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Synthesis and Structure of Silyl-Substituted Imidazol-2-ylidenes and Their Precursors[1]

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Abstract — Previously unknown heterocyclic carbenes and their precursors containing a silicon atom in the side chain were prepared. Their structures were studied by multinuclear ^{1}H, ^{13}C, ^{15}N, and ^{29}Si NMR spectroscopy.

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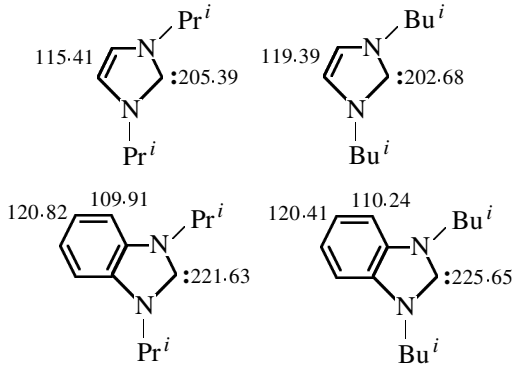
The unique properties of N-heterocyclic carbenes attract much researchers' attention [1–3]. For a long time it was believed that carbenes are so reactive that they can exist only as short-lived intermediate species. However, as early as 1962, Wanzlick suggested that these "intermediates" may be very stable [4]. It was his suggestion that the carbene center in position 2 of the imidazole ring should be stable owing to electron-donor effect of the neighboring nitrogen atoms; it provided the conceptual basis for the development of the chemistry of this class of compounds. Two decades later, Arduengo et al. isolated and described stable imidazol-2-ylidenes [5, 6]. This achievement stimulated extensive experimental and theoretical studies of the structure and properties of these unexpectedly stable nucleophilic carbenes which could be handled in an inert atmosphere at room temperature. Up to now, numerous N-heterocyclic carbenes, both saturated and unsaturated, have been synthesized.

Metal complexes of carbenes play an important role as homogeneous catalysts in such reactions as alkene rearrangements, Fischer–Tropsch reaction, polymerization of alkenes and alkynes. Carbene complexes are used as ligands in organometallic catalysts [7, 8]. Carbene ligands as compared to phosphines extend the field of their application as catalysts. They are less sensitive than their phosphine analogs to air and moisture. Recent experimental data show that catalysts based on various metal complexes of carbenes exhibit better characteristics than the corresponding phosphine complexes [9].

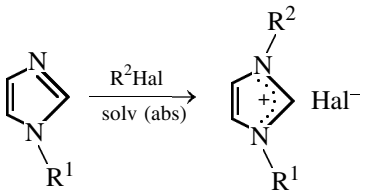
Previously we prepared, studied, and characterized 1,3-diisopropylimidazol-2-ylidene, 1,3-diisobutylimidazol-2-ylidene, 1,3-diisopropylbenzimidazol-2-ylidene, 1,3-dibutylbenzimidazol-2-ylidene, and their precursors [10, 11]. As a method for prompt identification of carbene compounds, we used ^{13}C NMR spectroscopy. This method is particularly informative in determining the structure of compounds having the carbene center. The chemical shift of the carbene carbon is characteristic and for the nitrogen-containing heterocyclic compounds is about 200 ppm. We have shown that the C^2 carbon atom of carbenes of the imidazole series resonates in the range 202–205 ppm, and that of carbenes of the benzimidazole series, at 220–226 ppm [10, 11].

The ^{13}C NMR chemical shifts (δ_C, ppm) of imidazole-series carbenes are shown below:



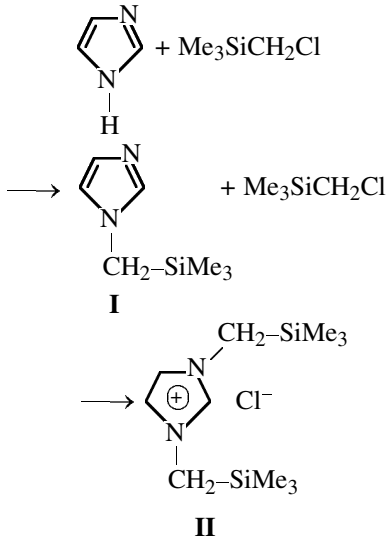
In this study we examined the previously unknown carbenes of the imidazole series and their precursors containing organosilicon substituents at the nitrogen atom, such as Me_3Si, Me_3SiCH_2.

