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Synthesis of Stable Pentacoordinate Silicon(IV)−NHC Adducts: An Entry to Anionic N-Heterocyclic Carbene Ligands

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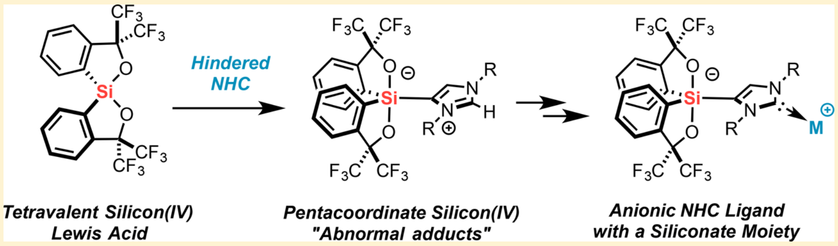
Supporting Information

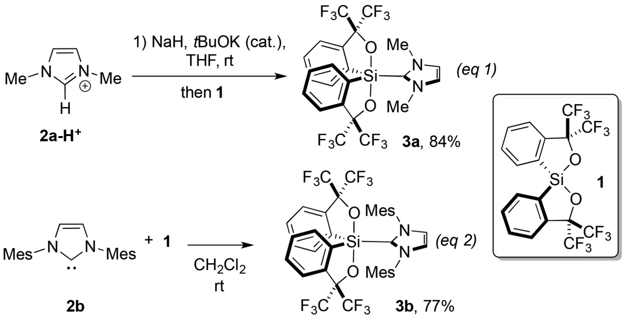


ABSTRACT: This work features the previously undescribed interactions of Martin's spirosilane with different types of N-heterocyclic carbenes (NHCs). The level of interaction proved to be strongly dependent on the size of the Lewis base and could vary from the formation of isolable classical Lewis adducts to abnormal Lewis adducts, as evidenced by X-ray diffraction structure analyses and NMR studies. It has been found that abnormal adducts could be used as precursors for the synthesis of anionic NHCs bearing a weakly coordinating siliconate component. Complexation of these new types of carbenes with gold(I) and copper(I) has been efficiently accomplished. DFT calculations performed on the siliconate-based anionic NHC ligands revealed a high-lying HOMO and therefore a strong σ-donor character.

The concept of Lewis acidity−basicity appears very early in the usual training of chemistry students. Intellectually simple and essentially important in all reactivity developments, it still enjoys important discoveries by playing with the nature of the partners or by involving it in unusual settings. When they are adequately substituted, tetravalent silicon derivatives can exert Lewis acidity, which has triggered versatile synthetic developments in organic chemistry.[1] Among the possible Lewis bases involved in donor−acceptor complexes, N-heterocyclic carbenes (NHCs)[2] have been employed with p-block elements in order to stabilize their low-valence states or to discover new reactivities.[3] Owing to the particular ability of silicon to reach hypercoordination,[4] NHCs have also been used with tetravalent silicon(IV) reagents in various chemical transformations involving putative transient pentacoordinate silicon(IV) intermediates.[5] Tetravalent halosilanes have received particular attention in this area, since they display sufficient electron deficiency to allow the isolation of relatively stable pentacoordinate NHC adducts.[6,7] As an extension, NHC-$SiCl_4$ compounds have judiciously served as precursors for the synthesis of NHC-stabilized silicon(0) species through potassium graphite reductions.[8] However, pentacoordinated Si-NHC adducts featuring nonhalogenated silane partners are very scarce.[9] We therefore considered the possibility to introduce Martin's spirosilane **1** in this forum, since it is an easily accessible derivative with a well-established Lewis acidic character.[10] Nucleophilic attack on the tetrahedral silicon atom of **1** triggers strain release, and synergic stabilization provided by the very electronegative bis-trifluoroalkoxy ligands leads in high yields to various trigonal-bipyramidal pentacoordinate adducts with charged nucleophiles.[11] Interestingly, NHCs have never been studied in this context, which aroused our curiosity.

