

Different electronic structure of phosphonyl radical adducts of *N*-heterocyclic carbenes, silylenes and germynes: EPR spectroscopic study and DFT calculations†‡

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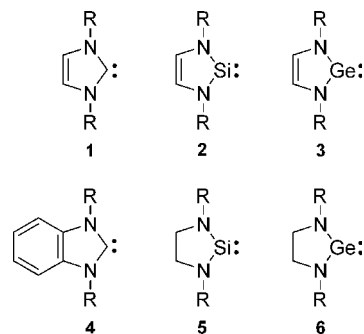
Stable *N*-heterocyclic carbenes and germynes were allowed to react with a phosphonyl radical, (*i*-PrO)₂(O)P[•] (**7**), generated by photolysis of [(*i*-PrO)₂(O)P]₂Hg. The products were identified by EPR spectroscopy. An unsaturated carbene (**1**) and germylene (**3**) react with **7** at the divalent atom to give unstable radical products ($\tau_{1/2} = 0.2$ s). A benzo-annulated carbene (**4**) and a saturated germylene (**6**) react with **7** to give more active radicals. An unsaturated (**2**) and a saturated silylene (**5**) undergo rapid reaction (in the dark) with [(*i*-PrO)₂(O)P]₂Hg to yield unusual silyl phosphites. In these cases only secondary radicals were observed. DFT (PBE0/TZVP//B3LYP/6-31+G(d)) calculations of the radical adducts of the different (C, Si, Ge) unsaturated *N*-heterocyclic divalent species with the phosphonyl radical show that the unpaired electron is delocalized over the five-membered ring; the spin density on the central atoms decreases in the order C, 39% > Si, 14% > Ge, 2%. These trends can be understood in terms of a zwitterionic structure of the radical adducts. The calculations of the radical adducts of **4**, **5** and **6** with **7** indicate larger spin density on the central atom, 47%, 58% and 42% on C, Si, Ge, respectively.

Introduction

Divalent compounds of group 14 elements are among the most important reactive intermediates.¹ For a long time species involving divalent carbon and its heavier congeners could only be directly observed by spectroscopic techniques, either in the gas phase² or in low-temperature matrices,³ but could not be isolated in macroscopic amounts at room temperature. Considerable progress in the chemistry of these compounds was achieved with the synthesis and isolation of stable *N*-heterocyclic carbenes^{4a–4c} and later of its heavier analogs.^{4d–4i}

These discoveries have stimulated research on the electronic structure of these novel divalent species and on the reasons for their unusual stability.⁵

Carbene **1** and its heavier group 14 congeners have lone pair electrons as well as a low-lying vacant $p\pi$ orbital, which implies that they can act both as electron donors, *e.g.*: in carbene–, silylene–, germylene–transition metal complexes,⁶ and as electron acceptors, *e.g.*: in reduction by alkali metals.⁷ These species therefore may possess high reactivity towards free radicals with different donor–acceptor properties. Interaction of the divalent species with radicals to form a new bond and change their



valency from two to three can involve, in the first step, a single electron transfer. An analogous case of interaction of free radicals with compounds containing lone pair electrons may be found in the radical chemistry of phosphites or phosphines, where radical addition to trivalent organophosphorus species leads to formation of four-valent, phosphorus-centered intermediates (eqn (1)).⁸



Although many reactions of stable *N*-heterocyclic divalent compounds have now been described,⁹ few reports on the chemistry of radicals of these compounds are available.¹⁰ Several radical adducts of unsaturated **1–3** with free radicals of different chemical nature, such as O-, P-, Re-, Co-, Mo-centered radicals (eqn (2)), have been studied by EPR and DFT calculations and were reported recently by us^{10a–c} and by other groups.^{10d–k} These adducts represent a new type of neutral radicals stabilized by various degrees of delocalization, which depend on the central

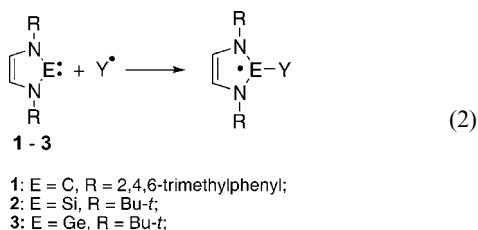
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† Dedicated to Professor Wataru Ando, a pioneer of silicon chemistry, on the occasion of his 75th birthday.

‡ Electronic supplementary information (ESI) available: Cartesian coordinates and energies of stationary points in the calculations of **2a**, **3a**, **4a**, **5a**, **6a** and Fig. S1–S7. See DOI: 10.1039/c0sc00143k

divalent atom.^{10a-c} The first isolations of diamagnetic products of free radical addition to silylenes and germylenes have been reported recently.^{10h,i}



We present here a first systematic study of phosphonyl radical $(i\text{-PrO})_2(\text{O})\text{P}^\bullet$ (**7**) adducts of *N*-heterocyclic stable carbenes, silylenes and germylenes by EPR spectroscopy and DFT calculations. We consider the following: (i) spectral features of the radical adducts, (ii) the effect of the divalent atom E (E=C, Si, Ge) on the spin density distribution in radical adducts, (iii) the effect of a saturated or unsaturated *N*-heterocycle on the electronic and molecular structure of the generated adducts. Additionally, we report a new type of reaction of silylenes **2** and **5** with phosphonyl mercury which yields silyl phosphites.

