

Free Radical Reactivity of a Phosphaalkene Explored Through Studies of Radical Isotopologues

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Abstract: Muonium (Mu), an H atom analogue, is employed to probe the addition of free radicals to the P=C bond of a phosphaalkene. Specifically, two unprecedented muoniated free radicals, MesP[•]-CMu(Me)₂ (**1a**, minor product) and MesPMu-C[•]Me₂ (**1b**, major product), were detected by muon spin spectroscopy (μ SR) when a solution of MesP=CMe₂ (**1**; Mes = 2,4,6-trimethylphenyl) was exposed to a beam of positive muons (μ^+). The μ^+ serves as a source of Mu (i.e. Mu = μ^+ + e⁻). To confirm the identity of the major product **1b**, its spectral features were compared to its isotopologue, MesPH-C(Me)CH₂Mu (**2a**). Conveniently, **2a** is the sole product of the reaction of MesPH(CMe=CH₂) (**2**) with Mu. For all observed radicals, muon, proton and phosphorus hyperfine coupling constants were determined by μ SR and compared to DFT-calculated values.

In recent years, phosphorus compounds displaying multiple bonding and/or low-coordination numbers have emerged from their purely fundamental roots to become attractive building blocks and synthons with applications ranging from catalysis to polymer and materials science.^[1] Of particular interest to us are phosphaalkenes, P=C analogues of olefins,^[2] which we have shown to be suitable monomers for radical-initiated homo- and co-polymerization.^[3,4] Despite the discovery of an unexpected microstructure for the polymer derived from MesP=CPh₂,^[5,6] the details of the simple free radical initiation remain unclear. Presumably, initiation involves the addition of neutral radicals to the P=C bond but such short-lived radical intermediates are extremely difficult to generate and characterize.

As an alternative to ESR, we have turned to muon spin spectroscopy (μ SR) to detect muoniated radicals, i.e. free radicals containing a muonium atom (Mu) in place of an H

atom.^[7] Mu is a single-electron atom, with a positive muon (μ^+) as nucleus, that may be envisaged as a light isotope of H (mass = 0.11 u). Thus, reacting low-coordinate compounds with Mu provides a rare opportunity to generate, and elucidate the structure of, radicals that could not otherwise be detected.^[8] μ SR offers several advantages over conventional methods: (i) muons can be injected into any sample; (ii) the muons arrive with almost 100% spin polarization, so very low quantities of muoniated species can be detected (10⁷, cf. 10¹² spins for ESR, 10¹⁸ for NMR); (iii) very short-lived muoniated radicals can be detected; and (iv) unlike conventional EPR or NMR, μ SR does not require an external electromagnetic field to stimulate spin-level transitions. Perhaps the most significant advantage of μ SR is its high selectivity of detection which minimizes complications from radiation damage and secondary radical species.

Despite the utility of Mu to probe novel radicals, there is no report of its reaction with low-coordinate phosphorus. The only muoniated P-radical was derived from tricoordinate phosphorus.^[9] This is particularly striking given the longstanding interest in development and applications of divalent phosphorus-based radicals.^[10,11] Even though there is growing interest in anionic and cationic radicals derived from phosphaalkenes,^[12] there is a dearth of information on the addition of neutral radicals to P=C bonds. Most pertinent to the present study is the EPR detection of a mixture of neutral P- and C-centred radicals and cationic phosphoniumyl radicals detected when single crystals of Mes^{*}P=CPh (Mes^{*} = 2,4,6-tri-*tert*-butylphenyl) were irradiated with X-rays, presumably reacting with adventitious H-sources.^[13]

Herein, we report two unprecedented radicals derived from the addition of Mu, a “light” H isotope, to phosphaalkene MesP=CMe₂ (**1**) in solution at ambient temperature.

The simple addition of Mu to the P=C bond of **1** is expected to result in the formation of up to two unique muoniated radicals, **1a** or **1b** (Scheme 1). Employing phosphaalkene **1** provides an advantage in elucidating the structures of these addition products since it exists in equilibrium with its alkene tautomer, MesPH(CMe=CH₂) **2** (ca. 22%),^[14] which can be independently studied in its pure form. In agreement with past studies of terminal alkenes,^[15] addition of Mu to the carbon-carbon double bond of **2** is expected to give the tertiary radical **2a** rather than the primary radical **2b** (Scheme 1). The Mu adduct of **2** (i.e. **2a**) is an isotopologue of **1b** with the only difference being the site of Mu substitution. Thus, **1b** and **2a** should have the same unpaired spin density at the carbon radical centre, leading to hyperfine coupling constants (hfcs) that differ only as a result of the isotopic substitution.^[16]

As a starting point, we exposed a THF solution of pure alkene **2** to a beam of positive muons (μ^+ + e⁻ gives Mu). The transverse-field muon spin rotation (TF- μ SR) spectrum (Figure 1) shows two radical precession signals (ν_1 and ν_2) in addition to the diamagnetic signal (ν_D). This observation suggests that the reaction of **2** with Mu affords a single radical product. The muon

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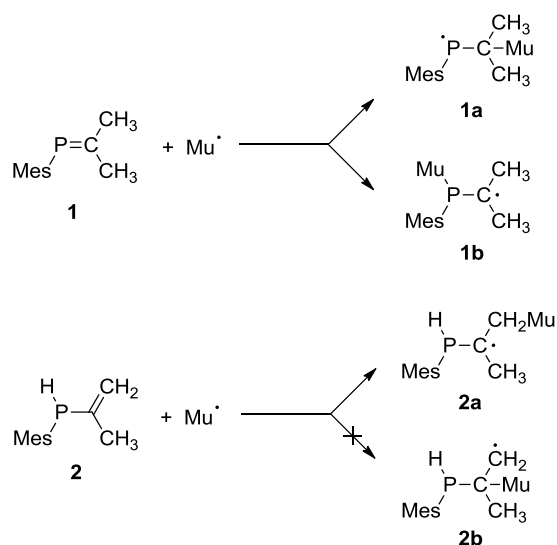
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hyperfine constant (A_{μ}) of this product is given by the difference between the two radical precession frequencies. At 25°C, the value of A_{μ} is 254 MHz but it varies with temperature (see the Supporting Information, Figure S5).



