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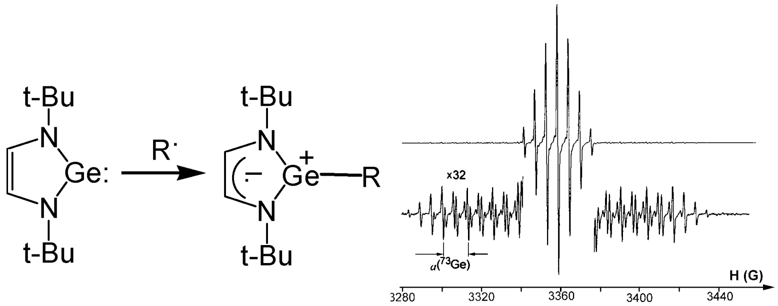

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Radical Reactions of a Stable *N*-Heterocyclic Germylene: EPR Study and DFT Calculation

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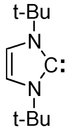
Although many reactions of stable unsaturated *N*-heterocyclic divalent compounds of group 14 elements (**1**−**4**) have now been described,[1−3] the radical chemistry of these compounds is relatively little known.[4−7] Several radical adducts of silylene **2** with free radicals of different chemical nature (TEMPO, $^{\bullet}P(O)(O^{i}Pr)_2$, $^{\bullet}Re(CO)_5$, $^{\bullet}MoCp(CO)_2$, $^{\bullet}WCp(CO)_3$, $^{\bullet}CH_2Ph$) have been studied by EPR and DFT calculations.[4] These adducts represent a new type of neutral silyl radicals stabilized by delocalization. The first synthetic results of free radical addition to silylenes and germylenes have also been reported recently. The products obtained by addition of 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO) to silylenes and germylenes differ depending upon the nature of the divalent atoms.[5,6] EPR study and DFT calculation of new radical intermediates may allow prediction of and explicate results of preparative synthesis.



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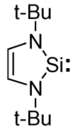

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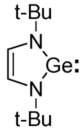

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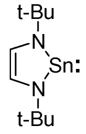

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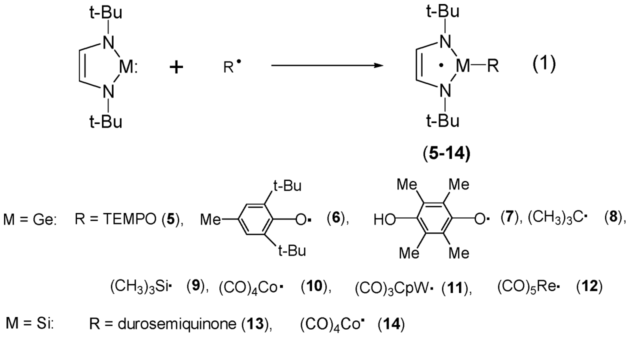
We present here preliminary results of EPR studies of adducts of stable germylene **3** with free radicals with different chemical structure (eq 1), including oxygen- (**5**−**7**), carbon- (**8**), silicon- (**9**), and metal-centered (**10**−**12**) radicals. To compare the EPR spectral parameters for derivatives of **3** and **2**, we have studied the EPR spectra of the new radical adduct of silylene **2** with durosemiquinone radical (**13**) and with $Co(CO)_4$ (**14**).



Results of the EPR study of radical derivatives of stable germylene **3** are summarized in Table 1. The main feature of the EPR spectra of **5**−**11** is a septet arising from equal hyperfine coupling (hfc) with two magnetically equivalent protons and two ^{14}N ($I = 1$) nuclei. Only in the EPR spectrum of **12** were the hfc's for the protons and nitrogen atoms sufficiently different that they could be observed separately.

Table 1. Hyperfine Coupling (G), *g*-Values for (**5**−**12**)[a] at 290 K

R	$a(2^{14}N)$	$a(2^{1}H)$	$a(^{73}Ge)$	$a(^{59}Co)$, $a(^{185,187}Re)$	*g*-factor
5	5.71	5.71	−	−	2.0015
6	5.5	5.5	16.0	−	2.0013
7	5.65	5.65	12.78	−	2.0013
8	5.7	5.7	−	−	2.0014
9	5.8	5.8	−	−	2.0013
10	5.1	5.1	11.4	5.1	2.0030
11	6.08	6.08	−	−	2.0013
12	7.29	4.68	−	36.07	2.0020

[a] Half lifetime (min) for radical (**5**−**9**, **11**): 8−15, (**12**): 120, (**10**): 1080.