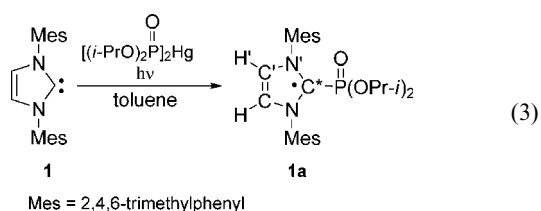
Results and discussion

In the following sections we discuss the structures and EPR spectra of radical adducts of **1–6** with the phosphonyl radical **7**. Selected calculated geometrical parameters are given in Table 1 and the *hfc* constants and spin density distribution are provided in Table 2.

Radical **7** is pyramidal and the unpaired electron occupies an orbital with nearly sp^3 hybridization.^{11a} (the EPR spectrum and a DFT calculated structure of **7** are presented in the ESI, Fig. S1†). The radical addition product of phosphonyl radicals in which the phosphorus atom is β to the radical center yield large a_{P} values (40–140 G), which are easy to detect. Thus, the EPR spectra can provide important information about the structures of the radical adducts.^{10c,11b-d}

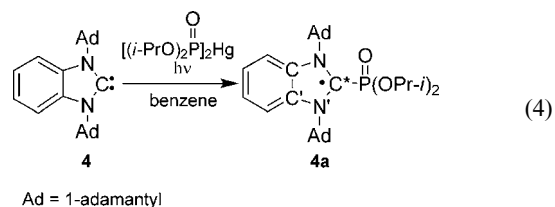
a) Carbene adducts

i) Radical adduct of carbene 1. In a preliminary communication^{10c} we reported the generation of radical **1a** (eqn (3)).



The following hyperfine coupling (*hfc*) constants were measured for radical **1a** ($g = 2.0027$, $\tau_{1/2} = 7.1$ s): $a(^{31}\text{P}) = 48.7$ G, $a(^{14}\text{N}) = 4.7$ G, $a(^2\text{H}) = 1.1$ G, $a(^{13}\text{C}^*) = 25.6$ G (Table 2). According to DFT calculations, the central carbon atom in **1a** is slightly pyramidal, $\Sigma\theta(\text{C}^*) = 352^\circ$ and the heterocycle is almost planar. The calculated Löwdin atomic spin density of **1a** shows that 39% of the spin density is localized on the central carbon atom (C^*) and 37% on the other ring atoms.

ii) Radical adduct of carbene 4. Unfiltered UV irradiation of the benzene solution of **4** and $[(i\text{-PrO})_2(\text{O})\text{P}]_2\text{Hg}$ (eqn (4)) leads to an EPR spectrum consistent with radical **4a** [$a(^{14}\text{N}) = 3.6$ G; $a(^{31}\text{P}) = 81.0$ G; $g = 2.0028$; $\tau_{1/2} < 1$ s] (Fig. 1a, Table 2). Hyperfine coupling of the unpaired electron with the $^{13}\text{C}^*$ nucleus was not observed due to a low signal-to-noise ratio.



To investigate the structure and the spin density distribution in radical **4a** DFT quantum mechanical calculations were carried out on a model radical (**4a'**), in which 1-adamantyl groups were replaced by *tert*-butyl groups. The heterocycle of **4a'** is nearly planar ($\angle \text{C}^*\text{NCC}' = -5.6^\circ$ and $\angle \text{C}^*\text{N}'\text{C}'\text{C} = 6.7^\circ$), with a more pyramidal central carbon atom ($\Sigma\theta(\text{C}^*) = 341^\circ$) than that in **1a** (Table 1). Calculations show that 47% of the spin density is localized on the central carbon atom, and 36% of the spin density is distributed on the other atoms of the heterocycle and annulated aromatic ring (Table 2). The difference between the calculated ($a_{\text{P}} = 122$ G) and experimental ($a_{\text{P}} = 81.0$ G) ^{31}P *hfc* constant can be attributed to conformational and vibrational averaging and general method error.

b) Germylene adducts

i) Radical adduct of germylene 3. Addition of phosphonyl radical **7** to germylene **3** in a toluene solution leads to an intense EPR spectrum consistent with radical **3a** (eqn (5)).

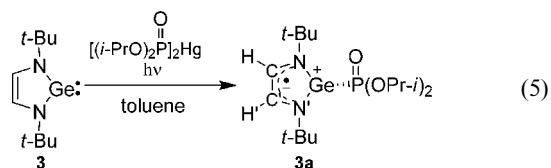


Table 1 Calculated sum of angles ($\Sigma\theta(\text{E})$) around the central atom [$^\circ$] and selected bond lengths (\AA) of radicals **1–6**

Radical	E	$\Sigma\theta(\text{E})$	E–P	E–N ^a	N–C ^b	C–C'
1a	C	352.3	1.781	1.421	1.395	1.349
4a	C	340.9	1.836	1.423	1.399	1.416
2a	Si	284.2	2.400	1.841	1.365	1.374
5a	Si	313.0	2.339	1.754	1.472	1.533
3a	Ge	270.0	2.493	1.961	1.348	1.390
6a	Ge	303.6	2.463	1.856	1.463	1.529

^a Average of E–N and E–N'. ^b Average of N–C and N'–C'.