[1] Dedicated to 85th anniversary of M.G. Voronkov.
[†] Deceased.



R^1, R^2 = $SiMe_3$, CH_2SiMe_3.

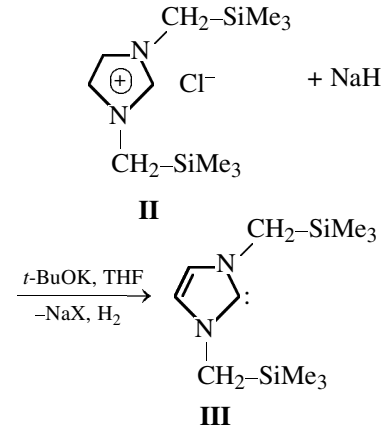
The reaction of imidazole with chloromethyltrimethylsilane in DMSO in the presence of KOH at 20°C yielded 1-methyltrimethylsilylimidazolium chloride **I**.



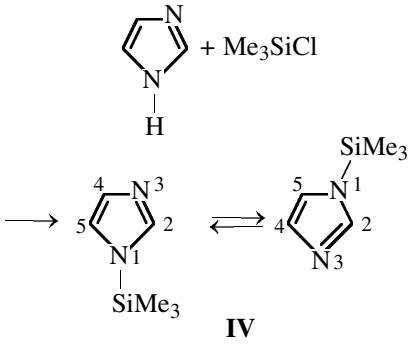
Further silylmethylation yields 1,3-bis(trimethylsilylmethyl)imidazolium chloride **II**. In the ^1H NMR spectra, two low-field signals of the imidazole ring protons are observed at δ 7.53 and 6.98 ppm, with 1 : 2 ratio of integral intensities; they can be assigned to protons H^2 and $H^{4,5}$, respectively. The high-field singlets at δ 4.23 and 0.53 ppm, taking into account their integral intensities, can be assigned to protons of the CH_2 and Me_3Si groups. The ^{13}C NMR spectrum is also consistent with the structure of the suggested salt **II**. Thus, the NMR data and elemental analysis prove that the reaction product is the 1,3-bis(trimethylsilylmethyl)imidazolium salt **II**.

Deprotonation of salt **II** in THF with sodium hydride in the presence of BuOK yielded a previously unknown stable carbene, 1,3-bis(trimethylsilylmethyl)-imidazol-2-ylidene **III**.

In the ^{13}C NMR spectrum, a characteristic low-field signal at 205 ppm is observed, which undoubtedly should be assigned to the carbene carbon atom.



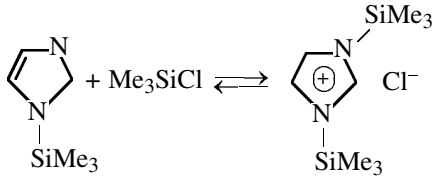
The reaction of imidazole with trimethylchlorosilane yields *N*-trimethylsilylimidazole **IV**, which, according to the NMR data, exists as a tautomeric equilibrium mixture.