Scheme 1. Muoniated radicals expected from Mu addition to a phosphoalkene **1** and the isomeric alkene **2**. Information on the radical geometries can be found in the Supporting Information.

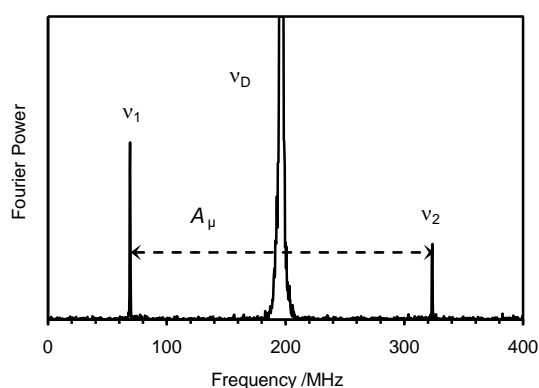


Figure 1. Transverse field μSR (TF- μSR) spectrum at 14.45 kG obtained from a 1:1 vol/vol solution of **2** in tetrahydrofuran at 25°C.

A different form of muon spin spectroscopy, muon avoided level-crossing resonance (μALCR), was employed to determine other hfc's, as explained in the Supporting Information. The μALCR spectrum obtained from the reaction of **2** with Mu is displayed in Figure 2. A total of four resonances are expected from **2a**, one due to ^{31}P ($I = 1/2$) and three associated with the inequivalent protons: PH , CH_2 , and CH_3 . The signal at 4.8 kG (Figure 2a) is readily assigned to phosphorus with hfc $A_{\text{P}} = 140$ MHz. The alternative assignment to one of the protons is unfeasible, because it would give $A_{\text{H}} = 164$ MHz, a value inconsistent with the proposed radical structure for **2a**. Moreover, its assignment as A_{P} is typical of known phosphinyl radicals (vide infra).

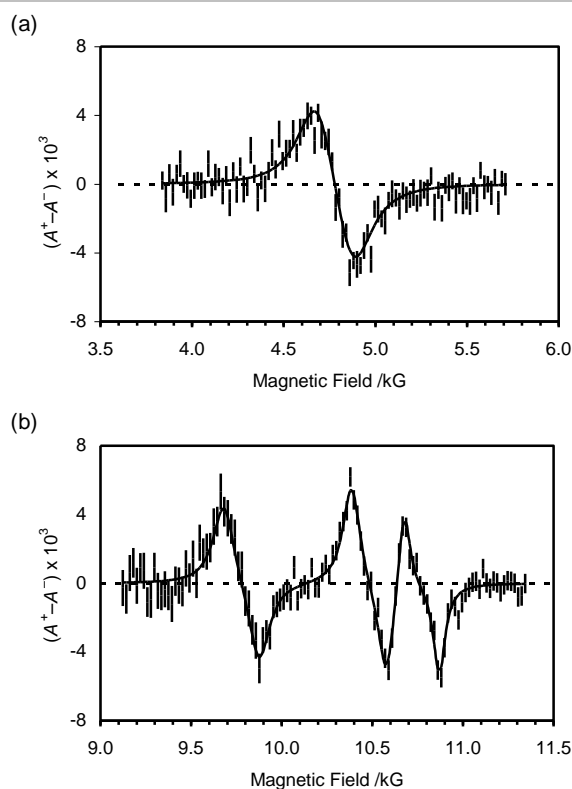


Figure 2. Segments of the muon avoided level-crossing spectrum (μALCR) of the radical formed from a 1:1 vol/vol solution of **2** in tetrahydrofuran at 25°C and subsequently identified as **2a**. The two field regions are consistent with assignments to (a) ^{31}P ; (b) three unique ^1H environments (i.e. CH_2 , CH_3 and PH).

Assignment of the three resonances attributed to protons is more complicated, and ultimately relies on comparison with computational prediction of the hfc's. However, some qualitative arguments can be made on the basis of isotope effects in the $-\text{CH}_2\text{Mu}$ group and the observed temperature dependence of the hfc's. A freely rotating $-\text{CH}_3$ group has three equivalent protons and averaging of the $\text{C}_{\alpha}(2p_z)\text{-CH}_3$ dihedral angles ϕ results in $\langle \cos^2\phi \rangle = 0.5$ and a proton hfc which is essentially temperature independent. In contrast, the preference of Mu for small dihedral angles in the muoniated methyl group $-\text{CH}_2\text{Mu}$ results in well-established temperature dependence: the muon hfc falls with temperature and the proton hfc increases with temperature.^[17] In addition, we can predict that the hfc of the protons in the $-\text{CH}_3$ group should be greater than those in the $-\text{CH}_2\text{Mu}$ group. Additional details of the temperature dependence are given in the Supporting Information. Based on the above, the four resonance field positions and the corresponding hfc's are assigned as shown in Table 1 and are fully consistent with the structure of **2a**. In particular, it was established that the H attached to phosphorus has $A_{\text{H}} = 71.4$ MHz. This is relevant to consideration of the isotopologue **1b**, which has Mu in this position. Scaling by the ratio of magnetic moments leads to a predicted muon hfc of about 230 MHz.

It is evident from the TF- μSR spectrum shown in Figure 3 that two different radicals ensue from the reaction of Mu with the phosphoalkene **1**. The more intense radical signal has $A_{\mu} = 304$ MHz at 299 K. This is 34% higher than estimated (230 MHz) but this could be due to an isotope effect (vide infra). The less

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intense signal (henceforth referred to as the minor radical) has a smaller muon hfc ($A_{\mu} = 135$ MHz). Moreover, the Fourier transform signal intensity varies with respect to the muon arrival time. This curious behaviour has been observed in other systems and, while not fully understood, it seems to indicate delayed formation of a radical.^[7b,18]

Table 1. Analysis of the muon avoided level-crossing (μ ALCR) spectrum obtained from **2** in tetrahydrofuran at 25°C and subsequently identified as **2a**.

