

## Mono- and Diaminocarbenes from Chloroiminium and -amidinium Salts: Synthesis of Metal-Free Bis(dimethylamino)carbene

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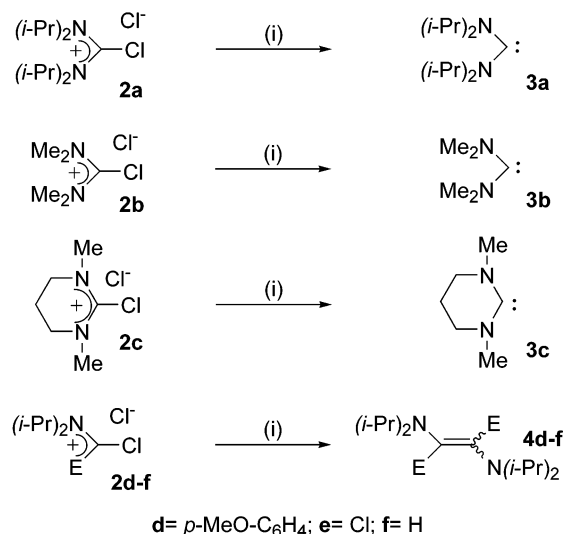
Deprotonation of formamidinium salts is by far the most popular way to generate diaminocarbenes.<sup>1</sup> A major advantage of this method is that deprotonation is a rapid reaction, even at low temperatures. However, hindered strong anionic bases are required, especially for open-chain diaminocarbenes, which have higher  $pK_a$  values<sup>2</sup> and are more susceptible to addition of nucleophilic species than imidazolium ions; yet side reactions are sometimes observed.<sup>3</sup> Moreover, for unhindered diaminocarbenes, the use of strong anionic bases carrying alkali metal counterions produces complexed carbenes.<sup>4</sup> All attempts so far to remove the metal from bis(dimethylamino)carbene have resulted in the destruction of the carbene;<sup>4a</sup> it has also been reported that even by using crown ethers, tertiary complexes involving the metal are formed.<sup>4a</sup> Alkali metal coordination to carbenes is particularly important with regard to the rate and mechanism of the dimerization. Alder suggested that metal ions might act as Lewis acid catalysts for dimerization, as is observed for protons,<sup>5</sup> but strong complexation might also eventually suppress dimerization.<sup>2a,5a,b</sup> All of the other methods known to generate diaminocarbenes, which includes desulfurization of thioureas,<sup>6</sup> involved drastic experimental conditions and are not easily applicable to unhindered carbenes. Here, we report a new synthetic route allowing for the formation of stable metal-free diaminocarbenes and transient monoaminocarbenes.

Bis(trimethylsilyl)mercury **1**<sup>7</sup> is known as a silylating agent<sup>8a</sup> and has been used to dechlorinate dichlorostannanes<sup>8b</sup> and boranes,<sup>8c</sup> allowing for the generation of stannylenes and borylenes. This reagent, which is highly soluble in classical solvents, appeared to be an interesting candidate for the generation of aminocarbenes from chloroamidinium and -iminium salts, themselves readily prepared from commercially available urea or amides.

To test the validity of this approach, we first added a THF solution of the mercury derivative **1** to a THF suspension of chlorotetra(isopropyl)formamidinium chloride **2a**<sup>9a</sup> at  $-78$  °C. After the mixture was warmed to room temperature, a clear yellow solution with a drop of mercury metal was observed. The mercury was readily separated, and after evaporation of the solvent and chlorotrimethylsilane,<sup>10</sup> carbene **3a** was obtained in near quantitative yield (Scheme 1).<sup>11</sup> The spectroscopic data for **3a** were identical to those previously reported,<sup>12</sup> but obviously in the case of **3a**, the buttressing effect of the isopropyl groups prevents complexation of alkali metals.

Having demonstrated the validity of our approach, we then study the reaction of **1** with the unhindered chlorotetramethylformamidinium chloride **2b**.<sup>9b</sup> The reaction was carried out in THF at  $-78$  °C and was monitored by <sup>13</sup>C NMR spectroscopy. Two signals were obtained at 259.7 and 42.2 ppm. As expected, the carbene carbon chemical shift is substantially deshielded as compared to those of the experimentally observed lithium complexes (238.4–244.0 ppm), but very close to the calculated values (246.9–265.1 ppm).<sup>2a,4a</sup>

Scheme 1<sup>a</sup>



<sup>a</sup> (i)  $\text{Hg}(\text{SiMe}_3)_2$  (1.1 equiv), THF,  $-78$  °C;  $-\text{Me}_3\text{SiCl}$ ,  $-\text{Hg}$ .

