. The ^1H NMR spectrum of **2** shows resonances that are quite different from those of **1** but close to those of free IPr.[16] The backbone proton of NHC **2** appears as a singlet (δ = 7.45 ppm) that is shifted downfield by $\Delta\delta$ = 0.83 and 1.08 ppm relative to those of IPr (6.62 ppm)[16] and **1** (6.37 ppm), respectively.[5] The new broad resonance appearing at 2.61 ppm is tentatively assigned to the amino proton. In addition to the other expected resonances, the appearance of a new resonance in the ^{13}C NMR spectrum of **2** at 224.21 ppm (C2, carbene carbon)[16] clearly revealed the formation of the new NHC **2**.

Silyl-substituted NHC **2** reacts in a similar way as a nonsubstituted NHC[17] with AdN_3 to form triazene **3**, which can also be prepared by treatment of **1** with 2 equiv of AdN_3 (Scheme 2). Formation of triazene **3** was accompanied by a large upfield shift of the NC*H* resonance in the ^1H NMR spectrum (δ = 5.88 ppm; $\Delta\delta$ = 1.57 ppm). Other ^1H NMR resonances were observed as expected.

Single-crystal X-ray structure analysis[18] confirmed the insertion of the aminosilyl group into the C−H bond at the C4 position of IPr to afford new NHC **2**, which crystallizes in the triclinic space group $P\bar{1}$ with a toluene molecule in the asymmetric unit (Figure 1). The observed imidazol geometry in **2** is very similar to that reported for free IPr.[16] For example, the C1−N1 and C1−N2 bond

10.1021/ja104386g

Scheme 2



distances are close to those in IPr. The N1−C1−N2 angle of 101.40(12)° is identical to that in IPr.[16]

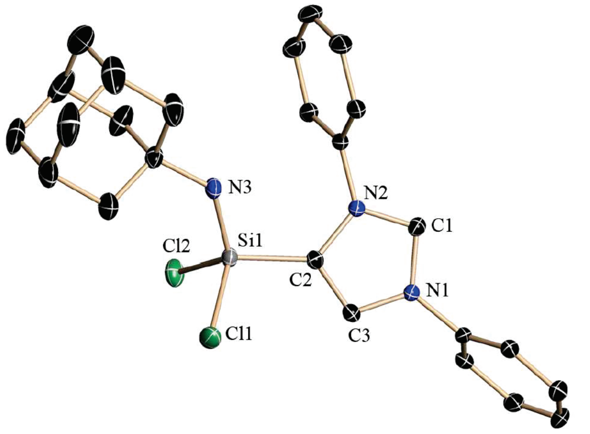


Figure 1. Molecular structure of **2**·PhMe (ellipsoids are shown at the 50% probability level; solvent toluene, isopropyl groups at the ortho positions, and H atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): C1−N2, 1.3654(19); C2−C3, 1.356(2); C2−N2, 1.4124(19); C2−Si1, 1.8417(16); Si1−Cl1, 2.0553(6); N3−Si1, 1.6726(14); N2−C1−N1, 101.40(12); N3−Si1−C2, 109.63(7); C2−Si1−Cl1, 107.50(5); Cl1−Si1−Cl2, 101.93(3).

Triazine **3** crystallizes in the triclinic space group $P\bar{1}$ with two toluene molecules in the asymmetric unit (Figure 2). Comparison of the crystallographic data for **3** with those for reported donor−acceptor triazines[17] revealed that **3** consists of a shorter N−N single bond [N4−N5, 1.380(3) Å] and a longer N−N double bond [N5−N6, 1.257(3) Å]. The C1−N4 bond in **3** is slightly shorter than those in unsubstituted NHC-derived triazenes,[17] indicating better acceptor properties of C1.

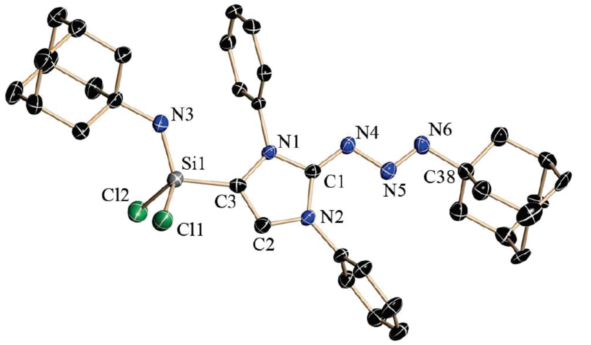


Figure 2. Molecular structure of **3**·2PhMe (ellipsoids are shown at the 50% probability level; solvent toluene, isopropyl groups at the ortho positions, and H atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): C1−N2, 1.382(4); C1−N4, 1.321(4); N4−N5, 1.380(3); N5−N6, 1.257(3); N6−C38, 1.480(4); C2−C3, 1.344(4); C3−N1, 1.406(4); C3−Si1, 1.847(3); Si1−Cl1, 2.0508(13); N3−Si1, 1.665(3); N1−C1−N2, 105.0(2); C1−N4−N5, 111.6(2); N4−N5−N6, 110.9(2); N5−N6−C38, 112.6(2); N3−Si1−C3, 111.51(14); C3−Si1−Cl1, 105.48(10); Cl1−Si1−Cl2, 102.75(6).

Compounds **2** and **3** show ^{29}Si NMR resonances (−30.01 and −34.34 ppm, respectively) consistent[19] with those reported for aminosilanes.

NHC-stabilized dichlorosilylene IPr·$SiCl_2$ **1** reacts in a unique way with 1-azidoadamantane to form aminosilyl-substituted NHC **2**, providing a new method for C4 or C5 functionalization of NHCs. This is the first example of a unique silylene reaction that might be associated with initial formation of unstable silaimine **2′**, which abstracts a proton from the IPr backbone to afford silyl-substituted NHC **2** via the intermediate **2″**. **2** behaves as a free NHC and yields triazene **3** upon reaction with AdN_3 via end-on addition of AdN_3.

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Supporting Information Available: Full experimental details; X-ray crystallographic data for **2** and **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Alternatively, formation of free unstable silaimine $\mathrm{Cl_2Si{=}NAd}$ and its insertion into the C−H bond at the C4 position of the free IPr to afford **2** cannot be ruled out.

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(18) Crystallographic details: Shock-cooled crystals were selected and mounted under a nitrogen atmosphere using X-TEMP2 (see: Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615–619). The structures were solved by direct methods (SHELXS) and refined on F^2 using full-matrix least-squares methods (SHELXL) (see: Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122). The crystal structure data have been deposited with the Cambridge Crystallographic Data Centre as CCDC nos. 7772443 (**2**) and 7772442 (**3**). Space group, cell parameters and R values with $I > 2\sigma(I)$ for **2**: $P\bar{1}$; $a = 11.4299(9)$ Å, $b = 12.0820(10)$ Å, $c = 15.5000(13)$ Å, $\alpha = 106.6130(10)°$, $\beta = 100.313(2)°$, $\gamma = 90.680(2)°$; $wR_2 = 0.0843$, $R_1 = 0.0378$. For **3**: $P\bar{1}$; $a = 11.9004(15)$ Å, $b = 15.3835(19)$ Å, $c = 15.9396(19)$ Å, $\alpha = 76.172(2)°$, $\beta = 73.774(2)°$, $\gamma = 69.913(2)°$; $wR_2 = 0.1409$, $R_1 = 0.0615$.

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