Radical Reactions of a Stable N-Heterocyclic Silylene: EPR Study and DFT Calculation

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Chemical species which involve divalent silicon atoms are key intermediates in numerous thermal and photochemical reactions of organosilicon compounds.[1] The field of stable silylenes commenced with the synthesis of stable N-heterocyclic compounds **1**, **2**, and **3**, and has led to an elaborate chemistry.[2,3]
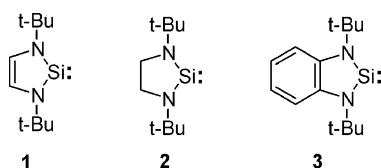
These silylenes act as Lewis bases, with the lone pair on silicon serving as the electron donor, for example in silylene−transition metal complexes.[4,5] According to spectroscopic studies, the stable silylene **1** behaves electronically like compounds of trivalent phosphorus.[6] Thus, it could be expected that stable silylenes, such as phosphites or phosphines[7] (eq 1) might react with free radicals to form radical intermediates (eq 2).[8]

$$X_3P: \quad + \quad Y\cdot \quad \longrightarrow \quad X_3\dot{P}{-}Y \qquad (1)$$
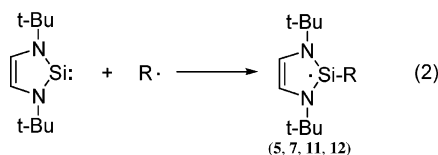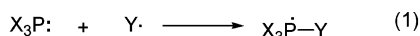
R = TEMPO (**5**), P(O)(OPr-i)$_2$ (**7**), Re(CO)$_5$ (**11**), CH$_2$Ph (**12**)

We present here preliminary results of EPR studies of adducts of stable silylene **1** with free radicals from different sources such as: 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) (**4**); Hg[P(O)-(OPr^i)$_2$]$_2$ (**6**); (CO)$_3$CpM−MCp(CO)$_3$, M = W (**8**), Mo (**9**); (CO)$_5$Re−Re(CO)$_5$ (**10**); and toluene.

Addition of stable nitroxyl radical **4** to toluene solution of **1** leads to formation of radical adduct **5**. The EPR spectrum of radical **5** (Figure 1a) is characterized by isotropic hyperfine coupling (hfc) with two ^{14}N and two ^{1}H nuclei: $a(2^{14}N) = 5.2$ G, $a(2^1H) = 6.3$ G, $g = 2.0049$. These data indicate that the unpaired electron in radical **5** is delocalized over the five-membered ring of the radical adduct.

Addition of **6** to a toluene solution of silylene **1** at 298 K gives rise to a new EPR signal of radical adduct (**7**) with additional hfc with the ^{31}P: $a(2^1H) = 5.6$ G, $a(2^{14}N) = 6.8$ G, $a(^{31}P) = 13.6$ G, $g = 2.0024$. Analogous reactions of silylene **1** with the dimers **8** and **9** lead to formation of the corresponding radical adducts. Their intense EPR spectra exhibit equivalent hfc of the unpaired electron with ^{14}N and ^{1}H nuclei at 298 K. For M = W the constants are

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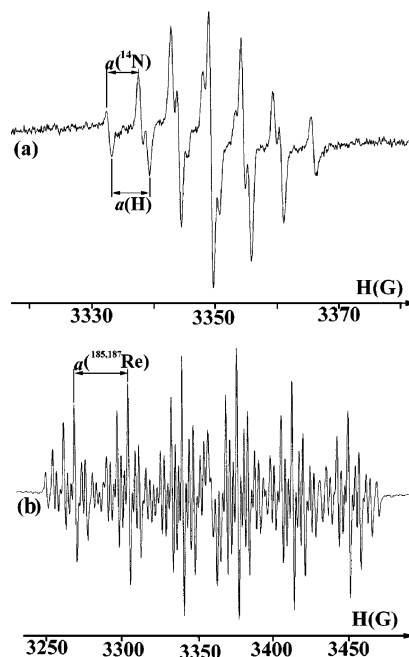‡ University of Wisconsin.

