Frustrated N-heterocyclic carbene–silylium ion Lewis pairs†

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The reaction of the N-heterocyclic carbene 1,3-di-tert-butyl-4,5-dimethylimidazolin-2-ylidene (1b) with trimethylsilyl iodide, triflate and triflimidate [Me₃SiX, X = I, CF₃SO₃ (OTf), (CF₃SO₂)₂N (NTf₂)] by mixing the neat, liquid starting materials afforded the corresponding 2-(trimethylsilyl)imidazolium salts [(1b)SiMe₃]X as highly reactive, white crystalline solids. Only the triflimidate (X = NTf₂) proved to be stable in solution and could be characterized by means of NMR spectroscopy (in C₆D₅Br) and X-ray diffraction analysis, whereas dissociation into free 1b and Me₃SiOTf was observed for the triflate system, in agreement with the trend derived by DFT calculations; the iodide was too insoluble for characterization. The compounds [(1b)SiMe₃]X showed the reactivity expected for frustrated carbene–silylium pairs, and treatment with carbon dioxide, tert-butyl isocyanate and diphenylbutadiyne gave the 1,2-addition products [(1b)CO₂SiMe₃]X (X = I, OTf, NTf₂), [(1b)C(NtBu)OSiMe₃]OTf and [(1b)C(Ph)C(SiMe₃)CCPh]OTf, respectively. Upon reaction with [AuCl(PPh₃)], metal–chloride bond activation was observed, with formation of the cationic gold(I) complexes [(1b)Au(PPh₃)]X (X = OTf, NTf₂).

Introduction

Frustrated Lewis pairs (FLPs), such as the well-studied phosphine–borane combination P(tBu)₃/B(C₆F₅)₃,¹–⁵ represent a growing class of systems that are capable of activating small molecules, most notably dihydrogen, as a result of the unquenched and mutual reactivity of the Lewis base and acid.⁶ Accordingly, exposure of an equimolar solution of P(tBu)₃ and B(C₆F₅)₃ in toluene to an atmosphere of H₂ swiftly affords the phosphonium borate [tBuPH][HB(C₆F₅)₃] under ambient conditions.¹,² Extensive theoretical studies³–⁵ of heterolytic dihydrogen splitting with this system consistently indicate the importance of secondary noncovalent interactions for the formation of an encounter complex (or prepared Lewis pair) in which the donor and acceptor sites are suitably pre-organized for synergistic interaction with an incoming H₂ molecule. A similar mechanistic proposal had been developed for the frustrated carbene–borane Lewis pair 1a/B(C₆F₅)₃,⁷ which exhibits a particularly strong propensity for heterolytic dihydrogen cleavage;⁷,⁸ this can be ascribed to an enhanced cumulative acid–base strength and to the strongly exergonic formation of the imidazolium salt 2a (Scheme 1).⁹

The high reactivity of this FLP was also exploited for the activation and fixation of numerous other small molecules,¹⁰ i.e. ammonia,⁸ tetrahydrofuran,⁷ alkynes,¹¹ white phosphorus,¹² sulfur,¹³ carbon dioxide and nitrous oxide,¹⁴ and it was also used as a dehydrogenation reagent.¹⁵ In the absence of substrates, however, 1a/B(C₆F₅)₃ does not become isolable as a weakly bound “normal” carbene–borane adduct, but

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Scheme 1 Reactivity of frustrated carbene–borane Lewis pairs.
slowly undergoes self-deactivation within 2 h at room temperature to form the significantly more stable “abnormal” adduct 3. Although initially unwanted, this observation triggered the development of anionic N-heterocyclic carbenes with a weakly coordinating anionic moiety (WCA-NHC), which can be formally derived from 3 by deprotonation. During our quest to prevent such deactivation reactions, numerous FLPs were studied with variation of the N-heterocyclic carbene (NHC), and also of the boron component. Thereby, carbene 1b proved particularly useful, since the presence of methyl groups in the 4,5-positions affords a sterically even more demanding carbene ligand, and self-deactivation of 1b/B(C6F5)3 is significantly slowed down in comparison with 1a/B(C6F5)3. Nevertheless, formation of the zwitterionic fluoro-borate 4 by C–F activation was found to proceed within 4 d at room temperature (Scheme 1). 