Table 2 Experimental and calculated ^{13}C , ^{29}Si , ^{73}Ge , ^{31}P and ^{14}N hfc constants (a , G), and calculated Löwdin atomic spin densities (SD)

	$a(\text{E})$ exp	$a(\text{E})$ calc	SD(E)	$a(\text{P})$ exp	$a(\text{P})$ calc	SD(P)	$a(2\text{N})$ exp ^a	$a(2\text{N})$ calc ^a	SD(2N) ^b
1a	25.6	21.9	39.3%	48.7	34.9	7.5%	4.7	3.1	34.3%
2a	— ^c	−75.0	14.4%	—	243.5	10.5%	—	4.4	45.8%
3a	15.0	−13.9	2.4%	186.0	182.9	8.1%	6.4	5.3	54.2%
4a^d	n/o ^e	46.8	46.7%	81.0	122.2	7.1%	3.6	2.5	27.3%
5a	—	−192.3	57.8%	—	264.0	11.6%	—	3.7	16.8%
6a	n/o	−78.3	42.0%	199.6	302.1	14.5%	7.6	4.6	23.7%

^a Average value on two atoms. ^b Sum of values on two atoms. ^c No experimental data. ^d Calculated data for model **4a'**. ^e Not observed due to low signal-to-noise ratio.

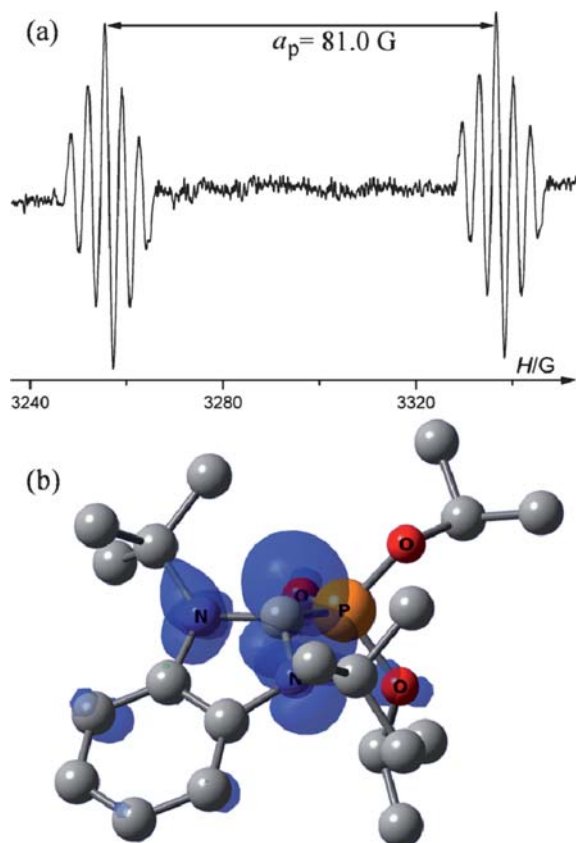


Fig. 1 (a) EPR spectrum of **4a** recorded under UV-irradiation at 298 K, (b) DFT calculated spin density of **4a'** at 0.003 au contour level. Calculated g -factor = 2.0032.

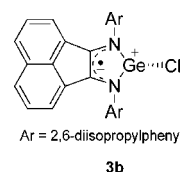
$[a(2\text{H}) = 4.4 \text{ G}; a(2^{14}\text{N}) = 6.38 \text{ G}; a(^{31}\text{P}) = 186.0 \text{ G}; a(^{73}\text{Ge}) = 15.0 \text{ G}; g = 2.0021]$ (Fig. 2, Table 2).

When the irradiating light is turned off a fast (and reversible) decrease in the intensity of the EPR signal of **3a** is observed ($\tau_{1/2} = 0.2 \text{ s}$) (Fig. S3†). The rate of decay of **3a** is not markedly dependent on temperature (230–290 K) and we believe that radical **3a** decays *via* dimerization (dimer structure unknown). We estimate the dimerization rate constant as $2k_{\text{dim}} = 5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.

According to DFT calculations, the heterocycle of **3a** is nearly planar ($\angle \text{GeNCC}' = -2.4^\circ$ and $\angle \text{GeN}'\text{C}'\text{C} = 1.4^\circ$), with a significant pyramidalicity at the germanium atom, $\Sigma\theta(\text{Ge}) = 270.0^\circ$. The calculated g -factor (2.0027), hfc constants

for ^{73}Ge , ^{14}N , ^1H , ^{31}P and the calculated spin density (Fig. 3, Table 2) show good agreement with the experimental EPR data of **3a**, indicating that only 2% of the spin density is localized on the germanium atom, and 81% of the spin density is distributed over the other atoms of the heterocycle. The calculations indicate that 12% of the spin density is localized on the phosphonyl group, accounting for the high hyperfine splitting by the ^{31}P nucleus. Thus, the spin density is transferred from germanium into the five-member ring and into the phosphonyl group, leading to an unusual zwitterionic structure (eqn (5)). An analogous case of a nearly complete transfer of spin density away from a heteroatom occurs in the phosphorus-centered radical $\cdot\text{PPh}(\text{OEt})_2(\text{O}i\text{-Bu})$, where the spin density is delocalized onto the aromatic ring.¹³

The hyperfine coupling of germanium in **3a**, $a(^{73}\text{Ge}) = 15.0$, is much smaller than that in the stable pyramidal radical $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ge}^\cdot$ (171.0 G),¹⁴ and in fact even smaller than reported for the planar radical $(t\text{-Bu}_2\text{MeSi})_3\text{Ge}^\cdot$ (20.0 G).¹⁵ The relatively low ^{73}Ge hyperfine coupling constant in radical **3a** is consistent with delocalization of the unpaired electron away from the Ge atom. Similar to **3a**, a low ^{73}Ge hyperfine coupling constant (9.6 G) was observed for the isoelectronic Cl-substituted germanium radical **3b**, which was isolated as deep red crystals in the reaction of the anion radical of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene and GeCl_2 .^{10j} We believe that in this case, full stabilization of the radical was achieved by additional delocalization of the unpaired electron over the annulated acenaphthene fragment of the molecule (a DFT calculated structure of **3b** is presented in the ESI, Fig. S4†).



