Free Radical Chemistry of Phosphasilenes

Kerim Samedov, Yannic Heider, Yuanjing Cai,* Philipp Willmes, Daniel Mühlhausen,
Volker Huch, Robert West, David Scheschkewitz,* and Paul W. Percival*

Abstract: *Understanding the characteristics of radicals formed from silicon-containing heavy analogues of alkenes is of great importance for their application in radical polymerization. Steric and electronic substituent effects in compounds such as phosphasilenes not only stabilize the Si=P double bond, but also influence the structure and species of the formed radicals. Herein we report our first investigations of radicals derived from phosphasilenes with Mes, Tip, Dur, and NMe₂ substituents on the P atom, using muon spin spectroscopy and DFT calculations. Adding muonium (a light isotope of hydrogen) to phosphasilenes reveals that: a) the electron-donor NMe₂ and the bulkiest Tip-substituted phosphasilenes form several muoniated radicals with different rotamer conformations; b) bulky Dur-substituted phosphasilene forms two radicals (Si- and P-centred); and c) Mes-substituted phosphasilene mainly forms one species of radical, at the P centre. These significant differences result from intramolecular substituent effects.*

$\mathbf{S}$ince the breakthrough isolation of the first disilene[1] and silene[2] in the early 1980s, silicon-containing heavy analogues of alkenes have moved into the focus of inorganic chemists. The initial emphasis was on the reactivity of Si=Si/Si=C containing molecules which can be polymerized and thence transformed into special high-performance inorganic materials (e.g. silicon carbide fibres).[3] Within a decade, a feasible method was developed to obtain the first isolable and structure-characterized stable phosphasilene (a molecule containing the $>$Si=P- fragment) by an elimination reaction.[4] From then on, acyclic and cyclic phosphasilenes have enjoyed increased attention regarding their exploitation in synthesis and exploration of the reactivity and properties of the Si=P bond.[5]

In view of the thermodynamic instability of the Si=P bond, a primary focus of phosphasilene chemistry has been on kinetic stabilization, by incorporation of peripheral bulky substituents,[5,6] and electronic stabilization via the introduction of electron-donors/acceptors[6d] or π-conjugated units,[6e,f] thus avoiding thermally induced oligomerization and other undesired transformations, such as cyclization, addition, and bond dissociation.[5a] Although steric protection of the silicon atom is more important than that of phosphorus,[5a] electronic stabilization is also necessary.[6e,f] Because silicon is less electronegative than phosphorus, the Si=P bond is σ-polarized. Electron-donating groups (e.g. silyl, NH₂) on the Si or P atom of phosphasilenes will electronically interact with the π-acceptor Si=P bond. Thus the Si=P–Si,[4a] P–P–Si=P,[4b] and Si–Si=P skeletons result in isolable and stable phosphasilenes with good yields.[7] Functionalized phosphasilenes have been developed for use as transfer reagents[8] and as catalysts in the form of π-accepting ligands in transition-metal complexes, either P-metalated via the phosphorus lone pair,[7a,9] or coordination of both the Si and P atoms with the transition metal centre.[10]

Although the recently developed synthetic method of 1,3-migration in the Si=Si–P skeleton has been used to generate stable phosphasilenes based on Si–Si=P,[5d,7b,e] phosphasilene chemistry is still restricted to small, neutral molecules. Despite recent advances in understanding the reactions of phosphasilenes,[5c] their reactivity towards free radicals seems to be unexplored. We decided to investigate this using an H-atom surrogate.

Our experimental technique is muon spin rotation (μSR), a form of magnetic resonance spectroscopy based on the spin precession of muons.[11] Muons are short-lived subatomic particles ($\tau = 2.2$ μs) which can be produced as highly spin-

[*] Dr. K. Samedov, Prof. Dr. Y. Cai
Beijing Advanced Innovation Center for Soft Matter Science and Engineering
Beijing University of Chemical Technology
Beijing 100029 (China)
E-mail: gardencyj@hotmail.com

Dr. K. Samedov
Department of Chemistry, University of British Columbia
2036 Main Mall, Vancouver, BC, V6T 1Z1 (Canada)

M. Sc. Y. Heider, Dr. P. Willmes, D. Mühlhausen, Dr. V. Huch, Prof. Dr. D. Scheschkewitz
Krupp-Chair for General and Inorganic Chemistry
Saarland University
Campus, C4.1, 66123 Saarbrücken (Germany)
E-mail: scheschkewitz@mx.uni-saarland.de

Prof. Dr. R. West
Department of Chemistry, University of Wisconsin-Madison
1101 University Avenue, Madison, WI 53706 (USA)