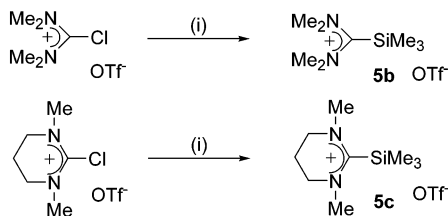
Importantly, the lithium complex of **3b** was reported to have a half-life at room temperature of a few hours in THF and a few days in toluene before the on-set of dimerization occurred.<sup>4a</sup> We observed a much shorter half-life, a few hours at  $0$  °C prior to decomposition that lead to a complex mixture, with no traces of dimer being detectable. These results clearly show that alkali metal complexation considerably stabilizes the carbene moiety. Moreover, although this does not demonstrate that free diaminocarbenes cannot dimerize in the absence of catalysts, it does raise the question.

Only one stable tetrahydropyrimid-2-ylidene, bearing bulky isopropyl groups at nitrogen, has been reported.<sup>4a</sup> To test the scope of our new synthetic method, we reacted **1** with 1,3-dimethyltetrahydropyrimidin-2-ium chloride **2c**.<sup>9c</sup> The metal-free carbene **3c**<sup>13</sup> was obtained, although with only 50% conversion. Carbene **3c** is perfectly stable at room temperature and can even be sublimed at  $40$  °C. However, traces of bis(trimethylsilyl)mercury **1** also sublimed under the same conditions, preventing the isolation of pure carbene **3c**. Not surprisingly, addition of 1 equiv of lithium, sodium, and potassium bis(trimethylsilyl)amide to toluene solutions of **3c** resulted in the formation of the corresponding complexes as shown by the resulting <sup>13</sup>C NMR data (Table 1). All of these complexes are stable at room temperature and show no tendency to dimerize.

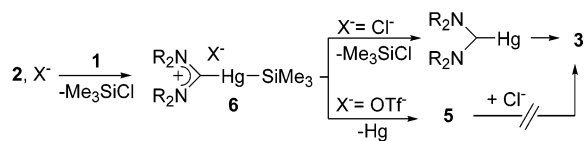
The bis(trimethylsilyl)mercury route is not limited to the preparation of stable carbenes. Indeed, with the same experimental conditions, the dimers of the *p*-methoxyphenyl- ( $E/Z = 90/10$ ), chloro- ( $E$ ), and hydrogen- ( $E$ ) diisopropylaminocarbene **4d–f** were obtained in good yields.<sup>13</sup> Obviously, the energy barrier for

**Table 1.**  $^{13}\text{C}$  NMR Data (ppm) of Metal-Free Carbene **3c**, and of Its Li, Na, and K Complexes

	C <sub>carbene</sub>	NCH <sub>2</sub>	NCH <sub>3</sub>	CH <sub>2</sub>
<b>3c</b>	242.7	43.9	41.4	20.9
<b>3c</b> -Li	219.4	47.4	42.1	20.8
<b>3c</b> -Na	224.9	47.3	41.8	20.9
<b>3c</b> -K	241.0	43.8	42.1	21.2

**Scheme 2**<sup>a</sup>

<sup>a</sup> (i)  $\text{Hg}(\text{SiMe}_3)_2$  (1.1 equiv), THF,  $-78^\circ\text{C}$ ;  $-\text{Hg}$ .

**Scheme 3**

the dimerization of carbenes **3d–f** is inferior to that for diamino-carbenes because the vacant carbene orbital is much lower in energy due to the donation of only one nitrogen lone pair.<sup>14</sup>

It is important to note that the counterion associated with the starting materials plays an important role. When the trifluoromethanesulfonate salts of **2b,c** were used instead of the chloride salts, carbenes **3b,c** were not obtained; instead, the trimethylsilyl amidinium salts **5b,c** were formed and isolated in almost quantitative yields (Scheme 2).<sup>10,13</sup>

The latter results shed light on the possible mechanisms involved in these reactions. As postulated independently by Mitchell<sup>8b</sup> and Eisch et al.,<sup>8c</sup> the first step is probably a metathesis reaction with formation of the mercury derivative **6**.<sup>15</sup> Then, chloride can induce the fast elimination of chlorotrimethylsilane, and subsequent decoordination of the metal affords the carbene **3**. In contrast, in the presence of a weakly coordinating species such as trifluoromethanesulfonate, the lifetime of **6** is sufficient for it to undergo elimination of mercury metal, giving the trimethylsilyl amidinium salts **5**. The latter does not react with chloride to afford **3**, showing that it is not the intermediate in the formation of carbenes (Scheme 3).

Despite the large number of routes known to generate stable or transient carbenes,<sup>1,6,16</sup> very few have as broad an applicability as the new synthetic method reported here. Because dechlorination occurs under very mild experimental conditions, we are currently investigating the possibility of preparing persistent halogeno- or even hydrogenaminocarbenes bearing a bulky amino group.