The structure of precursor **IV**, which is of interest itself, was studied by ^1H, ^{13}C, ^{15}N, and ^{29}Si multinuclear NMR spectroscopy. The correct interpretation of the chemical behavior and biological activity of these heterocyclic systems is impossible without knowing the structure of the tautomeric forms and factors governing their relative stability. In the ^1H and ^{13}C NMR spectra of trimethylsilyl derivative **IV**, the signals of protons H^4 and H^5 and of carbons C^4 and C^5 coalesce, which is indicative of fast exchange of the trimethylsilyl group between the N^1 and N^3 nitrogen atoms even at room temperature. In the ^{15}N NMR spectrum, only one resonance signal at –160 ppm is observed; it belongs to the N^1 and N^3 atom. This is also indicative of fast (in the NMR time scale) exchange of the Me_3Si group between the nitrogen atoms. Below are listed ^1H, ^{13}C, ^{15}N, and ^{29}Si chemical shifts (δ, ppm) of *N*-trimethylsilylimidazole **IV** in $CDCl_3$.

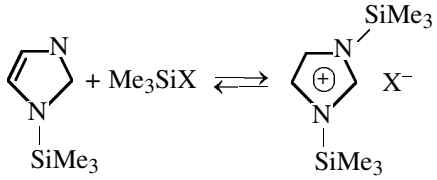
IV	δ^1H			$\delta^{13}C$			$\delta^{15}N$	$\delta^{29}Si$
	H^2	$H^{4,5}$	Me_3Si	C^2	$C^{4,5}$	Me_3Si	$N^{1,3}$	Si–N
	7.59	7.06	0.45	138.04	122.67	–0.24	–160.1	14.1

The subsequent silylation of 1-trimethylsilylimidazole **IV** with trimethylchlorosilane yields *N,N'*-bis(trimethylsilyl)imidazolium chloride **V**. The latter is in rapid degenerate exchange with the initial compound, the equilibrium being shifted to the right, toward salt **V**.



V

The formation of the related *N,N'*-bis(trimethylsilyl)imidazolium salts and their participation in the exchange processes was reported in [12, 13]. These processes are well studied by NMR spectroscopy [12, 13], conductometric titration [12], and X-ray diffraction analysis [14].



X = Cl, Br, I, OSO_2CF_2, $OClO_2$.

According to X-ray structural data, the crystalline 1 : 1 adduct prepared by the reaction of *N*-trimethylsilylimidazole with Me_3SiI is *N,N'*-bis(trimethylsilyl)-imidazolium iodide [14].

So far we failed to prepare carbenes from *N,N'*-bis(trimethylsilyl)imidazolium salts. Compound **V** is easily hydrolyzed and is very sensitive to atmospheric moisture. Probably, the presence of the bridging methylene group in compound **II** stabilizes the molecule of the precursor compared to **V**, which allowed us to perform its deprotonation with the formation of bis(trimethylsilylmethyl)imidazol-2-ylidene **III**. On the other hand, however, preparation of the complex of bis(trimethylsilylmethyl)imidazol-2-ylidene with palladium chloride leads to desilylation of the carbene with the formation of *N,N'*-dimethylimidazolium chloride.

The structure of the starting, intermediate, and final products was proved by multinuclear (^1H, ^{13}C, ^{15}N, ^{19}F, ^{29}Si) and dynamic NMR spectroscopy. The ^{13}C NMR spectroscopy was shown to be a unique tool for detection and identification of carbenes (characteristic signals of the carbene carbon atom are observed in the range 200–215 ppm).

EXPERIMENTAL

The ^1H, ^{13}C, ^{15}N, and ^{29}Si NMR spectra of the compounds prepared were recorded on Bruker DPX-400 and Bruker AV-400 NMR spectrometers with working frequencies of 400.13, 100.62, 40.56, and 79.5 MHz, respectively. The ^1H, ^{13}C, and ^{29}Si chemical shifts were measured relative to tetramethylsilane as an internal references, and the ^{15}N shifts were determined relative to an external reference, $CH_3{}^{15}NO_2$. All the spectra were taken at 27°C, the accuracy of the chemical shifts measurement was 0.01 and 0.02 ppm for ^1H and ^{13}C, respectively, and 0.1 ppm for ^{15}N and ^{29}Si. The ^{29}Si NMR spectra were obtained using the INEPT pulse sequence. The ^{15}N chemical shifts were measured from the inverse two-dimensional ^1H–^{15}N spectra using the HMBC-GP protocol. To assign the signals and determine the structure of the compounds, we used the ^1H, ^{13}C, ^{15}N 2D NMR techniques.