Resonance Field /kG	Hyperfine constant /MHz	Assignment ^[a]
4.779 ± 0.004	139.55 ± 0.09	<i>P-H</i>
9.778 ± 0.004	71.40 ± 0.08	<i>P-H</i>
10.481 ± 0.002	58.37 ± 0.04	<i>CH₃</i>
10.772 ± 0.002	52.98 ± 0.04	<i>CH₂Mu</i>

[a] The nuclear spin is denoted by italic font.

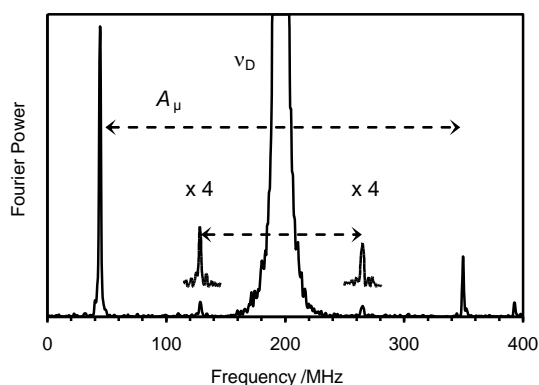


Figure 3. Transverse field μ SR spectrum at 14.45 kG obtained from a solution of **1** (0.5 M) in tetrahydrofuran at 3°C. The signals of two radicals are evident. The offsets show the weaker radical signal on an expanded scale (4 times Fourier power, being twice the signal amplitude). The small signal at 392 MHz is an artefact, an overtone of the intense diamagnetic signal.

The μ ALCR spectrum obtained from the reaction of **1** with Mu shows two resonances consistent with phosphorus (Figure 4(a)) and only one signal in the region where protons would give a resonance (Figure 4(b)). A single proton resonance is just what is expected for radical **1b**, which has six equivalent methyl protons. Assignment of the two ^{31}P signals is not so straightforward. As shown in Figure S6, this part of the spectrum is markedly temperature-dependent. The gradual broadening and disappearance of the 6.4 kG resonance at lower temperature suggests some temperature-mediated dynamic effect. Since isotopologue **2a** did not show this effect, we conclude that this unusual behavior is associated with the minor radical, namely the phosphinyl **1a**.

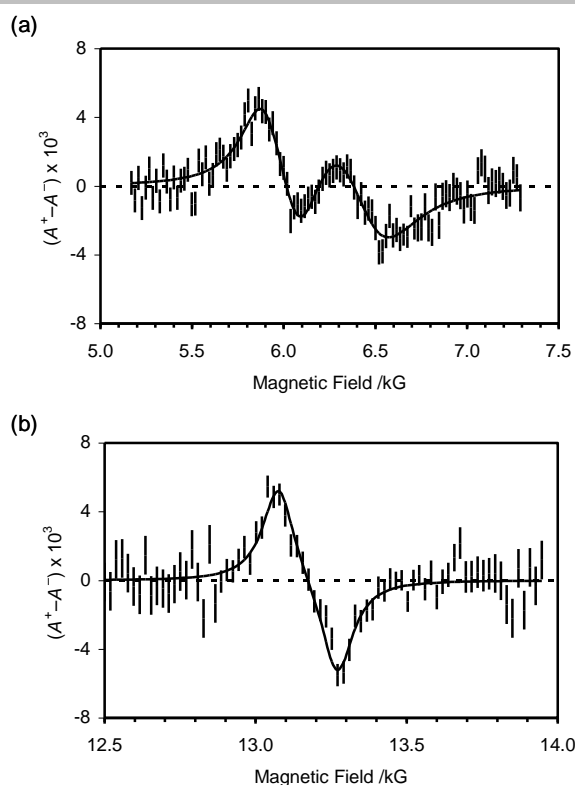


Figure 4. Segments of the μ ALCR spectrum of the radicals formed from a solution of **1** (0.5 M) in tetrahydrofuran at 26°C. The two field regions are consistent with assignments to (a) ^{31}P (one signal each from **1a** and **1b**); (b) six equivalent protons in **1b** (i.e. two CH_3 groups).

In principle, there is ambiguity in the translation of μ ALCR resonance fields to hfc's because the field position depends (Equation S1) on an absolute value, $|A_{\mu} - A_k|$, where k represents the relevant nucleus. In most cases it can safely be assumed that $A_{\mu} > A_k$, but this is not the case here. If the major radical ($A_{\mu} = 304$ MHz) is assigned to **1b**, and $A_{\mu} > A_P$, then the 6.0 kG resonance translates to $A_P = 160$ MHz, a value close to that of its isotopologue **2a** ($A_{\mu} = 254$ MHz, $A_P = 140$ MHz). It then follows that $A_{\mu} < A_P$ for the 6.4 kG resonance, which translates to $A_P = 285$ MHz for minor radical **1a** ($A_{\mu} = 135$ MHz). The near coincidence of the two phosphorus resonances is a consequence of the accidental degeneracy of $(A_{\mu} - A_P)$ and $(A_P - A_{\mu})$ for the two radicals. As far as we are aware, this is the first report of such a situation.