Radicals **6**, **7**, and **10**, which were obtained in relatively high concentration, showed at high gain additional satellite lines due to hyperfine interaction of the unpaired electron with ^{73}Ge nuclei. (Table 1). Thus, **7** gave a decet of septets from the 7.8% of ^{73}Ge ($I = {}^{9}/_{2}$) present in natural abundance (Figure 1a). **7** also shows hyperfine splitting to the hydrogens of two ^{t}Bu groups [$a(18H) = 0.085$ G] at high resolution (Figure 1a, inset).

The reaction of **2** with duroquinone under UV irradiation and the spontaneous reaction of **2** with $Co_2(CO)_8$ produced radicals **13** and **14**, respectively (Figures 1b and 2c), in somewhat lower concentration than for the corresponding germylene radicals. It is possible that the rate of addition of a second radical to the silylene to give diamagnetic products is greater than that for the corresponding germylene, allowing the germylene radicals to accumulate in higher concentration. Double addition of TEMPO to both silylenes and germylenes has been noted previously.[5]

The hyperfine couplings to germanium in **6**, **7**, and **10**, $a(^{73}Ge) = 11.4$ to 16.0 G, are much smaller than those in the stable pyramidal radical $[Me_3Si)_2N]_3Ge^{\bullet}$ (171.0 G),[8] and in fact even less than that reported for the planar radical $(tBu_2MeSi)_3Ge^{\bullet}$ (20 G).[9] The relatively low Ge hyperfine coupling in radicals **6**, **7**, and **10** is consistent with delocalization of the unpaired electron away from the Ge atom and onto the five-membered ring of the unsaturated germylene.

To investigate the effect of the central atom on the spin density in the unsaturated system we carried out DFT (B3LYP) quantum mechanical calculations[10] for model radicals containing different central atoms Ge (**15**), Si (**16**), and C (**17**) (Figure 3).

Radical **15** has a nearly planar structure, $\angle GeNCC' = -1.6°$ and $\angle GeN'C'C = 2.1°$, with a pyramidal germanium, $\Sigma\Theta(Ge) = 266.2°$. The calculated hfc constants for ^{73}Ge, ^{14}N, and H and spin density contributions for **15** (Figure 3) show good agreement with the experimental EPR data of **7**, confirming that the spin density is delocalized over the five-membered ring. An important result of

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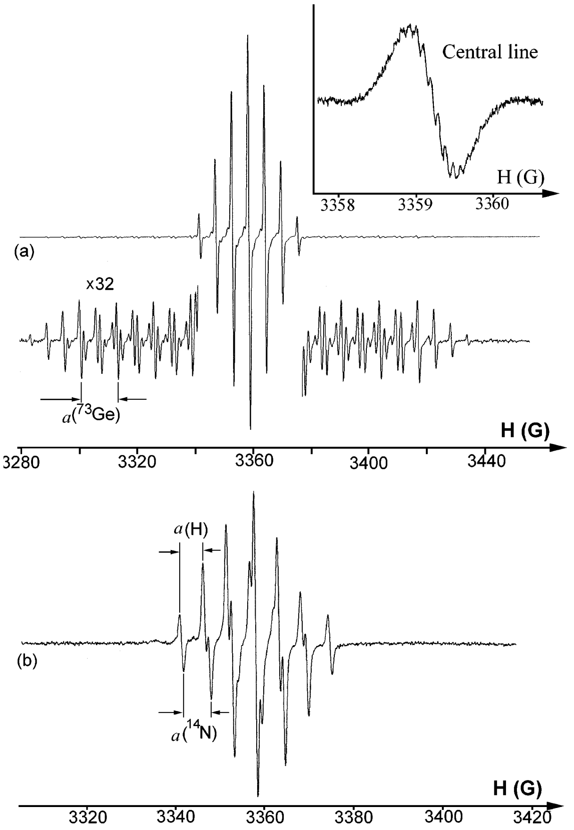

Figure 1. EPR spectra recorded on a Bruker EMX-10/12 spectrometer in toluene at 298 K under UV irradiation (λ = 300 nm). (a) Radical **7**. The inset shows the central line at high resolution. (b) Radical **13**; $a(2^{14}\mathrm{N})$ = 6.2 G, $a(2^{1}\mathrm{H})$ = 5.28 G.