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- (10) In contrast to  $\text{Me}_3\text{SiI}$ ,  $\text{Me}_3\text{SiCl}$  does not react with diamino-carbenes. Kuhn, N.; Kratz, T.; Blaser, R.; Boese, R. *Chem. Ber.* **1995**, *128*, 245.
- (11) General procedure for the synthesis of carbenes **3**: A THF-*d*<sub>8</sub> solution (2.0 mL) of **1** (0.8 mmol) was added dropwise at  $-78^\circ\text{C}$  to a THF-*d*<sub>8</sub> suspension (2.0 mL) of **2** (0.7 mmol). The reaction was monitored by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. After being stirred for 20 min at  $-78^\circ\text{C}$ , the mixture was warmed to room temperature, giving a clear solution containing a drop of mercury metal. The solution was transferred with a cannula and the solvent and  $\text{Me}_3\text{SiCl}$  were removed under vacuum, affording carbenes **3**. The same experimental procedure was used to prepare olefins **4** and trimethylsilyl derivatives **5**. WARNING: Mercury(0) and mercury derivatives are toxic.
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- (13) Selected NMR data, **3c** [toluene-*d*<sub>6</sub>],  $^1\text{H}$ : 1.33 (quint, 2H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 6.0$ ), 2.24 (t, 4H,  $\text{NCH}_2$ ,  $^3J_{\text{HH}} = 6.0$ ), 2.70 (s, 6H,  $\text{NCH}_3$ ),  $^{13}\text{C}$ : 20.94, 41.43, 43.87, 242.65. **4d** (E),  $^1\text{H}$ [ $\text{CD}_3\text{CN}$ ]: 0.88 (broad s, 24H,  $\text{CHCH}_3$ ), 3.29 (sept, 4H,  $\text{CHCH}_3$ ,  $^3J_{\text{HH}} = 6.6$ ), 3.91 (s, 6H,  $\text{OCH}_3$ ), 6.90 (d, 4H,  $\text{CH}$ ,  $^3J_{\text{HH}} = 8.5$ ), 7.48 (d, 4H,  $\text{CH}$ ,  $^3J_{\text{HH}} = 8.5$ ).  $^{13}\text{C}$ [ $\text{CDCl}_3$ ]: 23.51, 51.25, 55.39, 112.82, 132.48, 137.59, 139.00, 158.24. (Z),  $^1\text{H}$ [ $\text{CD}_3\text{CN}$ ]: 1.26 (d, 24H,  $\text{CHCH}_3$ ,  $^3J_{\text{HH}} = 7.0$ ), 3.78 (s, 6H,  $\text{OCH}_3$ ), 3.94 (sept, 4H,  $\text{CHCH}_3$ ,  $^3J_{\text{HH}} = 7.0$ ), 6.58 (d, 4H,  $\text{CH}$ ,  $^3J_{\text{HH}} = 9.0$ ), 7.07 (d, 4H,  $\text{CH}$ ,  $^3J_{\text{HH}} = 9.0$ ).  $^{13}\text{C}$ [ $\text{CDCl}_3$ ]: 24.30, 47.66, 55.16, 112.11, 133.33, 134.00, 136.71, 156.94. **4e** [THF-*d*<sub>8</sub>],  $^1\text{H}$ : 1.21 (d, 24H,  $\text{CHCH}_3$ ,  $^3J_{\text{HH}} = 6.7$ ), 3.38 (sept,  $\text{CHCH}_3$ , 4H,  $^3J_{\text{HH}} = 6.7$ ).  $^{13}\text{C}$ : 20.93, 22.14, 50.56, 138.07. **4f** [THF-*d*<sub>8</sub>],  $^1\text{H}$ : 1.02 (d, 24H,  $\text{CHCH}_3$ ,  $^3J_{\text{HH}} = 6.6$ ), 3.20 (sept,  $\text{CHCH}_3$ , 4H,  $^3J_{\text{HH}} = 6.6$ ), 5.17 (s, 2H),  $^{13}\text{C}$ : 21.75, 49.21, 119.21. **5b** [ $\text{CD}_3\text{CN}$ ],  $^1\text{H}$ : 0.51 (s, 9H,  $\text{SiCH}_3$ ), 3.16 (s, 12H,  $\text{NCH}_3$ ).  $^{13}\text{C}$ : 1.98, 45.59, 122.52 (q,  $\text{CF}_3$ ,  $^3J_{\text{CF}} = 321.5$ ), 186.02. **5c** [ $\text{C}_6\text{D}_6$ ],  $^1\text{H}$ : 0.25 (s, 9H,  $\text{SiCH}_3$ ), 1.63 (quint, 2H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 5.3$ ), 2.79 (s, 6H,  $\text{NCH}_3$ ), 2.85 (t, 4H,  $\text{NCH}_2$ ,  $^3J_{\text{HH}} = 5.3$ ).  $^{13}\text{C}$ : 1.62, 19.49, 43.50, 48.57, 122.34 (q,  $\text{CF}_3$ ,  $^3J_{\text{CF}} = 321.1$ ), 172.61.
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