Table 2 summarizes the analysis of the μ ALCR spectrum shown in Figure 4. The resonance at 13.2 kG is attributed to the methyl protons of **1b** ($A_H = 58$ MHz) and is supported by the fact that isotopologue **2a** displays the same hfc. In addition, the unpaired electron in **1a** is too far from any proton to give a significant hfc. Thus, both the phosphorus and proton hfc's lead to the conclusion that the major radical is **1b**. The limited literature data on comparable ^{31}P hfc's of α -phosphinoalkyl radicals supports this conclusion (178 MHz for $\text{Et}_2\text{P-}\dot{\text{C}}\text{HCH}_2\text{CMe}_3$ in solution at 300 K).^[19]

Having identified the major radical as **1b**, the minor radical can then be assigned to the phosphorus-centred radical **1a** ($A_{\mu} = 135$ MHz, $A_P = 285$ MHz). The large phosphorus hfc is consistent with ESR studies of similar phosphinyl radicals. For instance, Fullam et al. found a ^{31}P isotropic hfc of 271 MHz for

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(Me₂CH)₂P in a γ -irradiated solid at 77 K,^[11a] and Bhat et al. reported a ³¹P isotropic hfc of 333 MHz for Ar-P-CH₂Ph (Ar = 2,4,6-tri(*tert*-butyl)phenyl) in an X-irradiated crystal at room temperature.^[13]

Table 2. Analysis of the muon avoided level-crossing (μ ALCR) spectrum obtained from the reaction of **1** with Mu in tetrahydrofuran at 26°C.

Resonance Field /kG	Hyperfine constant /MHz	Assignment ^[a]
5.986±0.005	160.3±0.2	<i>PMu</i> (1b)
6.407±0.008	285.1±0.6	<i>P-CMu</i> (1a)
13.173±0.003	57.8±0.1	-C(<i>CH₃</i>) ₂ (1b)

[a] The nuclear spin is denoted by italic font.

To gain additional support for our assignments, density functional theory was employed to compute optimum geometries, vibrational frequencies and hyperfine constants of the radicals **1a**, **1b** and **2a**. The “reference” geometries of isotopologues **1b** and **2a** are identical within the Born-Oppenheimer Approximation, since they represent the minimum-energy nuclear configuration on the electronic potential surface. However, the vibrationally-averaged structures differ. Not only is there a small increase in bond length for the lighter isotope (P–Mu in **1b**; C–Mu in **1a**), there is also an effect on the dihedral angle about the P–C bond. Such effects are well-established for hydrocarbon radicals,^[15] but this is the first time that they have been explored for organophosphorus radicals. Details of the calculations are given in the Supporting Information and the key hfc’s are reported in Table 3, where they are compared to the experimental results. The calculations show that radical **1b** is 36 kJ mol⁻¹ less stable than **1a**.

In general there is good agreement between the calculated hfc’s and those determined by experiment. The apparent discrepancy for –CH₂Mu in the first two rows of Table 3 is rationalized by temperature dependence, as described in section B1 of the Supporting Information. One can define an average value for the group:

$$\bar{A}(\text{CH}_2\text{Mu}) = [2A_H + A_\mu] / 3 \quad (1)$$

where A_μ is the muon hfc corrected by a factor (γ_P/γ_μ) to account for the different gyromagnetic ratios of the proton and the muon. The average value is then 62 MHz for the experimental data, and 64 MHz for the calculated value, both slightly higher than the proton hfc for the unsubstituted methyl (58 MHz) found for **1b**.

Conformational effects also affect the hfc’s of PH (**2a**) and PMu (**1b**). The vibrationally-averaged bond length is slightly longer (1.4%) for the lighter isotope at 0 K, but more significantly there is also a 4.6° change in the dihedral angle, Me-C-P-Mu (**1b**) vs. Me-C-P-H (**2a**), resulting in an overall isotope effect of 36% on the calculated values of A_μ/A_H . A similar situation arises when Mu is attached to the carbon (**1a**). In this case, we calculate a 1.9% increase in bond length and a 4.6° change in dihedral angle Mes-P-C-Mu, resulting in a 33% hyperfine effect compared to its C–H isotopologue. These zero-point vibrational effects involve high frequency vibrations: almost 7000 cm⁻¹ for the P-Mu stretch, and 2600 cm⁻¹ and 2200 cm⁻¹ for the P-Mu wagging motions. In contrast, it is the lowest frequency

vibrations that have the largest effect on the temperature dependence of the hfc’s. Of particular relevance here is torsional motion about the P-C bond. This is only 35 cm⁻¹ for PMu–C in **1b** and 33 cm⁻¹ for P–CMu in **1a**. The floppiness of the radicals suggested by these low values results in significant uncertainty in the calculations. Nevertheless we are satisfied that our computational results support our spectroscopic assignments.

Table 3. Comparison of experimental and computed hyperfine constants (MHz).

Radical	Site ^[a]	Exp. ^[b]	Calc. ^[c]
2a	<i>CH₂Mu</i>	254	391
	<i>CH₂Mu</i>	53	35
	<i>CH₃</i>	58	57
	<i>PH</i>	71	58
	<i>PH</i>	140	136
1b	<i>CH₃</i>	58	58
	<i>PMu</i>	160	159
1a	<i>PMu</i>	304	241
	<i>P-CMu</i>	285	220
	<i>P-CMu</i>	135	141

[a] Nucleus indicated by italic font. [b] 298–299 K. [c] UB3LYP/TZVP at 0 K.

In closing, we have explored the reaction of the P=C bond of a phosphalkene with a hydrogen atom analogue, namely, muonium. For the first time, the products of radical addition at either the P- or the C-atom of the P=C bond have been detected, with the C-centred radical (**1b**) being the major species. This work is consistent with the proposed mechanism for the polymerization of MesP=CPh₂, where the first step appears to involve highly selective addition of radicals to the P-atom of the P=C bond to afford a C-centred radical intermediate.^[5] Future work will aim to use μ SR spectroscopy to gain additional insight into the propagation mechanism of phosphalkenes.

Acknowledgements

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Keywords: phosphalkenes • radicals • isotope effects • muon spin spectroscopy

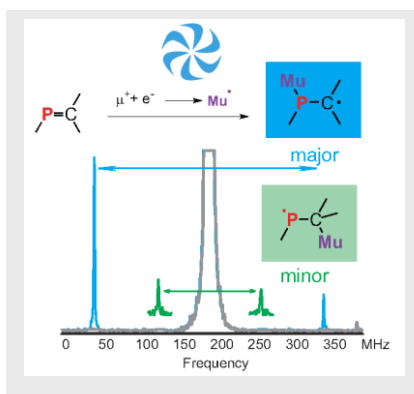
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Entry for the Table of Contents

COMMUNICATION

Phosphaalkene and Muonium Get

Radical: Muonium, an H-atom analogue, reacts with a phosphaalkene to form two radicals, a carbon-centred radical (major product) and a phosphinyl (minor product). Muon, proton and ^{31}P hyperfine coupling constants are reported for these radicals and an isotopologue generated from an alkene.