As an alternative to boranes, more strongly Lewis acidic silylium ions have also been introduced to FLP chemistry, and it was shown that triarylsilylum salts of the type [Ar3Si][B(C6F5)4] react with bulky tertiary phosphines to afford frustrated Lewis pairs that are able to split dihydrogen irreversibly if an encoun-
dered bulky carbene 1b reacts with bulky tertiary phosphines to afford frustrated Lewis pairs that are able to split dihydrogen irreversibly if an encounter complex with appropriate spatial requirements is formed. More recently, the thermally robust phosphine–silylium adduct [(Bu),P–Si(iPr)2][B(C6F5)3] was reported to undergo H2 and D2 cleavage at 90 °C with formation of the silane (iPr)3SiH and the phosphonium borate ([(Bu)3P]H)[B(C6F5)3]2. In view of these results, it was an obvious choice to aim at combining NHCs with silylium ions; however, for the present study, more readily available silylium sources such as the commercially available trimethylsilyl iodide, triflate and triflimidate were chosen. In previous reports, the reactions of Me3SiI and Me3SiOTf with wCO2 reduction with silanes or polymerisation of silicon-containing compounds.

### Results and discussion

#### Generation of carbene–silylium adducts

Our initial efforts to isolate the carbene–silylium adducts [(1b)SiMe3]X (X = I, OTf, NTf2) by mixing 1b with Me3SiX were ambiguous, and only the reaction with Me3SiNTf2 produced a precipitate of the triflimidate [(1b)SiMe3]NTf2 from hexane or toluene solution in satisfactory yield. Since the silyl reagents and also carbene 1b are liquid at room temperature, equimolar amounts of 1b and Me3SiX were mixed by blending in a Teflon vial under argon, resulting in immediate solidification to afford [(1b)SiMe3]I, [(1b)SiMe3]OTf and [(1b)SiMe3]NTf2 as colourless materials in quantitative yield and analytically pure form after careful washing with cold hexane in order to remove any trace of unreacted starting materials (Scheme 2). NMR spectroscopic characterisation in solution was hampered by the high reactivity of the compounds, which decompose rapidly in deuterated solvents such as CDCl3, C6D6, and THF-d8 and are only sparingly soluble in toluene-d8. However, instructive NMR spectra could be recorded for the triflate and triflimidate salts in deutero-bromobenzene (C6D5Br), although the samples always showed contamination with the corresponding imidazolium salt, in which a hydrogen atom replaces the Me3Si group. The 13C NMR spectra reveal distinct differences, since the spectrum of [(1b)SiMe3]OTf shows a resonance at 210.5 ppm, indicating the presence of the free carbene at 1.55 (tBu) and 2.09 ppm (Me) and also for the methyl groups of Me3SiOTf at 0.20 ppm. The formation of the free carbene in 1b with Me3SiOTf resulted in rapid formation of the 4-(trimethylsilyl)imidazolium triflate 8 (abnormal carbene–silylium adduct, Fig. 1). The latter reaction clearly forms a sterically even more stable abnormal adduct 8 in a similar fashion as described for 3 (vide supra). Therefore, the reactivity of 1b towards Me3SiX was investigated in the expectation that the presence of the 4,5-methyl substituents might render the carbene–silylium adducts [(1b)SiMe3]X (X = I, OTf, NTf2) more stable and even isolable. It should be noted that these studies are also highly relevant in view of the interest in NHC-mediated activation of tetravalent silicon compounds, since NHC–Si interactions have been hypothesized for the mechanistic course of various catalytic reactions such as cyanosilylation, CO2 reduction with silanes or polymerisation of silicon-containing compounds.