ii) Radical adduct of germylene 6. Unfiltered UV-irradiation of a toluene solution containing $[(i\text{-PrO})_2(\text{O})\text{P}]_2\text{Hg}$ and saturated germylene **6** leads to an EPR spectrum consistent with radical **6a** [$a(2\text{H}) = 2.5 \text{ G}; a(2^{14}\text{N}) = 7.64 \text{ G}; a(^{31}\text{P}) = 199.6 \text{ G}; g = 2.0036]$ (eqn (6), Fig. 4, Table 2). This spectrum demonstrates the interaction of the unpaired electron with only two methylene protons out of four. Evidently, the two pairs of methylene protons are not magnetically equivalent relative to the orbital of the unpaired electron (see calculations below). At room

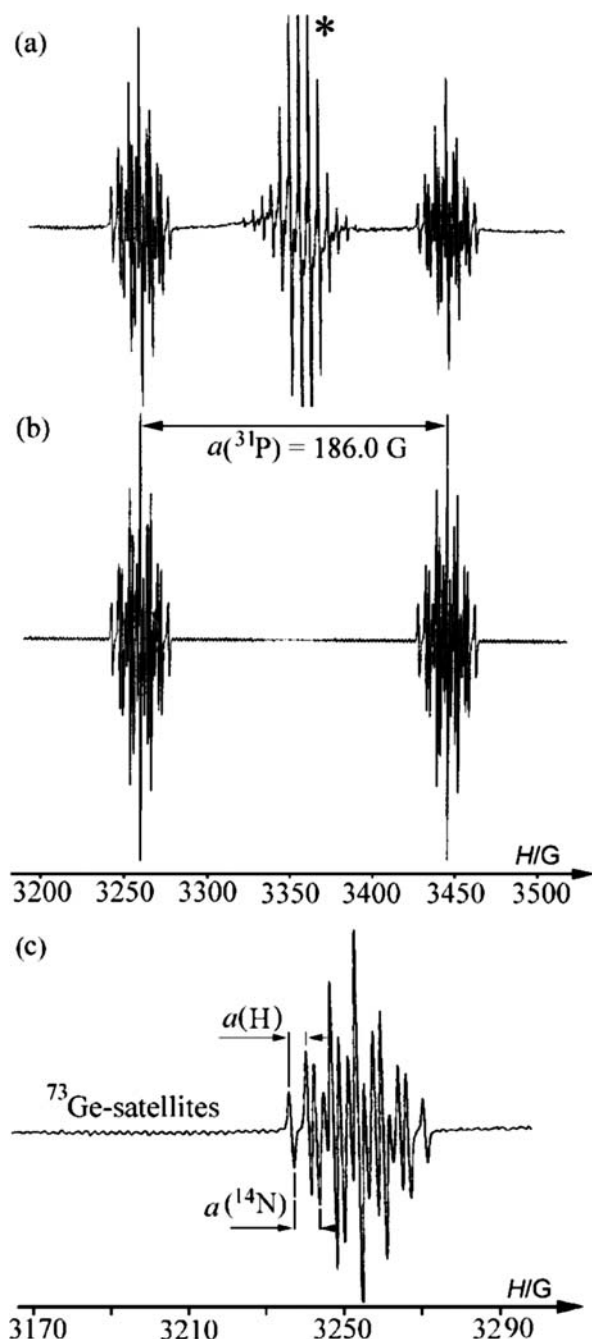


Fig. 2 (a) EPR spectrum of a toluene solution of **3a** recorded under UV-irradiation at 298 K (asterisk marks lines belonging to side products¹²), (b) simulated spectrum of **3a**, (c) expanded low field multiplet.

temperature the rate of dynamic conformational changes (ring inversion) of the saturated heterocycle (in the timescale of EPR) is not enough to average the hyperfine interaction with the four protons. This effect is typical for EPR spectra of saturated cyclic

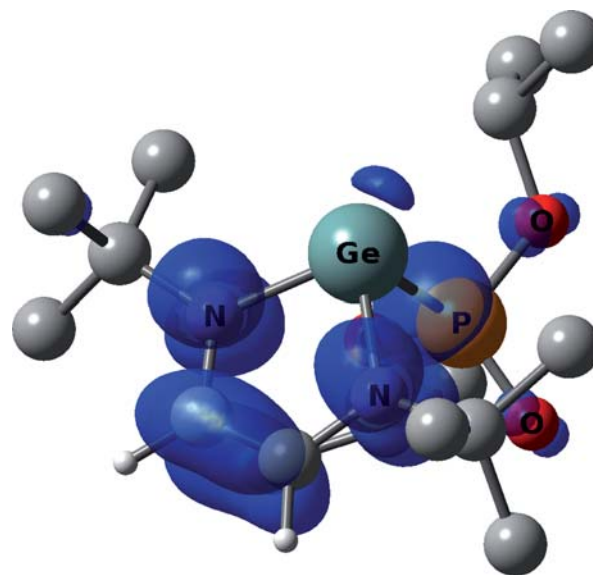
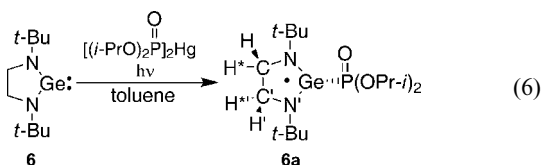