Figure 1. EPR spectra recorded on a Bruker EMX-10/12 spectrometer in toluene at 298 K: (a) radical **5**, (b) radical **11** after UV irradiation ($\lambda = 300$ nm).

$a(2^1H) = a(2^{14}N) = 5.65$ G, and for M = Mo, $a(2^1H) = a(2^{14}N) = 5.7$ G, $g = 2.0027$.

UV irradiation of a toluene solution of **1** containing **10** at 298 K gives rise to the EPR signal of **11**, the adduct of a rhenium-centered radical with **1**. The EPR spectrum of the reaction mixture shows six groups of lines (Figure 1b). We attribute those to an interaction of the unpaired electron with the ^{185,187}Re nuclei ($I = ^5/_2$) $a(^{185,187}Re) = 36.5$ G and $a(2^1H) = 4.7$ G, $a(2^{14}N) = 7.1$ G, $g = 2.0039$. The value of the hfc constant with ^{185,187}Re nucleus in radical **11** is similar to the corresponding constant for Re(CO)$_5$-containing nitroxides (40.9 G).[9]

An interesting observation is that the EPR spectra of the investigated radicals do not show hyperfine interaction of the unpaired electron with the ^{29}Si nuclei (4.67%) although the existence of hfc with ^{31}P in **7** and with ^{185,187}Re in **11** indicates the presence of spin density on the silicon atom. Key information for understanding the absence of satellite lines for the ^{29}Si nucleus was obtained upon EPR study of **12**, the adduct of silylene **1** with benzyl radical, obtained by UV irradiation of a toluene solution of **1** in the cavity of the EPR spectrometer. At 298 K the EPR spectrum of radical **12** exhibits hfc with two pairs of magnetically equivalent protons and two equivalent nitrogens and carbons [$a(4^1H) = 2.75$ G, $a(2^{14}N) = 8.6$ G, $a(2^{13}C) = 3.0$ G (satellite line), $g = 2.0027$] (Figure 2a).[10] However at 225 K some lines of the nitrogen multiplet
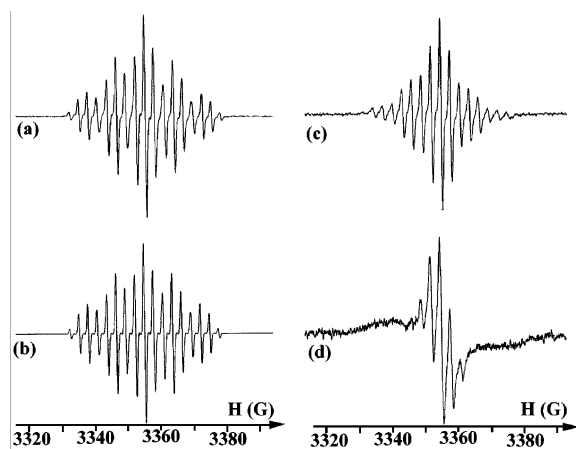
Figure 2. (a) Experimental EPR spectrum of **12** in toluene after UV irradiation at 298 K, (b) simulated EPR spectrum of **12** (SimFonia software), (c) at 225 K, (d) at 195 K.
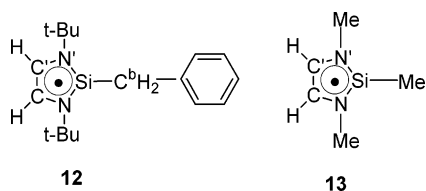