Prof. Dr. P. W. Percival
Department of Chemistry, Simon Fraser University
8888 University Drive, Burnaby, BC, V5A 1S6 (Canada),
and
Centre for Molecular and Materials Science, TRIUMF
4004 Wesbrook Mall, Vancouver, BC, V6T 2A3 (Canada)
E-mail: percival@sfu.ca

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/anie.202006289.

polarized beams at various particle accelerators (we use the TRIUMF facility, in Vancouver, Canada). In matter, the positive muon can act as the nucleus of the single-electron atom muonium (Mu). Although Mu has only one-ninth the mass of H, their atomic properties are very similar, and Mu can be considered as a light isotope of hydrogen.[12] In particular, Mu adds to low-valent molecules to form muoni-ated radicals (free radicals in which an H atom has been replaced by Mu).[11c, 13] Unlike ESR spectroscopy, the method of choice for persistent free radicals,[14] muon spin spectros-copy is ideal for the study of transient radicals. Because muon beams are spin-polarized, useful spectra can be obtained from as few as 10^7 radicals. Furthermore, μSR has been used to investigate free radical chemistry under conditions not amenable for study by more conventional spectroscopic techniques. Examples range from the gas phase[15] to super-heated, pressurized water.[16]

In recent years we have applied muon spin spectroscopy to study the radical chemistry of low-valent molecules containing silicon,[17] germanium,[17b, 18] and phosphorus.[19] By studying monomer radicals we are able to gain more insight into the mechanism of polymerization,[19] specifically the initial step of selective addition of radicals to different sites in the monomer. In addition, the structure of the parent compound can influence the possibility of migration of the radical centre, resulting in a different structure of the repeating unit of the polymer.[20] Thus, investigation of monomer radicals is important for the study of radical polymerization. However, to date there have been no investigations of radicals formed from phosphasilenes.

Herein, we report unprecedented radical species derived from phosphasilenes substituted with different bulky groups. All these compounds (**1–4** in Scheme 1), including the newly synthesized compounds **2** and **3**, were isolated pure and fully characterized (see the Supporting Information). They were studied in solution by μSR.
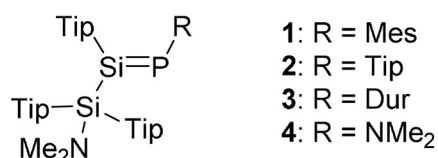
Scheme 1. Phosphasilenes investigated (CCDC No. 1989736 (for **2**) and 1989735 (for **3**). Mes = 2,4,6-trimethylphenyl, Tip = 2,4,6-triisopro-pylphenyl, Dur = 2,3,5,6-tetramethylphenyl, NMe₂ = dimethylamino.

The first phosphasilene which we investigated was **4** (Scheme 1). On the basis of prior experience of Mu reactions with silenes[17a,d,g] and phosphaalkenes[19] we expected two radicals, corresponding to Mu addition at the Si and P ends of the double bond, as shown in Scheme 2. However, the transverse-field μSR spectrum (Figure 1) obtained from a solution of **4** in hexane shows the characteristic precession signals of at least four muoniated radicals.

In principle, Mu could add to the phenyl rings of the Tip (2,4,6-triisopropylphenyl) substituents, but in this case muon hyperfine constants (hfcs) greater than 400 MHz would be
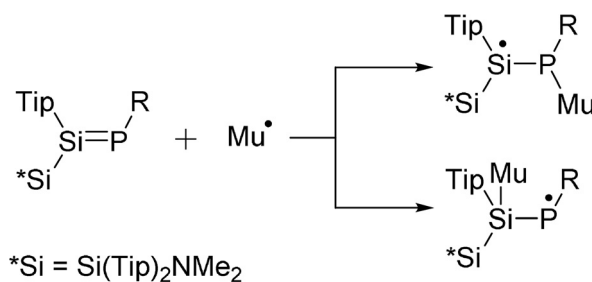
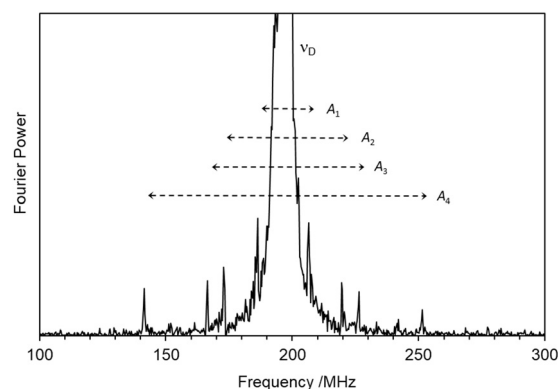**Scheme 2.** Reactivity pattern anticipated for phosphasilenes **1–4** in reaction with Mu.