Lalangi Chandrasena, Dr. Kerim Samedov, Dr. Iain McKenzie, Dr. Mina Mozafari, Prof. Robert West, Prof. Derek P. Gates, and Prof. Paul W. Percival**

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Free Radical Reactivity of a Phosphaalkene Explored Through Studies of Radical Isotopologues

Supporting Information

Free Radical Reactivity of a Phosphaalkene Explored Through Studies of Radical Isotopologues

Lalangi Chandrasena, Kerim Samedov, Iain McKenzie, Mina Mozafari, Derek P. Gates, Robert West and Paul W. Percival*

Abstract: Muonium (Mu), an H atom analogue, is employed to probe the addition of free radicals to the P=C bond of a phosphaalkene. Specifically, two unprecedented muoniated free radicals, MesP[•]-CMu(Me)₂ (**1a**, minor product) and MesPMu-C[•]Me₂ (**1b**, major product), were detected by muon spin resonance (μ SR) spectroscopy when a solution of MesP=CMe₂ (**1**: Mes = 2,4,6-trimethylphenyl) was exposed to a beam of positive muons (μ^+). The μ^+ serves as a source of Mu (i.e. Mu = μ^+ + e⁻). To confirm the identity of the major product **1b**, its spectral features were compared to its isotopologue, MesPH-C[•](Me)CH₂Mu (**2a**). Conveniently, **2a** is the sole product of the reaction of MesPH(CMe=CH₂) (**2**) with Mu. For all observed radicals, muon, proton and phosphorus hyperfine coupling constants were determined by μ SR spectroscopy and compared to DFT-calculated values.

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A. Experimental Procedures

1. Materials and methods

All manipulations of air- and/or water-sensitive compounds were performed under a nitrogen atmosphere by using standard Schlenk or glovebox techniques. Hexanes, and diethyl ether were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. Tetrahydrofuran (THF) and n-heptane were dried over sodium and benzophenone and distilled prior to use. DBU (1,8-Diazabicyclo(5.4.0)undec-7-ene) was dried over CaH_2 and distilled prior to use. Vinylmagnesium bromide (1.0 M in THF), 2-bromomesitylene, and LiAlH_4 were purchased from Sigma Aldrich and used as received. Dichloro-(2,4,6-trimethylphenyl)phosphine (starting material) and (1-methylethenyl)(2,4,6-trimethylphenyl)phosphine **2** were prepared according to known literature procedures^[1, 2]. (1-methylethylidene)(2,4,6-trimethylphenyl)phosphine **1** was generated via thermal conversion of **2** at 100 °C (24 h) in n-heptane in the presence of catalytic amounts of DBU as the major component of an inseparable ca. 3.5:1 mixture of **1** and **2** (as determined by ^{31}P NMR spectroscopy (see Fig. S1)). The identities of **1** and **2** were verified by comparison of obtained NMR data (^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy) with the data provided in the original reference.^[2] ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 25 °C on Bruker Avance 400 MHz. H_3PO_4 (85%) was used as an external standard ($\delta = 0$ for ^{31}P). ^1H NMR spectra were referenced to the residual protonated solvent signal.

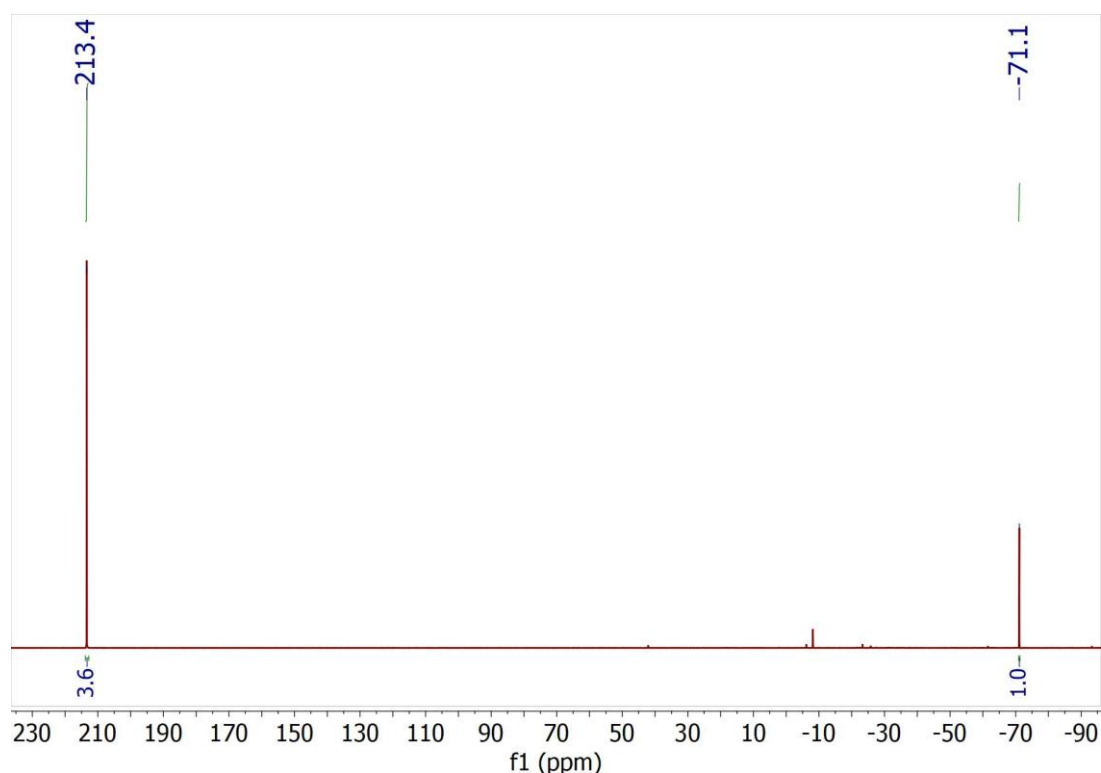


Figure S1. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) of the 3.5:1 mixture of **1** and **2**.