Fig. 3 DFT calculated spin density of **3a** at 0.003 au contour level. Calculated *g*-factor, absolute values of *hfc* constants and Löwdin atomic spin densities (in parentheses) at the particular nucleus of radical **3a**: *g* = 2.0027, *a*(¹³C) = 1.0 G (14.8%), *a*(¹³C') = 2.2 G (11.9%), *a*(¹H) = 4.1 G (−1.0%), *a*(¹H') = 3.5 G (−1.0%).

radicals.^{10a,16} The very large ³¹P-coupling constant of 199.6 G in **6a** is one of the largest observed for ³¹P nuclei in radical adducts of phosphonyl radicals.

After the irradiating light is turned off the signal of **6a** immediately disappears. The signal intensity of **6a** is lower by an order of magnitude than the signal of **3a** at a similar reactant concentration and condition of UV-irradiation. This fact indicates that the rate of **6a** dimerization is markedly faster than for **3a**.

DFT calculations of *hfc* constants in radical **6a** predict a somewhat larger *a_P* = 302.1 G. The calculated spin density distribution shows that in radical **6a** 42% of the spin density is localized on the central germanium atom, and 24% of the spin density is distributed on the ¹⁴N atoms (Fig. 5), in contrast to the spin density distribution in **3a** in which only 2% of the spin density resides on the Ge. Such a spin distribution difference between **3a** and **6a** is reasonable, because **6a** has no conjugated π-system which can delocalize the spin.

c) Silylene adducts

i) Reaction of silylene 2 with [(*i*-PrO)₂(O)P]₂Hg. In contrast to carbenes and germylenes, spontaneous reaction of a toluene solution of [(*i*-PrO)₂(O)P]₂Hg with unsaturated silylene in a 1 : 2 ratio begins immediately even at 200 K and gives an unexpected red-yellow Hg-containing product (**2b**), which was characterized by ¹H, ¹³C, ³¹P and ²⁹Si NMR spectroscopy (Scheme 1). **2b** is not stable at r.t. and completely disappears after 12 h (in the dark) forming a new compound **2c**, also observed by NMR spectroscopy. Additionally, traces of (*i*-PrO)₂(O)PH have been observed by NMR spectroscopy, indicating that radical processes are involved. Both products **2b** and **2c** are very air and moisture sensitive. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) of the reaction

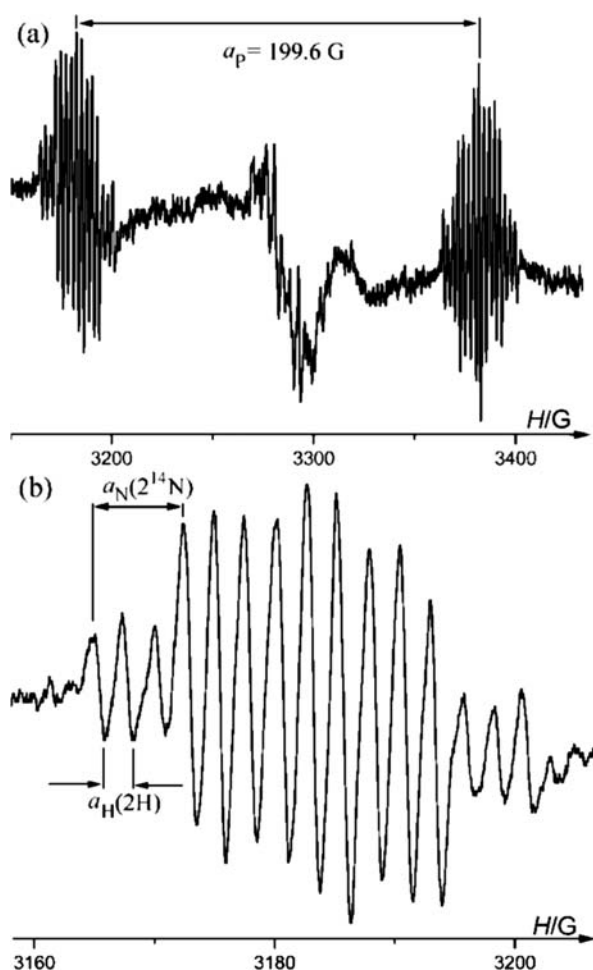


Fig. 4 (a) EPR spectrum of **6a** recorded under UV-irradiation at 298 K, (b) expanded low field multiplet.

mixture shows signals corresponding to **2c** and of the Hg-elimination product of **2b** (Fig. S5†).

Reactions of silylene with dialkylphosphite and its derivatives are new and interesting, however evidently, we cannot use $[(i\text{-PrO})_2(\text{O})\text{P}]_2\text{Hg}$ for formation of Si–P bonds in radical addition reactions.

The EPR monitoring of a toluene solution containing $[(i\text{-PrO})_2(\text{O})\text{P}]_2\text{Hg}$ and **2** in the dark and under UV irradiation reveals only minor secondary products of various radical reactions (for details see ESI, Fig. S6–S7†).