Figure 3. Calculated data for radical **12**: $a(^{14}N') = 5.7$ G (22.5% of spin density), $a(^{14}N) = 6.1$ G (22.7%), $a(^{29}Si) = -83.5$G (25.4%), $a(^{13}C) = 1.6$ G (7.5%), $a(^{13}C') = 1.2$ G (7.4%); **13** nonplanar: $(\angle SiNCC') = -6.9°$, $(\angle SiNCC') = 6.5°$, $a(^{14}N') = 7.0$ G, $a(^{14}N) = 7.2$ G, $a(^{29}Si) = -99.7$ G; **13** planar: $(\angle SiNN') = 0°$, $a(^{14}N') = 7.3$ G, $a(^{14}N) = 7.4$ G, $a(^{29}Si) = -105.4$ G.

broaden (Figure 2c) and at 195 K only a quintet remains (Figure 2d) with $a(4^1H) = 2.84$ G. The temperature effect is reversible.

We suggest that the differential broadening of the spectral lines results from the modulation of hyperfine coupling constants due to the decrease of the rate of dynamic conformational processes at low temperature.

The larger the difference between hfc constants in different conformations of the radical the greater is the frequency of conversion processes necessary for their averaging.[11] To support this explanation, and in particular the absence of satellite lines for ^{29}Si, we carried out DFT (B3LYP) quantum mechanical calculations[12] for **12** and model radical **13**.

Radical **12** (Figure 3) has a C_1 envelope-shaped structure ($\angle SiNCC' = -3.0°$ and $\angle SiN'C'C = 3.9°$) with a pyramidal silicon $\Sigma\Theta(Si) = 292.0°$. The calculated hfc constants for ^{14}N and ^{13}C and spin density contributions for **12** (Figure 3) show agreement with the experimental EPR data of **12** and indicate that the spin density is delocalized. However, the calculations predict a large hfc with ^{29}Si $a(^{29}Si) = 83.5$ G, which as mentioned above is not observed experimentally. This apparent discrepancy may be due to fast dynamic conformational processes. Calculations for the model radical **13** (Figure 3) show that on going from the envelope conformation to the ring-planar conformation the change in

$a(^{29}Si)$ is 5.7 G, 14 times larger than the change in $a(^{14}N)$ of 0.4 G. Calculations demonstrated that large ^{29}Si hyperfine coupling should be significantly more sensitive to the decrease of the rate of transition between the two conformations than that for ^{14}N. This suggests that the rate of flipping of the radical center relative to the ring may not be large enough on the EPR time scale to cause averaging of the values of $a(^{29}Si)$ at room temperature. Thus, we conclude that conformational inversion in all the radical adducts of **1** may be the cause of broadening and lack of observation of satellite lines of $a(^{29}Si)$.

In summary, we report here radical adducts of N-heterocyclic silylene **1**, representing a new type of neutral silyl radicals stabilized by delocalization. These were produced from a variety of precursors and studied by EPR spectroscopy and quantum mechanical calculations. The radicals persist at 298 K for 1–7 days, with lifetimes increasing in the order **5 < 7 < 11 < 12**.

Supporting Information Available: Experimental and simulated EPR spectra and calculational data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Reaction of a stable silylene with TEMPO has recently been reported without identification of a radical intermediate (which would not be stabilized by delocalization): Iwamoto, T.; Masuda, H.; Ishida, S.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2003**, *125*, 9300.
(9) Hudson, A.; Lappert, M. F.; Lednor, P. W.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* **1974**, 966.
(10) The structure of **12** was confirmed by an experiment using $C_6D_6CD_3$; the EPR spectrum reduces to a quintet of triplets, as expected (see Supporting Information). **12** was also observed as the eventual product in several independent experiments with silylene **1** in toluene solution with different radical sources, when the primary radicals were formed in high concentration [for example **11**, R = $Re(CO)_5$]. We suppose that the initially formed radicals react with toluene to form benzyl radicals, which then add to the silylene radical to produce **12**. The hfc constants for radical **12** differ somewhat from those for the other radicals reported here, perhaps due to different pyramidality at silicon.
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(12) For details of the calculations see the Supporting Information.

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