We first started our study by examining the reactivity of the smallest dimethyl NHC toward spirosilane **1**. Thus, after deprotonation of dimethylimidazolium and subsequent addition of **1**, full conversion of both starting partners was observed to afford the Lewis adduct **3a** in 84% yield after purification (Scheme 1, eq 1). The resulting adduct **3a** proved to be very stable and inert to moisture, as it could resist an aqueous workup, which attests to the strength of the interaction. The

Scheme 1. Interaction between Martin's Spirosilane 1 and NHCs 2a,b: Normal Adducts[a]



[a]Mes = 2,4,6-trimethylphenyl.

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pentacoordinate nature of the silicon atom was confirmed by ^{29}Si NMR spectroscopy, displaying a chemical shift of −83 ppm (δ 7.5 ppm for **1**), which is in accordance with other known pentacoordinate derivatives[12] and thus excluding the formation of adducts with other valences. Solid **3a** could be recrystallized, and an X-ray diffraction (XRD) analysis was performed, confirming the structure and showing as salient features a large O−Si−O angle of 181.9° (113.5° for **1**), an elongated Si−O bond (1.78 Å vs 1.65 Å for **1**), and a Si−C$_{NHC}$ distance of 1.94 Å (Figure 1).

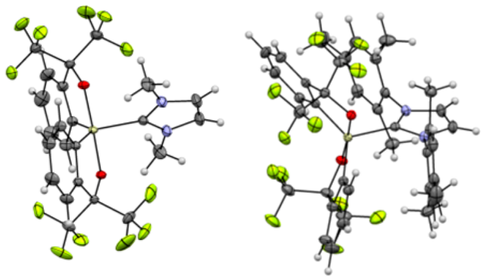
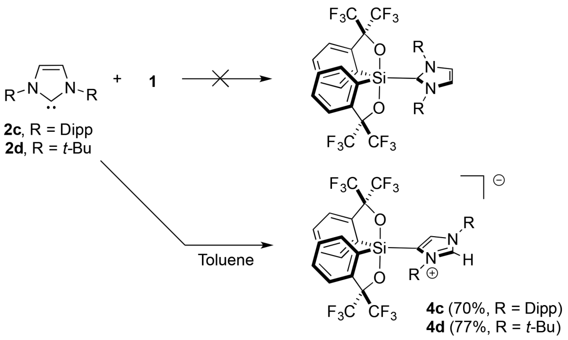


Figure 1. X-ray crystal structures of **3a** (left, CCDC 1523668) and **3b** (right, CCDC 1523669).

This structure represents one of the first well-defined neutral pentacoordinate silicon(IV) adducts formed between an NHC and a nonhalogenated silane derivative. As expected, bringing steric bulk to the NHC had some consequences. When the preformed IMes **2b** was mixed with silane **1**, the complete formation of the Lewis adduct **3b** was still observed (Scheme 1, eq 2), but it appeared to be less stable than **3a** since this adduct is hydrolyzed after a few hours in contact with water. XRD analysis confirmed a similar pentacoordinate silicon(IV) structure but with very slightly looser features in comparison to **3a** since the O−Si−O angle is now 183.7° and the Si−C$_{NHC}$ distance is 1.95 Å (Figure 1). These data reflect the greater steric congestion with the bulkier NHC. Interestingly, a remarkable "through space" C−F coupling[13] of 3.3 Hz between the trifluoromethyl groups and the aromatic *o*-methyls was observed by ^{13}C NMR spectroscopy,[14] suggesting a likely stabilizing interaction of the adduct.

The use of IDipp and ItBu carbenes **2c,d**, respectively, dramatically changed the scenario (Scheme 2). While B(C$_6$F$_5$)$_3$ is known to form a normal Lewis adduct with IDipp (**2c**),[15] no such formation was noticeable when the same NHC was confronted with Lewis acidic silane **1**. The abnormal adduct **4c** was instead smoothly obtained in 24 h at room temperature and was isolated.[16,17] The same behavior was observed with carbene **2d** bearing *t*-Bu groups, and abnormal adduct **4d** was obtained as the only product in only 8 h at room temperature. It is worth mentioning that these zwitterionic adducts are quite robust, since they could be purified by chromatography on silica gel.

Scheme 2. Interaction between Martin's Spirosilane 1 and IDipp (2c) or ItBu (2d): Formation of Abnormal Adducts



The X-ray crystallographic structure of **4c** featured a large O−Si−O angle of 189.2° and a short Si−C$_{NHC}$ distance of 1.91 Å (Figure 2).