Figure 1. Transverse-field μSR spectrum at 14.48 kG obtained from a solution of **4** in hexane at 50.6 °C. This Fourier transform corre-sponds to a 3 μs time window delayed by 85 ns. The truncated signal labeled ν_D is due to muons in diamagnetic molecules, whose spins precess at the muon Larmor frequency (196.15 MHz at this magnetic field). A_1, A_2, A_3, and A_4 denote the separation of the pairs of radical precession frequencies and thus comprise the muon hyperfine con-stants.

expected for the cyclohexadienyl-type products.[21] The much smaller hfcs observed are instead consistent with the original expectation of Mu addition at the Si=P bond. It is well established that rotation about a carbon–carbon bond affects the magnitude of muon hfcs in alkyl radicals, because overlap of the unpaired electron orbital (p_z) with the muon varies with the dihedral angle ϕ between C_β-Mu and $C_\alpha(2p_z)$.[22] The corresponding effect was invoked to explain hyperfine isotope effects in muoniated radicals derived from a phos-phaalkene,[19] and it seems reasonable that the conformational effect would also apply to Mu adducts of Si=P. Thus, the multiple radical signals obtained from **4** might be due to two or more conformers of each radical (Scheme 2). The possi-bility of identifying distinct conformers prompted our further investigations, both experimental and computational.

If conformation is important, then modifying the sub-stituents should have an effect on the muon hfcs. We therefore investigated a series of available phosphasilenes, **1–4**, which have different substituents on the P atom. The μSR spectra show strong differences, both in number of radical species and their hfcs (see Figure 2). These and additional spectra are included in the Supporting Information, together with lists of precession frequencies used to calculate the muon hfcs. The μSR spectra were found to depend on Fourier transform
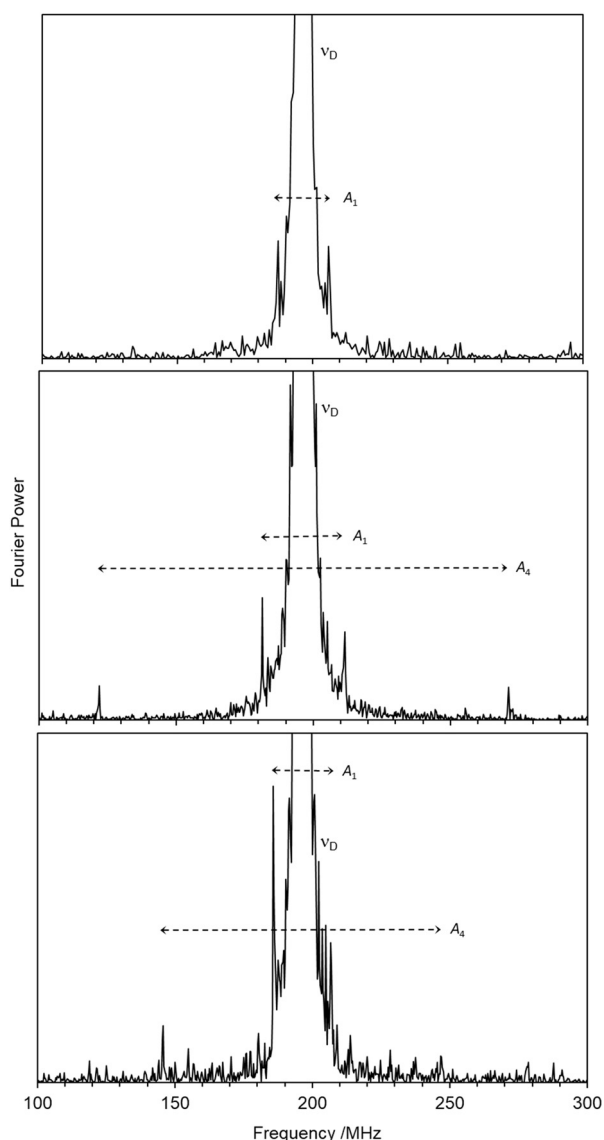
Figure 2. Transverse-field μSR spectra at 14.48 kG obtained from a solution of **1** in tetrahydrofuran at 53.5 °C (top), **2** in tetrahydrofuran at 53.7 °C (middle), and **3** in tetrahydrofuran at 54.6 °C (bottom).

conditions, specifically the time delay between the muon stop and the data time window used in the transform. This is not simply a result of delayed onset of some frequencies, because the amplitudes of the precession frequencies vary with delay time in a sinusoidal manner. A similar effect has been previously noted for muoniated radicals derived from heteroatomic double bonds: C=O,[23] Si=C,[17d] and P=C.[19] A practical consequence of this effect is that "standard" μSR display (no Fourier transform delay) can result in missing a particular signal. Thus, the spectrum derived from **2** shown in the middle panel of Figure 2 reveals only two radicals, whereas adjustment of the transform delay time reveals the precession signals of a third radical (compare Figures S16 and S17). Careful examination of all spectra by varying the Fourier transform delay revealed oscillations in signal amplitudes but no more radicals.