1-(Trimethylsilylmethyl)imidazole (I). To a solution of 5.6 g of KOH in 200 ml of DMSO, cooled to 10°C, 6.8 g of imidazole was added. The mixture was stirred for 5 min, and 12.25 g of trimethylchlorosilane was slowly added dropwise; the temperature did not exceed 20°C. The reaction mixture was stirred at room temperature for 5 h, diluted by a factor of 2 with distilled water, and extracted with chloroform (6 × 100 ml). The organic layer was washed with water and dried over $MgSO_4$; the solvent was removed, and the residue was distilled in a vacuum. bp 110°C (11 mm Hg). Yield 5.6 g (36.3%). ^1H NMR spectrum, δ, ppm: 7.18 s (1H, H^2), 6.86 d (1H, H^5), 6.64 d (1H, H^4), 3.36 s (2H, CH_2), 0.07 s (9H, Me_3Si). ^{13}C NMR spectrum, δ_C, ppm: 136.93 (C^2), 128.64 (C^5), 119.47 (C^4), 38.29 (CH_2), 3.12 (Me_3Si).

1,3-Bis(trimethylsilylmethyl)imidazolium chloride (II). To 5 g of 1-(trimethylsilylmethyl)imidazole in 10 ml of dry toluene, 5.9 g of trimethylchlorosilane was added dropwise with vigorous stirring over a period of 1 h; the mixture was stirred at 100°C for 15 h. The oil formed in the process crystallized on cooling. The precipitate was filtered off, washed with dry THF, and dried in a vacuum; mp 161–162°C. Yield 7.4 g (83%). ^1H NMR, δ, ppm: 9.83 s (1H, H^2), 7.31 s (2H, $2H^{4,5}$), 4.03 s (4H, CH_2), 0.14 s (18H, Me_3Si). ^{13}C NMR, δ_C, ppm: 136.64 (C^2), 124.49 ($C^{4,5}$), 43.68 (CH_2), 1.05 (Me_3Si).

1,3-Bis(trimethylsilyl)imidazol-2-ylidene (III). The reaction was carried out under dry argon. All the solvents were purified and degassed by standard procedures directly before use. To 0.001 mol of 1,3-bis(trimethylsilylmethyl)imidazole in 10 ml of THF,

0.012 mol of KOH was added. The mixture was allowed to stand for 3 min, after which 5 ml of a 1 M solution of potassium *tert*-butoxide in THF was added with vigorous stirring. The mixture was stirred for 4 h, the formed salt filtered off, and the filtrate was concentrated in a vacuum. ^{1}H NMR spectrum, δ, ppm: 7.12 s (2H, $H^{4,5}$), 3.91 s (4H, CH_2), 0.23 s (18H, Me_3Si). ^{13}C NMR spectrum, δ, ppm: 205.2 (C^2), 120.26 ($C^{4,5}$), 37.26 (CH_2), 0.93 (Me_3Si).

1-Trimethylsilylimidazole (IV). Imidazole, 8.16 g and 1,1,1,3,3,3-hexamethyldisilazane, 26.3 g, were mixed in an argon atmosphere and stirred for 12 h at 100°C. The resulting mixture was distilled in a vacuum; bp 75–77°C (7 mm Hg). Yield 9.7 g (58%).

1,3-Bis(trimethylsilyl)imidazolium chloride (V). To 5 g of 1-(trimethylsilyl)imidazole in 10 ml of dry toluene, 8.4 g of trimethylchlorosilane was added dropwise with vigorous stirring over a period of 1 h; the mixture was stirred at 100°C for 15 h. The oil formed in the process crystallized on cooling. The precipitate was filtered off, washed with dry THF, and dried in a vacuum.

ACKNOWLEDGMENTS

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