Although we could not observe the primary radical adducts (**2a**) of the phosphonyl radical with **2**, we carried out computations for radical **2a** in order to compare it with the analogous adducts of the carbenes and germylenes discussed above. DFT calculations of the structure (Scheme 1) and $h\nu$ constants in **2a** predict $a(^{31}\text{P}) = 243.5$ G. Fig. 6 shows the calculated structure of **2a** and its spin density. The heterocycle of **2a** is planar ($\angle \text{SiNCC}' = -0.5^\circ$ and $\angle \text{SiN}'\text{C}'\text{C} = 0.5^\circ$), with a pyramidal central silicon, $\Sigma\theta(\text{Si}^*) = 284.2^\circ$. The calculated spin densities show that in primary radical **2a** 14% of the spin density is localized on the central silicon atom and 65% of the spin density is distributed on the other atoms of the heterocycle. The spin delocalization pattern is similar to that in radical **3a** ($\text{E} = \text{Ge}$), but with slightly higher spin density on the central silicon atom.

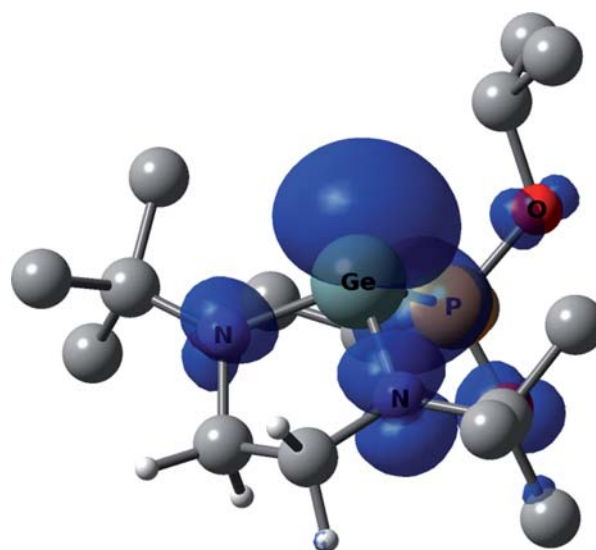
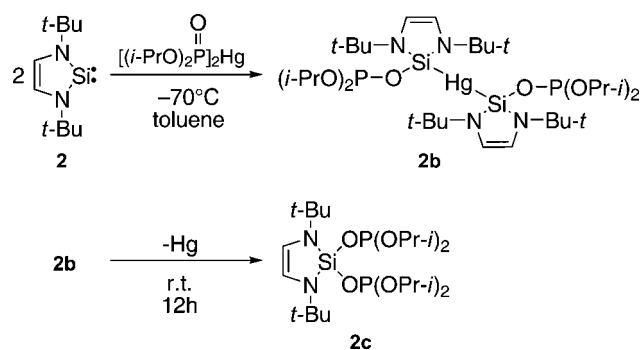


Fig. 5 DFT calculated spin density of **6a** at 0.003 au contour level. Calculated g -factor, absolute values of $h\nu$ constants and Löwdin atomic spin densities (in parentheses) at the particular nucleus of radical **6a**: $g = 2.0031$, $a(^{13}\text{C}) = 0.5$ G (0.7%), $a(^{13}\text{C}') = 0.4$ G (−0.2%), $a(^1\text{H}) = 0.8$ G (−0.1%), $a(^1\text{H}^*) = 2.3$ G (0.2%), $a(^1\text{H}') = 5.6$ G (0.7%), $a(^1\text{H}^{*'}) = 7.5$ G (0.9%).



Scheme 1

ii) **Radical adduct of silylene 5.** Saturated silylene **5** reacts with $[(i\text{-PrO})_2(\text{O})\text{P}]_2\text{Hg}$ similarly to unsaturated silylene **2** (Scheme 2). However, the reaction is slower and less clean, and additional unidentified minor products were observed.

As we did for **2a**, we studied computationally the radical adduct (**5a**) of phosphonyl radical **7** to silylene **5**. The DFT calculations predict $a(^{31}\text{P}) = 264.0$ G. The calculated spin density distribution shows that in radical **5a** 58% of the spin density is localized on the central silicon atom, and 19% of the spin density is distributed over the other atoms of the heterocycle (Fig. 7).

Conclusions

Radical reactions of phosphonyl radicals with stable N -heterocyclic carbenes, silylenes and germylenes were studied by EPR spectroscopy and by DFT calculations. The calculations show that for unsaturated radicals **1a**, **2a** and **3a**, the degree of pyramidity at the radical center increases in the order: C ($\Sigma\theta = 352^\circ$) \ll Si ($\Sigma\theta = 284^\circ$) $<$ Ge ($\Sigma\theta = 270^\circ$), which is

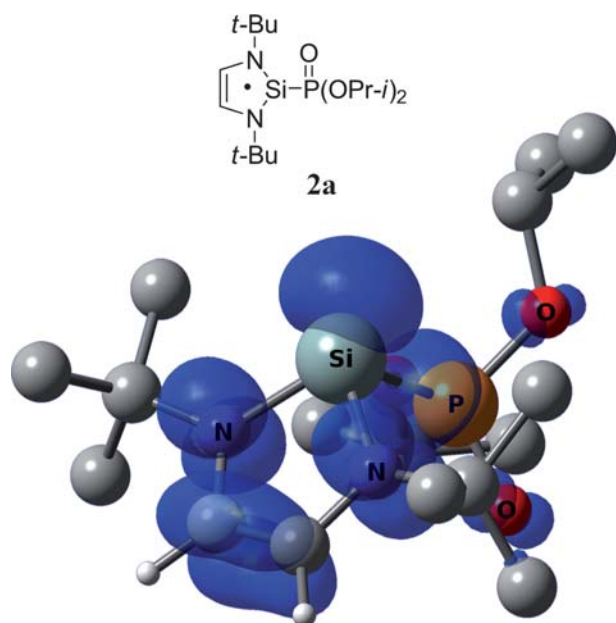
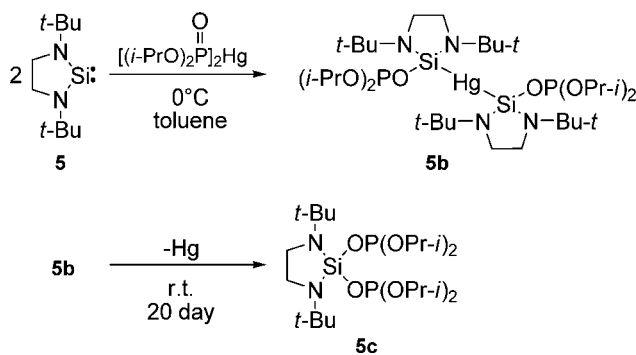