A summary of the muon hfcs for all radicals detected is given in Table 1. The data are grouped into columns with similar values, labeled A_1–A_4, although the largest entry for **2** appears to be an outlier and possibly represents a different structure to the others in the A_4 column. The effect of varying the substituent on P is best seen in the A_1 column. There is also a clear effect of temperature. Both observations suggest that the bulk of the substituent (R in Schemes 1 and 2) influences the relevant dihedral angle ϕ. The effect is strongest for the smallest hfcs (A_1) because those correspond to values of ϕ close to 90°, and β hyperfine constants depend on $\cos^2 \phi$.[24] The temperature dependence of the other sets of hfcs is small, consistent with larger dihedral angles. There is also a small solvent dependence, evident in the spectra taken at 25 °C. These findings all suggest that the significant differences in the hfc results arise from intramolecular effects.

Table 1: Summary of muon hyperfine constants determined from μSR spectra.

Sample[b]	T [°C]	Muon hyperfine constants [MHz][a]			
		A_1	A_2	A_3	A_4
1	53.5	19.0(1)	–	–	–
2	53.7	30.1(1)	–	61.7(1)	149.0(1)
3	54.6	21.3(1)	—	-	101.9(1)
4	25.3	15.0(1)	48.5(1)	60.4(1)	111.9(1)
4′	6.3	13.8(2)	48.3(1)	62.0(2)	112.8(1)
4′	25.2	16.4(2)	47.4(1)	61.1(1)	111.6(1)
4′	50.6	19.9(1)	46.3(1)	60.2(1)	110.1(1)

[a] The decimal digits in parentheses denote statistical fit uncertainties.
[b] THF solvent except for **4′** for which the solvent was hexane.

To assign the muon hfcs to individual radical structures and conformations, DFT calculations were carried out for phosphasilenes **1**–**4** and the radicals formed by adding an H atom to either end of the Si=P bond. Molecular geometries were optimized, and relaxed potential energy surface (PES) scans were performed for rotation about the Si—P bond of each radical. Computational details are given in the Supporting Information. Within the Born–Oppenheimer approximation an electronic PES should apply to all nuclear isotopes, so the equilibrium radical geometries were assumed to apply to the analogous muoniated radicals as well. Similarly, proton hfcs were simply scaled by the ratio of the muon/proton magnetic moments (3.183) to estimate muon hfcs; no attempt was made to account for mass-dependent isotope effects.[12b] This limitation should be taken into consideration when comparing experimental hfcs with predictions. In the absence of extensive vibrational analysis, computed hfcs correspond to the geometry at the minimum of the electronic potential surface. Zero-point vibrational effects can result in significant isotope effects for a light atom such as muonium.[12b]