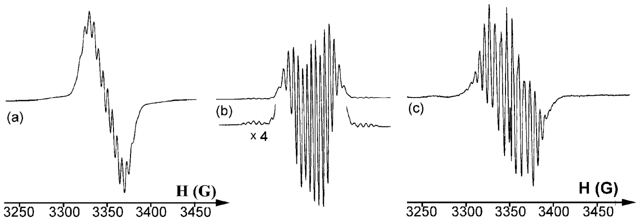

Figure 2. EPR spectra at 290 K: (a) radical **10** (first derivative), (b) radical **10** (second derivative), (c) radical **14** (first derivative); $a(2^{14}\mathrm{N}) \approx a(2^{1}\mathrm{H})$ = 5.3 G, $a(^{59}\mathrm{Co})$ = 6.4 G ($I = {}^{7}/_{2}$).

the calculation is that only 2% of the unpaired electron spin density is localized on the Ge atom. The spin density is transferred from germanium into the five-membered ring and thereby is delocalized over the two nitrogen atoms and two carbon atoms of the unsaturated heterocycle, leading to an unusual zwitterionic structure, **18**. An analogous case of nearly full transfer of spin density away from a heteroatom may be found in the phosphorus-centered radical $\mathrm{PhP^{\bullet}(OEt_2)_2OtBu}$, where the spin density is delocalized onto the aromatic ring.[11]

Larger spin densities on the central atom were calculated for the silicon radical **16** (15.4%) and the carbon radical **17** (52.4%). Thus, the spin density on the central atoms decreases in the order C > Si > Ge, and the degree of spin delocalization to the five-membered ring increases along the opposite order of Ge > Si > C. This is quite surprising in view of the poor conjugation usually exhibited by Si and Ge relative to C[12] and the pyramidality at the central atom for Si and Ge. However, these trends can be understood in terms of zwitterionic structure **18**, as the thermodynamic stability of $\mathrm{MR_3}(+)$ follows the order Ge > Si > C.[13]

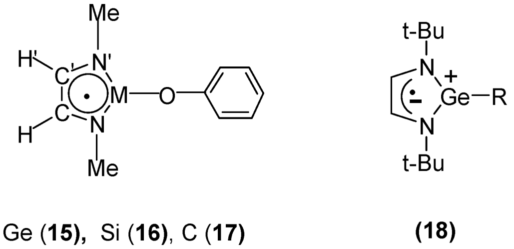

Figure 3. Calculated data for radicals **15**−**17**. **15**: $a(^{14}\mathrm{N}')$ = 6.7 G (28.5% of spin density), $a(^{14}\mathrm{N})$ = 6.7 G (28.4%), $a(^{73}\mathrm{Ge})$ = −11.5 G (1.9%), $a(^{13}\mathrm{C})$ = 4.7 G (18.0%), $a(^{13}\mathrm{C}')$ = 4.9 G (18.3%), $a(\mathrm{H}')$ = $a(\mathrm{H})$ = 5.0 G. **16**: $a(^{14}\mathrm{N}')$ = $a(^{14}\mathrm{N})$ = 7.5 G (25.5%), $a(^{29}\mathrm{Si})$ = −83.1 G (15.4%), $a(^{13}\mathrm{C})$ = 3.4 G (13.6%), $a(^{13}\mathrm{C}')$ = 3.5 G (13.7%), $a(\mathrm{H}')$ = $a(\mathrm{H})$ = 4.0 G. **17**: $a(^{14}\mathrm{N}')$ = $a(^{14}\mathrm{N})$ = 10.6 G (15.4%), $a(^{13}\mathrm{C})$ = 139.1 G (52.4%), $a(^{13}\mathrm{C})$ = $a(^{13}\mathrm{C}')$ = 2.5 G (2.7%) $a(\mathrm{H}')$ = $a(\mathrm{H})$ = 0.7 G.

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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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