#### Scheme 2

Reaction of 1b with trimethylsilyl iodide, triflate and triflimidate; mixing liquid 1b and liquid Me3SiX affords quantitatively solid [(1b)SiMe3]X.
of “frustration”.

Theoretical calculations of carbene–silylium adduct formation

To rationalize the reactivity of the carbene 1b towards the reagents Me₅SiX (X = I, OTf, NTf₂), the thermodynamics of adduct formation were calculated for the ion pairs [(1b)SiMe₅]⁺ and also for the corresponding adducts [(1c)SiMe₅]⁺ containing the sterically less encumbered carbene 1,3,4,5-tetramethylimidazolin-2-ylidene (1c). The anions were generally placed underneath the plane of the resulting 2-(trimethylsilyl)imidazolium salt, and the structures were freely refined. We employed the functionals M05-2X, M06-2X and B97-D, which were developed by Zhao and Truhlar

and by Grimme to describe conveniently noncovalent and long-range dispersion interactions that can be expected to contribute significantly to the overall binding, in particular for the sterically congested adducts of carbene 1b. Table 1 summarizes the enthalpies (ΔH) and Gibbs free energies (ΔG) at 298 K for the formation of the adducts [(1b)SiMe₅]X and [(1c)SiMe₅]X, and Fig. 3 shows a bar diagram for the values derived with the B97-D functional.

In addition, the gas-phase association energies were calculated for the reaction of the carbene 1b and 1c with a “naked” [Me₅Si]⁺ cation in the absence of any counterion (Table 1). Since the reverse reaction, the dissociation of [(1b)SiMe₅]⁺ and [(1c)SiMe₅]⁺ into the free carbene and [Me₅Si]⁺, can be defined as the trimethylsilylum affinity (TMSA = ΔH), high TMSA values of ca. 75 kcal mol⁻¹ for 1b and ca. 92 kcal mol⁻¹ for 1c can be derived for both carbones as expected for the combination of very strong nucleophiles and electrophiles. Nevertheless, the TMSA value of 1b is significantly smaller than that of 1c, which confirms the lower stability (by ca. 17 kcal mol⁻¹) of the sterically overcrowded system. Notably, all calculations reproduce the highly distorted structure of the cation [(1b)SiMe₅]⁺ found in the solid state (Fig. 2).†

Table 1. Enthalpies (ΔH) and Gibbs free energies (ΔG) at 298 K in kcal mol⁻¹ for the formation of carbene–silylium adducts

<table>
<thead>
<tr>
<th>Adduct</th>
<th>M05-2X</th>
<th>M06-2X</th>
<th>B97-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(1b)SiMe₅]⁺</td>
<td>ΔH</td>
<td>ΔG</td>
<td>ΔH</td>
</tr>
<tr>
<td>[(1b)SiMe₅]OTf</td>
<td>-0.2</td>
<td>14.6</td>
<td>-1.8</td>
</tr>
<tr>
<td>[(1b)SiMe₅]NTf₂</td>
<td>-11.2</td>
<td>4.1</td>
<td>-14.0</td>
</tr>
<tr>
<td>[(1b)SiMe₅]⁺</td>
<td>-73.7</td>
<td>-56.8</td>
<td>-75.4</td>
</tr>
<tr>
<td>[(1c)SiMe₅]</td>
<td>-22.8</td>
<td>-10.2</td>
<td>-23.4</td>
</tr>
<tr>
<td>[(1c)SiMe₅]NTf₂</td>
<td>-35.3</td>
<td>-22.4</td>
<td>-36.5</td>
</tr>
<tr>
<td>[(1c)SiMe₅]⁺</td>
<td>-92.3</td>
<td>-77.2</td>
<td>-93.8</td>
</tr>
</tbody>
</table>


§ M05-2X, M06-2X, and B97-D/6-311G(d,p) enthalpies and Gibbs free energies at 298 K. ‖ 1b = 1,3-di-tert-butyl,4,5-dimethylimidazol-2-ylidene; 1c = 1,3,4,5-tetramethylimidazol-2-ylidene; if present, the anion X was placed underneath the plane of the resulting 2-(trimethylsilyl)imidazolium salt, and the structure was freely refined.