2. Samples for muon spin spectroscopy

A 3.5:1 mixture of phosphalkene **1** and terminal alkene **2** was dissolved in dry and oxygen-free tetrahydrofuran (THF) and sealed under inert atmosphere in a stainless-steel cell equipped with a thin stainless-steel window for muon spin spectroscopy experiments. The concentration of the major component was ca. 0.5 M. Pure alkene **2** was dissolved in an equal volume of THF and sealed in a similar sample cell.

3. Muon spin spectroscopy

Muon spin spectroscopy experiments were carried out at TRIUMF in Vancouver, Canada, at the M15 beam line using the HELIOS spectrometer.^[3] Two spectroscopic techniques were used: transverse-field muon spin rotation (TF- μ SR) and avoided muon level-crossing resonance (μ ALCR). HELIOS incorporates a superconducting magnet whose field is oriented along the muon beam direction. For TF- μ SR experiments the muon spin polarization of the beam is adjusted to be transverse to the field, whereas in μ ALCR the spin polarization is parallel to the magnetic field.

In TF- μ SR muons injected into a sample precess in a plane perpendicular to the applied magnetic field (see Figure S2). When each individual muon decays, its positron is emitted in a direction influenced by its instantaneous spin orientation, i.e. the asymmetric probability distribution has a maximum along the spin direction. As the muon spins precess this decay distribution sweeps past fixed positron detectors (four in HELIOS, arranged in phase quadrature). A histogram of lifetime events is recorded for each detector direction and the resulting muon decay curve is modulated by the muon spin precession frequency. In the simplest case of muons in a diamagnetic environment, the muon spins precess at the muon Larmor frequency (13.55 kHz per Gauss, or 196 MHz at 14.4 kG, the field used in the TF- μ SR experiments described in this paper). In muonium (Mu) or muoniated free radicals there are hyperfine interactions with the unpaired electron spin, and these give rise to additional precession frequencies. At sufficiently high magnetic field the μ SR spectrum for a muoniated radical exhibits two precession frequencies, which are situated almost symmetrically about the diamagnetic signal. The difference between the two radical precession frequencies is the muon hyperfine coupling constant (hfc), A_μ . The various precession frequencies can be conveniently displayed in a Fourier power spectrum (e.g. Figure S3), but quantitative data is obtained by fitting the μ SR histogram in time space.

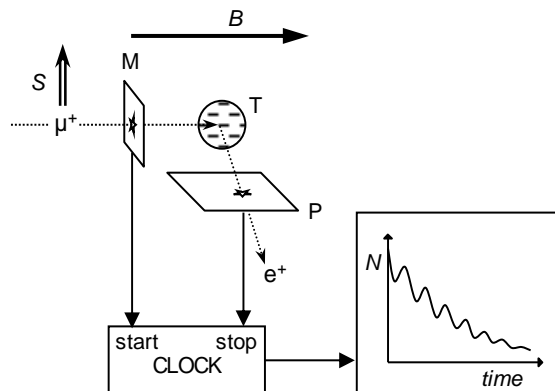


Figure S2. A typical transverse-field μ SR experimental set-up. The muon beam has spin polarization (S) transverse to the applied magnetic field (B). M and P are plastic scintillator detectors which detect the passage of each muon and the subsequent emission of the positron generated when the muon decays in the target sample (T). The elapsed time between the muon arrival and decay is recorded in a histogram. Taken from Ref. [4].

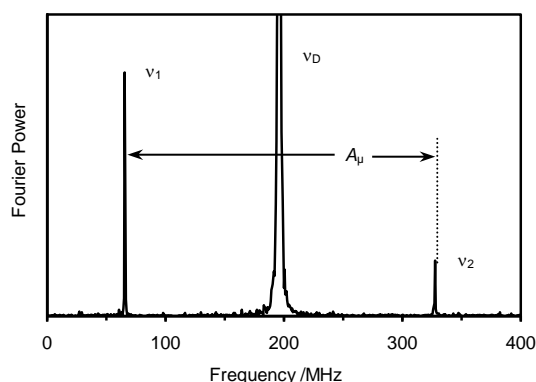


Figure S3. A typical transverse-field μ SR spectrum. The truncated peak ν_D is due to muons decaying in a diamagnetic environment; it precesses at the muon Larmor frequency. The pair of frequencies about the diamagnetic signal are due to a muoniated free radical. The hyperfine splitting constant A_μ is given by $\nu_2 - \nu_1$. Taken from Ref [4].

In μ ALCR the muon spin polarization is monitored by recording the asymmetry in positron counts in the two directions parallel and antiparallel to the applied magnetic field. Resonances occur at specific fields where spin states mix, resulting in loss of muon spin polarization. In practice this means that each magnetic nucleus in the muoniated radical gives rise to a resonance at a field, B_{res} , whose value (to first order of approximation) is determined by the difference between its hyperfine constant, A_k , and the

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muon hyperfine constant, A_μ (see Eq. S1). γ_e , γ_μ and γ_k are the gyromagnetic ratios for the electron, muon and the nucleus in question. The muon asymmetry is plotted as a function of magnetic field, and the signal has a roughly first-derivative line shape (see Figure S4), due to the field-modulated mode of detection, similar to conventional EPR.

$$B_{\text{res}} = \frac{1}{2} \left| \frac{A_\mu - A_k}{\gamma_\mu - \gamma_k} - \frac{A_\mu + A_k}{\gamma_e} \right| \quad (\text{S1})$$

Equation S1 is appropriate for a single nucleus with nuclear spin $I = 1/2$, but needs to be modified for the case of equivalent nuclear spins:^[5]

$$B_{\text{res}} = \frac{1}{2} \left| \frac{A_\mu - A_k}{\gamma_\mu - \gamma_k} - \frac{A_\mu^2 - 2MA_k^2}{2\gamma_e(A_\mu - A_k)} \right|, \quad (\text{S1}')$$

where $(1 - I^k) \leq M \leq I^k$. The 6 protons in **1b** result in a total of 12 resonances (some degenerate) giving 6 different values of the resonance field. However the shifts are much smaller than the linewidth and they are symmetrically arranged about the value predicted from equation S1.