Fig. 6 DFT calculated spin density of **2a** at 0.003 au contour level. Calculated *g*-factor, absolute values of *hfc* constants and Löwdin atomic spin densities (in parentheses) at the particular nucleus of radical **2a**: *g* = 2.0032, *a*(¹³C) = 0.9 G (13.4%), *a*(¹³C') = 1.6 G (9.5%), *a*(¹H) = 3.0 G (−0.86%), *a*(¹H') = 2.4 G (−0.61%).



Scheme 2

accompanied by a decrease in the spin density on the central atom (C (39.3%) \gg Si (14.4%) > Ge (2%)) and an increased spin delocalization over the 5-membered ring (C \ll Si < Ge, highest delocalization). These trends can be understood in terms of a larger contribution of zwitterionic resonance structure **B** (eqn (7)) along the series Ge > Si \gg C. This trend is consistent with the strength of np -SOMO(E) $\rightarrow \pi^*(N-C=N)$ conjugation which also follows the order Ge > Si > C, as the SOMO(E) energy in *e.g.*, H₃E[•] increases along the series C (−10.5 eV) \ll Si (−9.1 eV) < Ge (−8.9 eV) (UHF/6-311+G//UB3LYP/6-311+G(d)). In all these trends large differences are observed

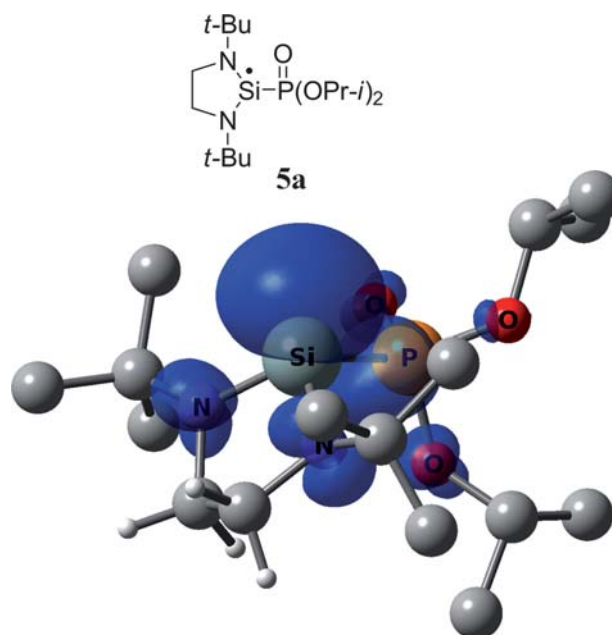
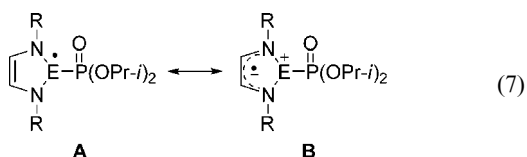


Fig. 7 DFT calculated spin density of **5a** at 0.003 au contour level. Calculated *g*-factor, absolute values of *hfc* constants and Löwdin atomic spin densities (in parentheses) at the particular nucleus of radical **5a**: *g* = 2.0032, *a*(¹³C) = 2.3 G (0.9%), *a*(¹³C') = 1.1 G (0.1%), *a*(¹H) = 0.7 G (0.06%), *a*(¹H*) = 2.9 G (0.29%), *a*(¹H') = 1.7 G (0.24%), *a*(¹H'*) = 5.0 G (1.1%).

between C and Si while the differences between Si and Ge are small.

In saturated radicals **5a** and **6a**, lacking the possibility for cyclic electron delocalization, the calculated spin density at the central atom is much higher (Si, 58%; Ge, 42%) than in the corresponding unsaturated radicals **2a** and **3a**, as expected.

Silylenes, in contrast to carbenes and germylenes react spontaneously with [(*i*-PrO)₂(O)P]₂Hg to yield unusual mercury-containing silyl phosphites. This new reaction opens interesting synthetic perspectives (*e.g.* synthesis of metallasilyl phosphite compounds).

The geometry, spin density distribution and reactivity of radical adducts of group 14 imidazol-2-ylidene and imidazolin-2-ylidene demonstrate a strong dependence on the nature of the heterocycle and on the divalent central atom. Such dependence is unprecedented in radical chemistry. We are continuing to explore this interesting new class of radical reactions.

Experimental section

Standard Schlenk techniques in a vacuum (10^{−2} torr) were used for the preparation and manipulations of all samples.