Figure 3 shows the PES scans for the two radicals formed from **4**. In both cases there are radical conformations with similar energies. Similar scans for the radicals formed from the other phosphasilenes can be found in the Supporting Information. In all cases Mu addition to Si gives the lower-energy radical. However, only the scans for **4** include equiergic minima, indicating pairs of radical conformations
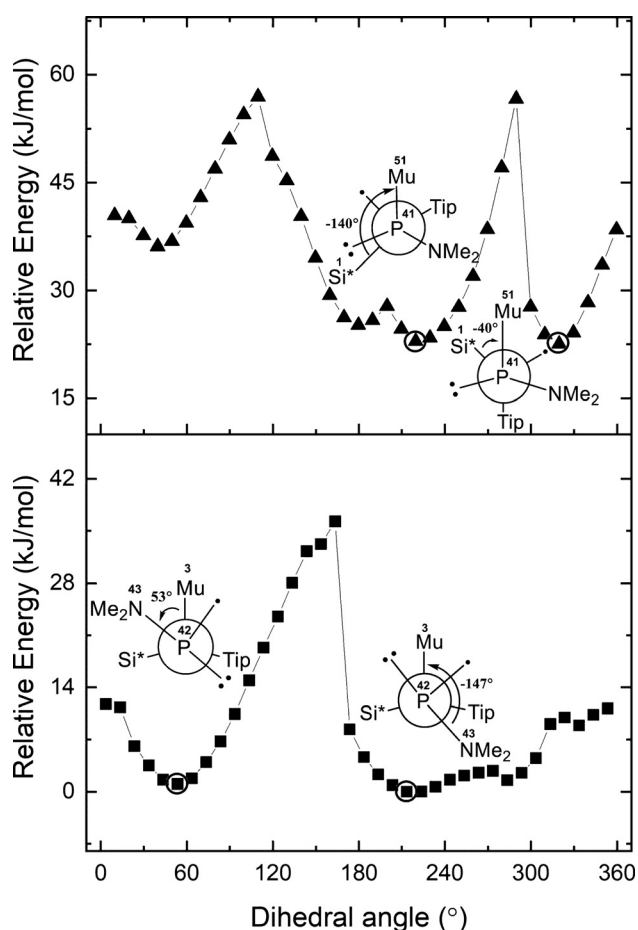
53° and 213°) and two rotamers of **4-PMu** (dihedral angles Mu[51]-P[41]-Si[2]-Si[1] 220° and 320°).

Similar considerations apply to the assignment of the radical signals detected from phosphasilenes **1–3** (see the Supporting Information) and the results are summarized in Table 2.

Table 2: Summary of radical assignments and conformations.

Radical	Hyperfine constant [MHz]		Assignment	
	Expt.	Calcd.	Dihedral angle [°]	Energy [kJ mol^{-1}][a]
4-SiMu	46	43	Mu^3-Si^2-P^{42}-N^{43} [b]: 213/−147	−242.7
	110	90	Mu^3-Si^2-P^{42}-N^{43}: 53	−241.6
4-PMu	60	57	Mu^{51}-P^{41}-Si^2-Si^1: 220/−140	−219.7
	20	19	Mu^{51}-P^{41}-Si^2-Si^1: 320/−40	−219.7
2-SiMu	30	31	Mu^{56}-Si^2-P^3-C^4: 34	−251.6
	149	141	Mu^{56}-Si^2-P^3-C^4: −66	−232.9
3-SiMu	21	21	Mu^{65}-Si^2-P^3-C^4: 30	−250.8
3-PMu	102	81	Mu^{27}-P^3-Si^2-Si^1: 109	−226.6
1-SiMu	19	22	Mu^{62}-Si^2-P^3-C^4: 30	−248.8

[a] Reaction energy, $\Delta E = E(\text{radical}) - E(\text{parent}) - E(\text{H})$. [b] The superscript digit denotes the atom number in the calculation.

One general result is that P-centred radicals are formed from all phosphasilenes (i.e. Mu attack on Si). As evident from the final column of Table 2, these are the lowest-energy products (presumably due to enhanced delocalization of the π system). However, Si-centred radicals were also detected for **4** and **3**. Since these are over 20 kJ mol^{-1} higher in energy than the P-centred radicals, it follows that radical formation must be kinetically controlled. The rates of the competitive reactions depend on their activation energies, and since the radical signals are similar in intensity (Figure 1) we conclude that there is not much difference in the activation energies. The radical formation reactions are all exoergic (Table 2), so energy dissipation must be faster than any equilibration processes between the multiple products detected. It should be pointed out that the nondetection of Si-centred radicals from **1** and **2** does not completely rule out their formation. For example, the lowest-energy conformer of **2-PMu** is predicted to have a muon hfc of 17 MHz (see the table on page S26), which means that weak precession signals could be swamped by the diamagnetic peak (see Figure S16).

Electronic and bulky substituent effects not only stabilize phosphasilenes in different ways, but also result in derived radicals with various characteristics. The electron-donating dimethylamino group in **4** electronically stabilizes the structures of Si- and P-centred radicals in different conformations when Mu adds to the Si=P double bond; thus multiple rotamers are observed. However, the situation is different for the bulky phenyl-substituted phosphasilenes **1–3**, because bulkier groups tend to lock in preferred conformations.[25] Thus, of the Mes-, Tip-, and Dur-substituted phosphasilenes **1–3**, the Tip-substituted compound **2** has the bulkiest substituent, so the preferred conformations of its radicals should

Figure 3. Potential energy surface scans for rotation about the Si–P bonds of radicals formed by Mu addition to phosphasilene **4** at the Si atom (lower) or the P atom (upper). The circled points denote radical conformations detected by muon spin spectroscopy.

with the same energy. This may be why there are more radicals detected from **4** than the other phosphasilenes.