§ TMSA (trimethylsilylum affinity).
The calculations for the ion pairs \([1b]\text{SiMe}_3X\) and \([1c]\text{SiMe}_3X\) reveal a marked influence of the counterion X, and in particular, the triflimidates (X = NTf$_2$) of both systems are significantly more stable than the corresponding triflates and iodides; this reflects the effect of a highly delocalized counteranion,

but might also indicate a favourable interaction with the 2-(trimethylsilyl)imidazolium cation. Since such interactions also play an important role in the solid state, we believe that the gas-phase calculations at hand will allow us to predict or substantiate trends in reactivity. All three functionals produce qualitatively similar results, with the B97-D values, which are assembled in Table 2, consistently yielding lower energies. The following discussion will be restricted to the B97-D values, which are assembled in Fig. 3. For \([1c]\text{SiMe}_3X\), the formation of all adducts is markedly exothermic and exergonic, which clearly suggests that frustrated Lewis pair behaviour cannot be expected for the combinations \(1c/\text{TMSX}\) and that complete formation of ion pairs can be expected. In contrast, the adducts \([1b]\text{SiMe}_3X\) are significantly less stable, with their stability following the order \([1b]\text{SiMe}_3I\) (\(\Delta H = -5.8\) kcal mol$^{-1}$) < \([1b]\text{SiMe}_3\)OTf (\(\Delta H = -9.0\) kcal mol$^{-1}$) < \([1b]\text{SiMe}_3\)NTf$_2$ (\(\Delta H = -19.0\) kcal mol$^{-1}$). Although entropy effects should not be overestimated, it can be stated that the formation of the triflimidate was calculated to be slightly exergonic (\(\Delta G = -3.9\) kcal mol$^{-1}$), whereas the triflate (\(\Delta G = 6.1\) kcal mol$^{-1}$) and iodide (\(\Delta G = 9.3\) kcal mol$^{-1}$) form endergonically. These theoretical results are in full agreement with the experimental observation that dissolution of the triflate in bromobenzene leads to predominant dissociation into \(1b/\text{Me}_3\text{SiOTf}\), whereas the starting materials \(1b/\text{Me}_3\text{SiNTf}_2\) are not observed for the triflimidate; this allowed us to characterize the latter by means of NMR spectroscopy and X-ray diffraction analysis (vide supra).

To establish a potential pathway for the formation of the 2-(trimethylsilyl)imidazolium salts \([1b]\text{SiMe}_3X\), we assumed that the initial binding between the Lewis basic carbene \(1b\) and the Lewis acidic \(\text{Me}_3\text{SiX}\) reagent will occur according to the established model of n-$\pi^*$ interaction,\(^{26,29}\) which leads to polarization of the adjacent Si-X bond by formation of a hyper-valent silicon species. In the case of strong polarization, this may be followed by subsequent heterolytic Si-X bond cleavage and ionization. Since the same considerations are valid for the reverse reaction, we obtained suitable starting geometries based on the calculated structures of \([1b]\text{SiMe}_3X\) (C), which were modified by placing the counterion X opposite to the carbene ligand. Full refinement without any geometrical constraints afforded a second set of ionic minimum structures B with weak Si-X interactions, which are 15.8 (X = I), 13.4 (X = OTf) and 13.0 kcal mol$^{-1}$ (X = NTf$_2$) higher in energy than the global minima. For all three systems, we were then able to locate transition states (TS), which connect the ionic local minima B with covalent adducts of the type \(1b/\text{Me}_3\text{SiX}\) (A). The transition state structures exhibit hypercoordinate silicon atoms with distorted trigonal-bipyramidal geometries (C$_{\text{carbene}}$-Si-I = 178.2°, C$_{\text{carbene}}$-Si-O = 178.1° and C$_{\text{carbene}}$-Si-N = 170.5°), in which the trigonal-planar [Me$_3$Si]$_i^+$ cation (C-Si-C angle sums = 360°) is flanked by loosely bound counterions and carbene ligands (C$_{\text{carbene}}$-Si = 2.434 Å for X = I, C$_{\text{carbene}}$-Si = 2.401 Å for X = OTf, C$_{\text{carbene}}$-Si = 2.612 Å for X = NTf$_2$). It is particularly noteworthy that very low barriers are found for the iodide and triflate systems (\(\Delta \Delta E \approx 0\) kcal mol$^{-1}$, X = I; \(\Delta \Delta E = 0.8\) kcal mol$^{-1}$, X = OTf),\(^{10}\) which can be expected to rearrange readily to \(1b/\text{Me}_3\text{SiX}\), whereas moderately higher barriers are found for both the formation and cleavage of \([1b]\text{SiMe}_3\)NTf$_2$. The resulting adducts A are located -8.8 (X = I), -10.8 (X = OTf) and -9.0 kcal mol$^{-1}$ (X = NTf$_2$) below the energy of the free, isolated starting materials, but, surprisingly, they do not display any direct C-Si contacts between the carbene carbon and the silicon atoms, as indicated by very long C$_{\text{carbene}}$-Si distances of 3.965 Å for X = I, 4.117 Å for X = OTf and 3.933 Å for X = NTf$_2$. Instead, the TMS groups display a series of short intermolecular C-H···C and C-H···N contacts in the range 2.53-2.78 Å, which probably contribute significantly to the overall binding energy.