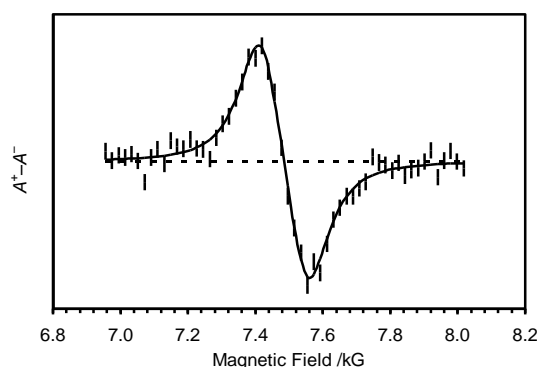


Figure S4. A typical μ LCR spectrum. The solid line represents a fit to the data (points with error bars); the differential-like lineshape is due to field modulation. Taken from Ref [4].

B. Additional Spectroscopic Results

1. Temperature-dependent hyperfine constants for the muoniated methyl group

Temperature dependence is typical for a muoniated methyl group attached to a radical center, e.g. in the β -muoniated ethyl^[6] and tert-butyl^[7] radicals. It arises from averaging over the vibrational mode corresponding to internal rotation of the methyl about the carbon-carbon bond. At low temperature the preferred conformation has maximum overlap between C_{β} -Mu and the p_z -orbital containing the unpaired electron on the α -carbon. Since β -hyperfine constants depend on dihedral angle,^[8]

$$A_{\beta} = A_0 + B \langle \cos^2 \phi \rangle, \quad (\text{S2})$$

the muon hfc falls with temperature as a larger range of angles is accessed. The line through the points in Figure S5 is the best fit of the empirical equation^[9]

$$A_{\mu} = A_{T=\infty} + (A_{T=0} - A_{T=\infty}) [1 - \exp(-E_a / RT)], \quad (\text{S3})$$

and gives an approximate barrier height for rotation of $E_a = 760 \text{ J mol}^{-1}$.

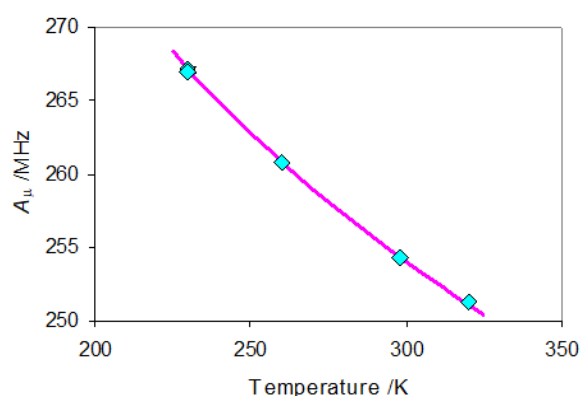


Figure S5. Temperature dependence of the muon hyperfine constant for the radical formed from **2**, subsequently identified as **2a**. The line through the points represents a fit to Eq. S3, as described in the text.

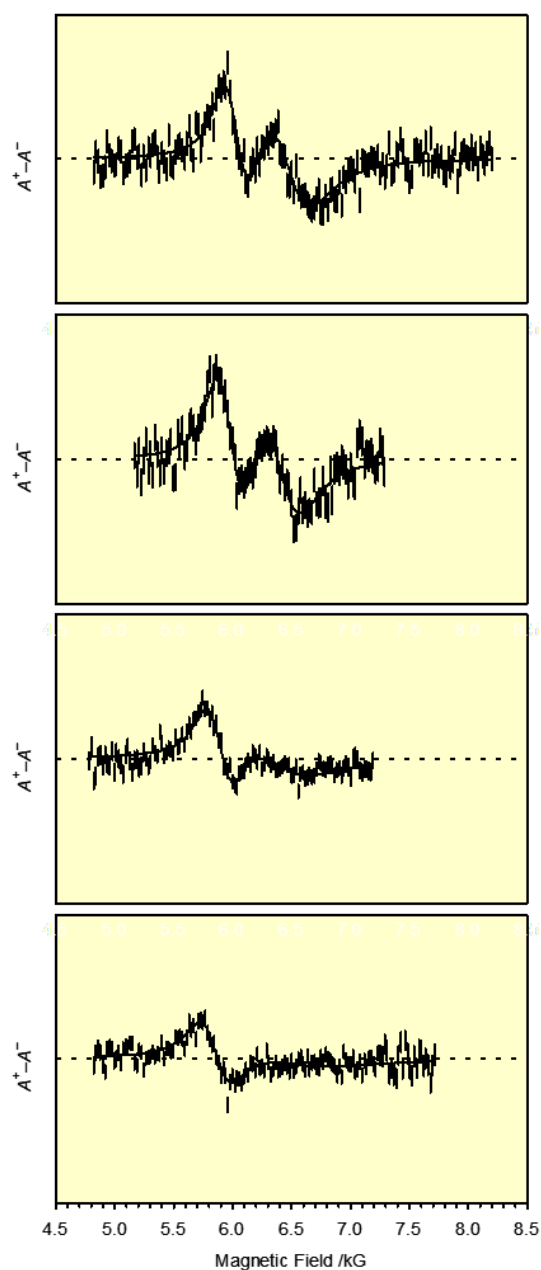
2. Temperature-dependent μ ALCR spectra arising from the radicals formed from **1**

Figure S6. Temperature variation of the phosphorus resonances in the muon avoided level-crossing spectrum of the radicals formed from **1** in tetrahydrofuran at temperatures (top to bottom) 320 K, 299 K, 265 K and 230 K. The x-axes are identical; the y-axes are the same as in Figs. 2 and 4 (in the main paper).