Assignment of the radical signals to specific rotamers involves comparison of the experimental hfcs (Table 1) with computed values. For ease of discussion the two radicals will be denoted **4-SiMu** and **4-PMu**. The muon hfcs calculated for **4-SiMu** are 90 MHz and 43 MHz for dihedral angles 53° and 213°, respectively. For the lowest-energy rotamers of **4-PMu** the calculated hfcs are 57 MHz and 19 MHz for dihedral angles 220° and 320°, respectively. There is also a local minimum in the **4-PMu** PES at 40°. Its calculated hfc is 115 MHz, close to one of the experimental values (110 MHz). However, the stability of that rotamer is questionable (there is a low barrier for conversion to the 320° rotamer), and any isotope effect would give a higher experimental hfc than the computed value. The three smallest experimental hfcs (20, 46, and 60 MHz) have good matches with predictions, suggesting that the largest value corresponds to **4-SiMu** at 53°. The isotope effect (90 MHz calculated, 110 MHz observed) is typical for alkyl radicals[12b] but equivalent data for a phosphorus-centred radical is limited.[19]

On balance, therefore, we assign the four detected radicals to two rotamers of **4-SiMu** (dihedral angles Mu^3-Si^2-P^{42}-N^{43}

be the most stabilized. The detection of two rotamers of the P-centred radical supports this point, and is consistent with the two clearly defined potential minima evident in the lower panel of Figure S23. In contrast, a single radical (Mu addition to Si) is observed in the less bulky Mes-substituted phosphasilene **1**, where there is only one clear minimum (Figure S22).

Since phosphasilenes **1–3** have similar substituents, it is not surprising that the resulting P-centred radicals have similar geometry and characteristics: muon hfcs in the range 20–30 MHz, a Mu-Si-P-C dihedral angle of 30°, and the lowest energy of ca. -250 kJ mol^{-1}. NBO analysis (Table S3 in the Supporting Information) shows that the half-filled orbital has almost pure p character, and the magnitude of the hfc depends on the extent of overlap with the Si—Mu bond.

Based on the above experimental and computational results, we have established that substituent effects influence the characteristics of the formed radicals. This is important because the relationship between the substituted phosphasilenes and the identity and structures of the formed radicals can lead to a new perspective for guiding the design and synthesis of phosphasilene monomers in radical polymerization.

In conclusion, we have synthesized phosphasilenes with various bulky phenyl substituents (**1–3**) and an electron-donating amino group (**4**), and explored how the various substituents influence radical formation via the reaction with muonium. All phosphasilenes form P-centred radicals, and two of them (**3** and **4**) also form more energetic Si-centred radicals, suggesting that radical formation is kinetically controlled. Remarkably, for the first time, radicals with different rotamer conformations were identified in the products of **2** and **4**. A single P-centred radical was detected as the product of **1**. This work demonstrates the potential influence of substituents on the phosphasilene radical characteristics, which should foster understanding of the selective design and synthesis of monomers for stereoregular radical polymerization. For further investigation of the intramolecular substituent effect on the identity and structure of radicals derived from silicon-containing heavy analogues of alkenes, we plan to extend our μSR studies to silenes.

Conflict of interest

The authors declare no conflict of interest.

[1] a) R. West, M. J. Fink, J. Michl, *Science* **1981**, *214*, 1343–1344; b) R. West, *Science* **1984**, *225*, 1109–1114.

[2] a) A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. K. Kallury, *J. Chem. Soc. Chem. Commun.* **1981**, 191–192; b) A. G. Brook, S. C. Nyburg, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. Krishna, M. R. Kallury, Y. C. Poon, Y.-M. Chang, W.-N. Winnie, *J. Am. Chem. Soc.* **1982**, *104*, 5667–5672.

[3] a) T. Ishikawa, Y. Kohtoku, K. Kumagawa, T. Yamamura, T. Nagasawa, *Nature* **1998**, *391*, 773–775; b) N. Patil, X. Zhao, N. K. Mishra, M. A. Saed, M. Radovic, M. J. Green, *ACS Appl. Mater. Interfaces* **2019**, *11*, 46132–46139.

[4] a) M. Drieß, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1022–1024; *Angew. Chem.* **1991**, *103*, 979–981; b) H. R. G. Bender, E. Niecke, M. Nieger, *J. Am. Chem. Soc.* **1993**, *115*, 3314–3315.