It should be emphasized that the potential-energy profiles shown in Fig. 4 can be expected to be strongly affected by solvent effects, since a transition from covalent to ionic structures is undergone, which proceeds via strongly polarized transition states. Nevertheless, we believe that the gas-phase calculations at hand allow us to rationalise the different reactivities of the \(1b/\text{Me}_3\text{SiX}\) systems, with the most weakly coordinating triflimidate ion affording a persistent ionic compound \([1b]\text{SiMe}_3\)NTf$_2$, whereas the corresponding iodide and triflate only form by mixing the neat starting materials, but are readily cleaved upon dissolution.

Reactivity of carbene–silylium Lewis pairs – addition reactions

The structural distortions determined experimentally and theoretically for the carbene–silylium adducts \([1b]\text{SiMe}_3X\), together with their obvious lability, prompted us to investigate their behaviour as potential frustrated Lewis pairs. However, dihydrogen cleavage with the triflate and triflimidate systems
proved unsuccessful under the conditions described for isolable phosphine–silylim adduct [(Bu)2P·Si(iPr)2][B(C6F5)4].24 In view of the general interest in the reduction of carbon dioxide by silanes, which can for instance be mediated by frustrated Lewis pairs,41 silylium ions,42 and N-heterocyclic carbenes,43 carbon dioxide fixation was studied by purging the Me3SiI system. TS = transition state.

Although slow decomposition in chlorinated solvents was observed in a similar fashion as described for carbene–borane systems,14,44 satisfactory NMR spectra could be recorded in CD2Cl2, affording 13C NMR signals for the carboxylic group at ca. 158 ppm, similar to the value for the adducts 1b·CO2 (165.5 ppm)14 and 1b·CO2·B(C6F5)3 (157.7 ppm)14 and shifted by approximately 33 ppm to lower field compared to free CO2.45 Crystals of [9]OTf suitable for X-ray diffraction analysis were obtained from THF solution at ~30 °C; the resulting molecular structure is shown in Fig. 5. The structural features of the CO2 moiety, with C–O bonds of 1.2083(16) and 1.3090(15) Å, are identical within error limits to the values found for the carbene–borane adduct 1b·CO2·B(C6F5)3, and the same perpendicular orientation (86.5°) to the imidazole plane is also observed.14