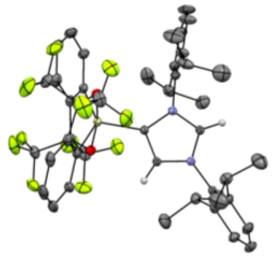
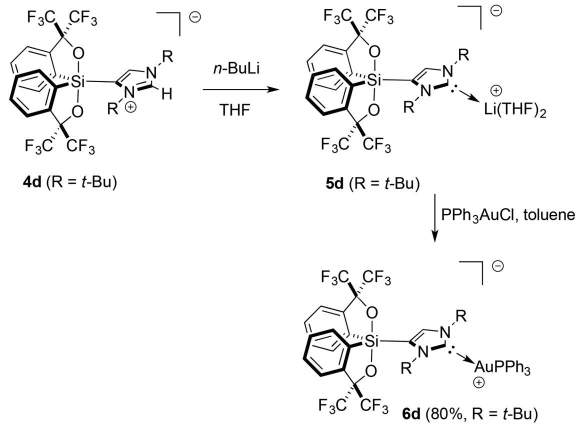


Figure 2. X-ray crystal structure of **4c** (except for the imidazolium ring, hydrogens have been omitted for clarity; CCDC 1523670).

Abnormal adducts **4c,d** are neutral species that could be regarded as imidazolium rings functionalized by a weakly coordinating anion.[18] At this stage, we anticipated the possibility to use these species as precursors of anionic NHCs.[19] Such NHCs bearing weakly coordinating anions are emerging as a new class of promising ligands, since they can deeply modify the physical and chemical properties of metal complexes.[20] To the best of our knowledge, no NHC with a silicon-based anion has been reported so far.[21] To our delight, deprotonation of the abnormal adduct **4d** was cleanly achieved using *n*-butyllithium[16b] as a base, affording the isolable lithium−carbene complex **5d** (Scheme 3). It is noteworthy that similar anionic NHCs bearing a tris(pentafluorophenyl)borate have been previously prepared by Tamm and co-workers[19d] using an alternative indirect route[22] due to difficulties to deprotonate the corresponding borate abnormal adducts. This striking difference clearly points out the robustness of the siliconate moiety, especially toward strong nucleophilic reagents. We next turned our attention to the complexation of the NHC-siliconates toward transition metals. Gratifyingly, the lithium complex **5d** reacted smoothly with (triphenylphosphine)gold(I) chloride. The anionic nature of the ligand and the presence of the lithium cation seem to favor the

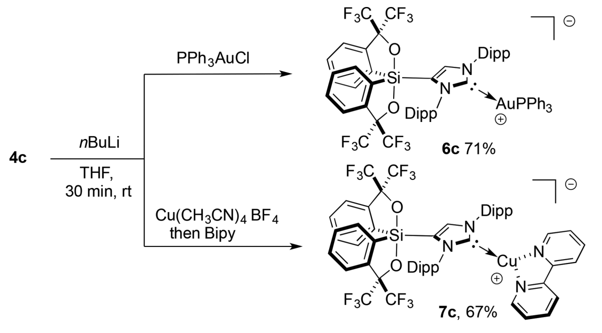
Scheme 3. Deprotonation of Neutral Imidazolium 4d and Synthesis of Gold Complex 6d



chloride dissociation, providing the neutral gold complex **6d**, as confirmed by XRD analysis.

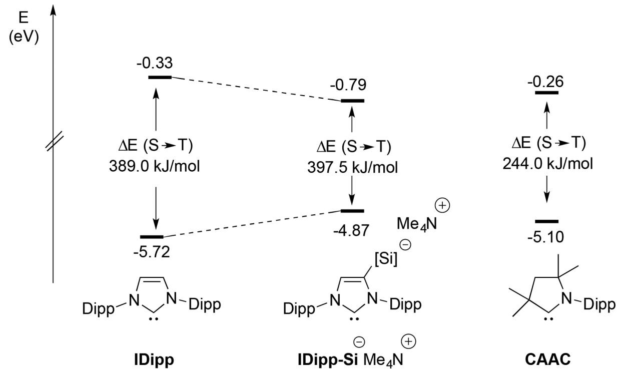
In a similar approach, we could efficiently synthesize the neutral gold complex **6c** and the three-coordinate Cu(I)-NHC complex **7c** from the abnormal adduct **4c** bearing diisopropylphenyl groups (Scheme 4).