[5] a) M. Driess, *Coord. Chem. Rev.* **1995**, *145*, 1–25; b) N. C. Breit, T. Szilvási, S. Inoue, *Chem. Eur. J.* **2014**, *20*, 9312–9318; c) V. Nesterov, N. C. Breit, S. Inoue, *Chem. Eur. J.* **2017**, *23*, 12014–12039; d) Y. Heider, P. Willmes, D. Mühlhausen, L. Klemmer, M. Zimmer, V. Huch, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2019**, *58*, 1939–1944; *Angew. Chem.* **2019**, *131*, 1958–1964.

[6] a) C. N. Smit, F. M. Lock, F. Bickelhaupt, *Tetrahedron Lett.* **1984**, *25*, 3011–3014; b) C. N. Smit, F. Bickelhaupt, *Organometallics* **1987**, *6*, 1156–1163; c) M. Driess, H. Pritzkow, U. Winkler, *J. Organomet. Chem.* **1997**, *529*, 313–321; d) R. Corriu, G. Lanneau, C. Priou, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1130–1132; *Angew. Chem.* **1991**, *103*, 1153–1155; e) B. Li, T. Matsuo, D. Hashizume, H. Fueno, K. Tanaka, K. Tamao, *J. Am. Chem. Soc.* **2009**, *131*, 13222–13223; f) S. Inoue, W. Wang, C. Präsang, M. Asay, E. Irran, M. Driess, *J. Am. Chem. Soc.* **2011**, *133*, 2868–2871.

[7] a) M. Driess, S. Block, M. Brym, M. T. Gamer, *Angew. Chem. Int. Ed.* **2006**, *45*, 2293–2296; *Angew. Chem.* **2006**, *118*, 2351–2354; b) P. Willmes, M. J. Cowley, M. Hartmann, M. Zimmer, V. Huch, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2014**, *53*, 2216–2220; *Angew. Chem.* **2014**, *126*, 2248–2252; c) V. Y. Lee, S. Aoki, M. Kawai, T. Meguro, A. Sekiguchi, *J. Am. Chem. Soc.* **2014**, *136*, 6243–6246; d) A. W. Kyri, P. K. Majhi, T. Sasamori, T. Agou, V. Nesterov, J.-D. Guo, S. Nagase, N. Tokitoh, R. Streubel, *Molecules* **2016**, *21*, 1309; e) P. Willmes, L. Junk, V. Huch, C. B. Yildiz, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2016**, *55*, 10913–10917; *Angew. Chem.* **2016**, *128*, 11074–11078.

[8] K. Hansen, T. Szilvási, B. Blom, S. Inoue, J. Epping, M. Driess, *J. Am. Chem. Soc.* **2013**, *135*, 11795–11798.

[9] a) S. Yao, S. Block, M. Brym, M. Driess, *Chem. Commun.* **2007**, 3844–3846; b) B. Li, T. Matsuo, T. Fukunaga, D. Hashizume, H. Fueno, K. Tanaka, K. Tamao, *Organometallics* **2011**, *30*, 3453–3456; c) K. Hansen, T. Szilvási, B. Blom, M. Driess, *Organometallics* **2015**, *34*, 5703–5708.

[10] N. C. Breit, T. Szilvási, T. Suzuki, D. Gallego, S. Inoue, *J. Am. Chem. Soc.* **2013**, *135*, 17958–17968.

[11] a) K. Nagamine, *Introductory Muon Science*, Cambridge University Press, Cambridge, **2003**; b) A. Yaouanc, P. D. de Réotier, *Muon Spin Rotation, Relaxation, and Resonance: Applications to*

Condensed Matter, OUP Oxford, Oxford, **2011**; c) I. McKenzie, *Annu. Rep. Prog. Chem. Sect. C* **2013**, *109*, 65–112.

[12] a) C. J. Rhodes, *J. Chem. Soc. Perkin Trans. 2* **2002**, 1379–1396; b) E. Roduner, in *Isotope Effects In Chemistry and Biology*, CRC Press, Boca Raton, FL, **2005**, pp. 433–450; c) M. Goli, S. Shahbazian, *Phys. Chem. Chem. Phys.* **2015**, *17*, 7023–7037.

[13] E. Roduner, *The Positive Muon as a Probe in Free Radical Chemistry,* Lecture Notes in Chemistry No. 49, Springer, Berlin, **1988**.

[14] a) F. Gerson, W. Huber, *Electron Spin Resonance Spectroscopy of Organic Radicals*, Wiley, New York, **2003**; b) P. Rieger, A. Rieger, D. Collinson, B. C. Gilbert, D. M. Murphy, C. W. Pantelides, H. R. T. Philip, R. G. Lawler, *Electron Spin Resonance : Analysis and Interpretation*, Royal Society of Chemistry, Cambridge, **2007**.