The fixation of the CO2 congener tert-butyl isocyanate was also studied, and its addition to a suspension of [(1b)SiMe3]-OTF in diethyl ether afforded the adduct [10]OTf as a colourless solid in 79% yield (Scheme 3). The 1H NMR spectrum (in CD2Cl2) exhibits four singlets at 0.22, 1.35, 1.73 and 2.42 ppm in a 9:9:18:6 ratio, which can be assigned to the Me3Si and two independent cations and anions in the asymmetric unit at 30 °C; the resulting NMR spectra could be recorded in the three different types of methyl groups, respectively. Single crystals of [10]OTf were obtained from Et2O/CH2Cl2 solution at ~30 °C, and the molecular structure was established by X-ray diffraction analysis (Fig. 6). The compound crystallizes with two independent cations and anions in the asymmetric unit with very similar structural parameters, which will be discussed for cation 1 only. The trimethylsilyl group is bound to the oxygen atom with Si–O = 1.7103(10) Å, which affords a shorter C1–C14 bond length of 1.5038(18) Å and a longer C14–O1 bond length of 1.3564(16) Å in contrast to neutral NHC-isocyanate adducts.46 The entire isocyanate moiety (Si–O1–C14–N3–C15) is planar and adopts a perpendicular orientation (89.4°) to the imidazole ring.

Scheme 3 Addition reactions of [(1b)SiMe3]X with carbon dioxide, tert-butyl isocyanate and diphenylbutadiyne.

Fig. 4 Potential–energy profile for the reaction of 1b with Me3SiX (X = I, blue; X = OTf, green; X = NTF2, red). Values correspond to ΔE = zero-point uncorrected B97-D/6-311G(d,p) electronic energies; ΔH = enthalpies at 298 K (round brackets, and ΔG = Gibbs free energies at 298 K (square brackets). Stick models are provided for the stationary points of the 1b/Me3Si system. TS = transition state.

Fig. 5 ORTEP diagram of cation in [9]OTf with thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (°): Si–O1 1.7399(10), Si–C16 1.8417(16), Si–C17 1.8469(15), Si–C15 1.8507(15), C1–C14 1.5129(17), N1–C1 1.3506(16), C14-O1 1.3090(15), C14–O2 1.2083(16), O1–Si–C16 101.30(6), O1–Si–C17 108.30(6).
Reactivity of carbene–silylium Lewis pairs – activation of metal–halide bonds

The high reactivity of the carbene–silylium pairs prompted us to employ \([\text{[1b]}\text{SiMe}_3\text{]}\text{OTf}\) and \([\text{[1b]}\text{SiMe}_3\text{]}\text{NTf}_2\) as metal-free carbene-transfer reagents by taking advantage of the favourable formation of volatile trimethylsilyl halides.\(^{50}\) In view of the prominent role of cationic gold(i) complexes in homogeneous catalysis,\(^{51}\) the gold(i) chloride complex \([\text{AuCl}(\text{PPh}_3)]\) was chosen as model system. Treatment of this starting material with \([\text{[1b]}\text{SiMe}_3\text{]}\text{OTf}\) and \([\text{[1b]}\text{SiMe}_3\text{]}\text{NTf}_2\) in chlorobenzene solution furnished the complexes \([\text{[1b]}\text{Au}(\text{PPh}_3)\text{]}\text{X}\), \([\text{[12]}\text{X} = \text{OTf}, \text{NTf}_2\), in high yield as colourless solids, which were isolated by precipitation with hexane and filtration (Scheme 4). NMR spectra were recorded in \(\text{CD}_2\text{Cl}_2\) solution, revealing \(^{31}\text{P}\) NMR signals at ca. 38 ppm and \(^{13}\text{C}\) NMR signals at ca. 184 ppm with \(\delta_{\text{CP}} = 125\), which is in agreement with the data reported for other NHC-phosphine gold(i) complexes.\(^{52}\)