Scheme 4. Formation of Gold(I) Complex 6c and Copper(I) Complex 7c



Lithium tetrafluoroborate salt is eliminated during the reaction to afford the neutral copper(I) complex **7c**, stabilized by a bispyridine and an anionic NHC ligand (Scheme 5). The X-ray crystal structures of the neutral gold(I) complex **6c** and copper(I) complex **7c** are shown in Figure 3.

Scheme 5. Frontier Molecular Orbital Comparison of Carbenes IDipp (2c), IDipp-Si$^-$Me$_4$N$^+$, and CAAC at the B3LYP-D3/def2-SV(P) Level



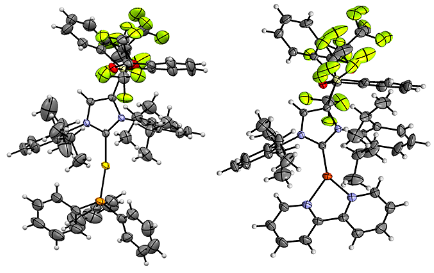


Figure 3. X-ray crystal structure of Au(I) complex **6c** (CCDC 1575949) left and Cu(I) complex **7c** (CCDC 1575951).

Figure 4 displays the HOMO of the anionic NHC-Si **IDipp-Si$^-$**, the deprotonated form of abnormal adduct **4c**, calculated at the B3LYP-D3/def2-SV(P) level of theory, with Me$_4$N$^+$ as a countercation to compensate the charges and make it possible to compare neutral and charged carbenes.[23]

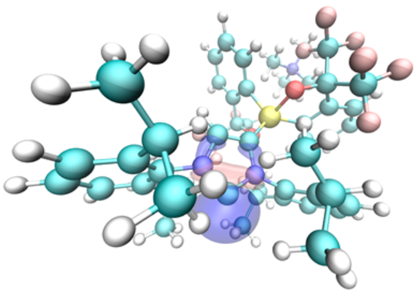


Figure 4. Vizualisation of the HOMO of **IDipp-Si$^-$** with Me$_4$N$^+$ calculated at the B3LYP-D3/def2-SV(P) level of theory and plotted at an isosurface value of 0.05 au.

We choose Me$_4$N$^+$, since it is a noncoordinating cation, and placed it close to the siliconate moiety to avoid spurious interactions with the carbene. It shows that the siliconate moiety, while influencing the carbene, does not modify the ability of this type of divalent carbon to be a σ donor. Frontier orbital energy levels for two classical carbenes (IDipp and CAAC) and our newly developed anionic siliconate NHC (**IDipp-Si$^-$**) have also been calculated and are presented in Scheme 5, along with the corresponding singlet−triplet gap. In comparison to IDipp **2c**, the **IDipp-Si$^-$** carbene displays a much higher lying HOMO (−4.87 vs −5.72 eV), which indicates a stronger σ-donor character.

According to the DFT studies, the HOMO of **IDipp-Si$^-$** carbene is even higher than that calculated for CAAC-Dipp (−5.10 eV), known to be a very strong σ-donor NHC. However, the singlet−triplet gap of **IDipp-Si$^-$** ressembles more that of IDipp than that of CAAC.

In conclusion, this study describes the sterically dependent interactions of Martin's spirosilane with different NHCs, allowing for the isolation of different types of novel neutral pentacoordinate silicon(IV)−NHC adducts to zwitterionic abnormal adducts in the case of bulky Lewis bases. The resulting functionalized imidazolium rings were used as precursors of unprecedented siliconate-based anionic NHCs. Gold(I) and copper(I) complexes bearing these new anionic ligands were cleanly obtained and fully characterized by X-ray diffraction. Finally, DFT calculations revealed a strong σ-donor character that suggests promising applications for further developments in metal catalysis, which may also involve the stereogenicity brought by the siliconate moiety.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00838.

Full experimental details and characterization data (PDF)
Cartesian coordinates of the calculated structures (PDF)

Accession Codes

CCDC 1523668−1523670, 1575949, and 1575951 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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