[15] P. W. Percival, J. C. Brodovitch, S. K. Leung, D. Yu, R. F. Kiefl, D. M. Garner, D. J. Arseneau, D. G. Fleming, A. Gonzalez, J. R. Kempton, M. Senba, K. Venkateswaran, S. F. J. Cox, *Chem. Phys. Lett.* **1989**, *163*, 241–245.

[16] P. W. Percival, J.-C. Brodovitch, K. Ghandi, B. M. McCollum, I. McKenzie, *J. Am. Chem. Soc.* **2005**, *127*, 13714–13719.

[17] a) B. M. McCollum, T. Abe, J.-C. Brodovitch, J. A. C. Clyburne, T. Iwamoto, M. Kira, P. W. Percival, R. West, *Angew. Chem. Int. Ed.* **2008**, *47*, 9772–9774; *Angew. Chem.* **2008**, *120*, 9918–9920; b) B. M. McCollum, J. C. Brodovitch, J. A. C. Clyburne, A. Mitra, P. W. Percival, A. Tomasik, R. West, *Chem. Eur. J.* **2009**, *15*, 8409–8412; c) A. Mitra, J.-C. Brodovitch, C. Krempner, P. W. Percival, P. Vyas, R. West, *Angew. Chem. Int. Ed.* **2010**, *49*, 2893–2895; *Angew. Chem.* **2010**, *122*, 2955–2957; d) R. West, P. W. Percival, *Dalton Trans.* **2010**, *39*, 9209–9216; e) P. W. Percival, J. C. Brodovitch, M. Mozafari, A. Mitra, R. West, R. S. Ghadwal, R. Azhakar, H. W. Roesky, *Chem. Eur. J.* **2011**, *17*, 11970–11973; f) P. W. Percival, B. M. McCollum, J. C. Brodovitch, M. Driess, A. Mitra, M. Mozafari, R. West, Y. Xiong, S. L. Yao, *Organometallics* **2012**, *31*, 2709–2714; g) R. West, K. Samedov, P. W. Percival, *Chem. Eur. J.* **2014**, *20*, 9184–9190; h) K. Samedov, R. West, P. W. Percival, J. C. Brodovitch, L. Chandrasena, M. Mozafari, R. Tacke, K. Junold, C. Kobelt, P. P. Samuel, R. Azhakar, K. C. Mondal, H. W. Roesky, M. Driess, W. Wang, *Organometallics* **2015**, *34*, 3532–3537.

[18] R. West, K. Samedov, A. Mitra, P. W. Percival, J.-C. Brodovitch, G. Langille, B. M. McCollum, T. Iwamoto, S. Ishida, C. Jones, J. Li, *Can. J. Chem.* **2014**, *92*, 508–513.

[19] L. Chandrasena, K. Samedov, I. McKenzie, M. Mozafari, R. West, D. P. Gates, P. W. Percival, *Angew. Chem. Int. Ed.* **2019**, *58*, 297–301; *Angew. Chem.* **2019**, *131*, 303–307.

[20] a) D. Bravo-Zhivotovskii, S. Melamed, V. Molev, N. Sigal, B. Tumanskii, M. Botoshansky, G. Molev, Y. Apeloig, *Angew. Chem. Int. Ed.* **2009**, *48*, 1834–1837; *Angew. Chem.* **2009**, *121*, 1866–1869; b) B. Farhadpour, J. Guo, D. W. Hairsine, J. B. Gilroy, K. M. Baines, *Polym. Chem.* **2019**, *10*, 4887–4894.

[21] E. Roduner, G. A. Brinkman, P. W. F. Louwrier, *Chem. Phys.* **1982**, *73*, 117–130.

[22] M. J. Ramos, D. McKenna, B. C. Webster, E. Roduner, *J. Chem. Soc. Faraday Trans. 1* **1984**, *80*, 267–274.

[23] M. Mozafari, L. Chandrasena, I. McKenzie, K. Samedov, P. W. Percival, *Radiat. Phys. Chem.* **2020**, *168*, 108532.

[24] C. Heller, H. M. McConnell, *J. Chem. Phys.* **1960**, *32*, 1535–1539.

[25] Y. Cai, L. Du, K. Samedov, X. Gu, F. Qi, H. H. Y. Sung, B. O. Patrick, Z. Yan, X. Jiang, H. Zhang, J. W. Y. Lam, I. D. Williams, D. L. Phillips, A. Qin, B. Z. Tang, *Chem. Sci.* **2018**, *9*, 4662–4670.