The molecular structures of both complexes were established by X-ray diffraction analyses, revealing almost identical structural parameters. Fig. 8 shows an ORTEP diagram of the cation in \([\text{[12]}\text{NTf}_2\), and further discussion will be confined to this compound. On first glance, the structural characteristics are unremarkable, with the cation displaying an almost linear C1–Au–P axis of 174.43(10)° and Au–C1 and Au–P distances of 2.063(3) and 2.2777(9) Å, which fall in the ranges found for related systems.\(^{16,17,52}\) For instance, gold–carbon and gold–phosphorus bond lengths of 2.044(4) Å and 2.275(1) Å were reported for the closely related complex \([\text{Au(1a)}(\text{PPh}_3)\text{]}\text{PF}_6\).\(^{53}\) However, closer inspection of the structures reveals distinct differences, since the carbene ligand in the latter complex shows the expected coplanar orientation with the C–Au–P axis, whereas pronounced twisting is observed for \(\text{12}\), with the gold atom being displaced by 0.753(6) Å from the imidazole plane, providing a remarkably large “pitch angle” of 20.5°.\(^{54}\) In
addition, two conspicuously short Au–H contacts of ca. 2.4 Å are found, involving a methyl hydrogen atom of each tert-butyl group (at C6 and C13, Fig. 8). These are among the shortest gold–hydrogen bonds known, and their occurrence, together with the overall structural distortion, can be ascribed to hindered rotation of the tBu substituents due to steric interaction with the 4,5-methyl groups (buttressing effect). It is anticipated that coordination to other metal ions such as Ru(iii), Rh(i) or Ir(i) might lead to C–H activation and formation of cycloammediated NHC complexes.

DFT calculations were carried out to assess the energy difference between the twisted structure found in the solid state and a structure with a coplanar orientation of the imidazole plane towards the C1 atom (analogous to the known inversion process of amines), which interconverts the two twisted structures A and B, and the small barrier of 2.9 kcal mol⁻¹ indicates that the observation of this process cannot be monitored by NMR spectroscopy.

Conclusions

It was demonstrated that the stability of trimethylsilylium adducts of the sterically demanding N-heterocyclic carbene is strongly affected by the nature of the counterion and increases with decreasing nucleophilicity of the ion X or with increasing Lewis acidity of the silylating agent Me₃SiX (X = I, OTf, NTf₂). For all systems 1b/Me₃SiX, the reactivity expected for frustrated Lewis pairs, such as CO₂ fixation, was observed, but it is unclear whether the reactions occur by insertion into the C–Si bond of an isolable carbene–silylium adduct or proceed by stepwise addition of Lewis acid and base, and the reaction path is again likely to depend on the counterion X. Accordingly, the term “frustrated Lewis pair” has to be used with caution, since the carbene and the counterion compete for the Lewis acid component, the trimethylsilylium ion, which cannot be expected to be freely available at any time. This might also explain the inability of these systems to split dihydrogen. Alternatively, these carbene–silylium combinations can also be regarded as tamed silylium ions, which have found numerous applications in Lewis acid catalysis, and in view of numerous reports on NHC-mediated activation of silicon(v) compounds, the potential use of carbene–silylium Lewis pairs for applications in catalysis can be envisaged. As demonstrated for the preparation of cationic NHC–gold(i) complexes, the systems 1b/Me₃SiX promote metal–halide bond activation and allow for the simultaneous introduction of carbene and a weakly coordinating counterion such as triflate or triflimidate, which might become a useful method for the preparation of coordinatively unsaturated and/or catalytically active transition metal complexes.

Acknowledgements

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Notes and references

32 [(1b)SiMe3][Br(C4F9)] was prepared by reaction of the FLP 1b[B(3,5-C6H4F3)2] with trimethylsilyl azide; 7 was prepared as previously described.† The X-ray crystal structures of both compounds are presented in the ESI.†
40 Furthermore, this indicates a very shallow potential energy surface (PES), which might be held responsible for the fact that the transition state for the triflate (green line) has a lower Gibbs free energy than the second ionic minimum structure B. Since all thermodynamic data are computed by means of statistical thermodynamics, and vibrations are treated as harmonic oscillators, especially for low frequency modes, large errors can be expected, see: P. Y. Ayala and H. B. Schlegel, *J. Chem. Phys.*, 1998, **108**, 2314–2325.