Typical EPR experiment

The phosphonyl radical **7** was generated photolytically *in situ* from [(*i*-PrO)₂(O)P]₂Hg. UV-irradiation of solutions containing the *N*-heterocyclic metallylenes and [(*i*-PrO)₂(O)P]₂Hg in a Pyrex tube within the cavity of the EPR spectrometer gave rise to the radical adducts of metallylenes whose spectra were recorded.

The typical concentration of the metallylenes was 10^{-2} M and of $\text{Hg}[\text{P}(\text{O})(\text{OPr-}i)_2]_2$ was 3×10^{-3} M.

Materials

The synthesis of **2**,^{4d} **3**,^{4h} **4**,^{4b} **5**,^{4f} **6**^{4h} and $[(i\text{-PrO})_2(\text{O})\text{P}]_2\text{Hg}^{17}$ is described elsewhere. Toluene and benzene were degassed, kept on *t*-BuLi in a vacuum and distilled prior to use.

EPR spectroscopy

EPR spectra were recorded on a Bruker EMX-10/12 X-band ($\nu = 9.4$ GHz) digital EPR spectrometer equipped with a Bruker N₂-temperature controller. Samples were irradiated with the focused and filtered ($\lambda > 300$ nm) or unfiltered ($\lambda > 250$ nm) light of a high-pressure mercury lamp (1 kW) (ARC lamp power supply model 69920) in the resonator of the EPR spectrometer.

EPR spectra were recorded at microwave power 0.5–1.0 mW, 100 kHz magnetic field modulation of 0.05–1.00 G amplitude. Digital field resolution was 2048 points per spectrum, allowing all hyperfine splitting to be measured directly with an accuracy of better than 0.1 G. Spectra processing and simulation were performed with Bruker WIN-EPR and SimFonia Software. The *g*-factors values were determined using 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) as reference ($g = 2.0058$).

NMR spectroscopy

NMR spectra were recorded at room temperature in benzene solutions in J. Young vacuum NMR tubes equipped with DMSO-*d*₆ capillary as external standard, using Bruker Avance 300 and Bruker Avance 500 instruments. NMR shifts are given in ppm.

2b: ¹H NMR (benzene, DMSO-*d*₆ capillary): δ 5.95 (4H, s), 4.91 (4H, m, $J_{\text{H-H}} = 5.9$ Hz), 1.41 (36H, s), 1.30 (24H, m, $J_{\text{H-H}} = 5.9$ Hz); ²⁹Si NMR: δ 65.7 (d, $J_{\text{Si-P}} = 12.7$ Hz); ³¹P NMR: δ 129.3; ¹³C NMR: 113.0, 65.4 (d, $J_{\text{C-P}} = 10.9$ Hz), 51.6, 32.0, 24.8.

2c: ¹H NMR (benzene, DMSO-*d*₆ capillary): δ 5.71 (2H, s), 4.52 (4H, m, $J_{\text{H-P}} = 6.3$ Hz, $J_{\text{H-H}} = 6.2$ Hz), 1.41 (18H, s), 1.19 (24H, dd, $J_{\text{H-P}} = 2.0$ Hz, $J_{\text{H-H}} = 6.2$ Hz); ²⁹Si NMR: δ -71.2 (t, $J_{\text{Si-P}} = 1.3$ Hz); ³¹P NMR: δ 126.2; ¹³C NMR: δ 110.4, 65.5 (d, $J_{\text{C-P}} = 11.1$ Hz), 51.3, 30.6, 24.5.

5b: ¹H NMR (benzene, DMSO-*d*₆ capillary): δ 4.94 (4H, m, $J_{\text{H-H}} = 6.0$ Hz), 2.94 (8H, s), 1.39 (36H, s), 1.33 (24H, d, $J_{\text{H-H}} = 6.0$ Hz); ²⁹Si NMR: δ 67.9 (d, $J_{\text{Si-P}} = 16.4$ Hz); ³¹P NMR: δ 129.7; ¹³C NMR: 65.0 (d, $J_{\text{C-P}} = 10.9$ Hz), 51.2, 44.1, 30.8, 24.8.

5c: ¹H NMR (benzene, DMSO-*d*₆ capillary): δ 4.55 (4H, m, $J_{\text{H-P}} = 6.0$ Hz, $J_{\text{H-H}} = 6.3$ Hz), 2.90 (4H, s), 1.66 (18H, s), 1.22 (24H, dd, $J_{\text{H-P}} = 5.2$ Hz, $J_{\text{H-H}} = 6.3$ Hz); ²⁹Si NMR: δ -69.1 (t, $J_{\text{Si-P}} = 3.2$ Hz); ³¹P NMR: δ 126.0; ¹³C NMR: δ 65.2 (d, $J_{\text{C-P}} = 10.8$ Hz), 50.9, 41.5, 29.3, 25.0.

Computational methods

Geometry optimizations were performed at the DFT B3LYP/6-31+G(d) level. This level was demonstrated to be reliable in predicting ground state geometries of radicals.¹⁸ All structures were confirmed as local minima by calculating second order derivatives. Orbital energies were calculated for optimized

geometries using the UHF method because KS energies tend to overestimate the experimental values. However, trends are consistent within the methods.¹⁹ These calculations were carried out using the Gaussian03²⁰ series of programs.

Isotropic hyperfine coupling constants and *g*-factors were calculated using the PBE0 functional²¹ in conjunction with an uncontracted TZVP²² basis set using the ORCA 2.6.35 software package developed by F. Neese.²³ The PBE0/TZVP level produces more accurate predictions of *hfc* constants and *g*-factors.^{23b,24}

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