3. Summary of hyperfine constants determined at various temperatures

Table S1. Hyperfine constants (in MHz)^[a] determined for radical **2a** identified as MesPH-C(CH₃)CH₂Mu.

Temp./K	A_{μ}	A_{P}	$A_{\text{H(PH)}}$	$A_{\text{H(CH}_3\text{)}}$	$A_{\text{H(CH}_2\text{)}}$	$\bar{A}(\text{CH}_2\text{Mu})^{[b]}$
230	267.1	144.9	69.5	57.9	50.8	61.8
265	259.8	142.6	71.1	58.7	52.6	62.3
298	254.3	139.5	71.4	58.4	53.0	61.9
320	251.1	137.2	70.8	57.8	52.9	61.6

[a] Statistical uncertainties all ≤ 0.1 MHz. [b] Average hfc for the -CH₂Mu group, defined by

$$\bar{A}(\text{CH}_2\text{Mu}) = [2A_{\text{H}} + A_{\mu}(\gamma_{\text{p}} / \gamma_{\mu})] / 3$$

Table S2. Hyperfine constants (in MHz)^[a] determined for the major radical from **1** identified as **1b** MesPMu-C(CH₃)₂.

Temp. /K	A_{μ}	A_{P}	$A_{\text{H(CH}_3\text{)}}$
230	306.9	166.3	57.6
265	305.5	163.2	57.4
299	303.9	160.3	57.8
320	302.8	158.1	57.7
320	302.8	158.1	57.7

[a] Statistical uncertainties all ≤ 0.1 MHz.

Table S3. Hyperfine constants (in MHz)^[a] determined for the minor radical from **1** identified as **1a** MesP-CMu(CH₃)₂.

Temp. /K	A_{μ}	A_{P}
230	139.9 ^[b]	289(2)
265	137.3	286.7(5)
299	135.3	285.1(6)
320	134.3	285.5(6)

[a] Statistical uncertainties ≤ 0.5 MHz except where indicated.

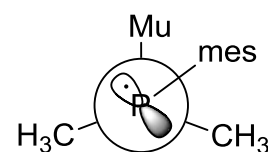
[b] extrapolated from higher temperatures.

C. DFT Calculations

Calculations were performed with Gaussian 16, Revision B.01^[10]. Optimized molecular geometries, molecular vibrations, and hyperfine frequencies were calculated at the UB3LYP/TZVP level. Coordinates and hyperfine constants calculated at the reference geometry (energy minimum) are listed below for the H isotopologues of **1a** and **1b**. The values for **2a** are not separately listed because within the Born-Oppenheimer Approximation there is no difference between **1b** and **2a**. To predict hyperfine constants for the muoniated isotopologues, muonium was treated as an isotope of H with mass 0.113429 u and magnetic moment 8.890597 μ_N . The effect of vibrational averaging was taken into account by using the Freq=Anharmonic and Fermi keywords.

Table S4. Cartesian coordinates (Å) and hyperfine constants (MHz) for the reference geometry of **1a**.

	Cartesian coordinates			hfc
P	0.00000000	0.00000000	0.00000000	219
C	0.00000000	0.00000000	1.89721648	-12
C	1.42388836	0.00000000	2.46876683	34
C	-0.80880342	1.20225210	2.39563010	
C	0.71812799	-1.66827873	-0.38704761	-16
C	-0.02386042	-2.85239870	-0.19753518	20
C	0.53462096	-4.07678196	-0.56537935	
C	1.80503849	-4.17197910	-1.12487415	
C	2.51769636	-2.99180569	-1.32525506	
C	1.99784456	-1.74595457	-0.97965844	20
C	-1.41767078	-2.84681122	0.38587343	7
C	2.37496355	-5.50315518	-1.54341900	
C	2.83141397	-0.51281194	-1.24063653	9
H/Mu	-0.49760365	-0.91787600	2.22103215	33/106
H	1.39231108	-0.01656987	3.56279420	10
H	1.99208398	-0.87057338	2.13800957	
H	1.96956394	0.89851981	2.16893456	
H	-0.84033789	1.21772341	3.48881832	
H	-1.83773665	1.17803298	2.03088803	
H	-0.36169783	2.14360654	2.06456145	
H	-0.04708420	-4.98110483	-0.41647467	3
H	3.50712124	-3.04008353	-1.76864607	3
H	-1.98162048	-1.96310528	0.08043305	
H	-1.39825291	-2.85867884	1.47938375	
H	-1.97307078	-3.72877062	0.06398483	4
H	2.17167032	-5.70198819	-2.60024833	2
H	1.93993407	-6.32151837	-0.96753659	
H	3.45796366	-5.53232678	-1.41014635	
H	3.13582606	-0.02477011	-0.31144928	
H	2.28144666	0.22993754	-1.82322076	8
H	3.73658430	-0.77077938	-1.79178485	6

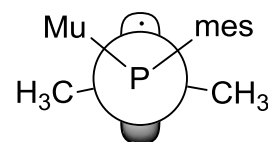


Sum of electronic and zero-point Energies = -809.340273 a.u.

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Table S5. Cartesian coordinates (Å) and hyperfine constants (MHz) for the reference geometry of **1b**.

	Cartesian coordinates			hfc
P	-1.634401	0.502360	-0.939539	132
C	-2.626143	-0.100217	0.457785	103
C	-2.304214	0.341198	1.850562	-26
C	-4.022932	-0.568141	0.186351	-27
C	0.131341	0.149812	-0.455156	30
C	0.637871	-1.160418	-0.319126	
C	1.977373	-1.338681	0.025966	3
C	2.835744	-0.263849	0.243171	
C	2.317833	1.020524	0.111618	
C	0.985900	1.249373	-0.237117	-2
C	-0.214953	-2.386040	-0.534165	
C	0.512148	2.680996	-0.353816	
C	4.286813	-0.487176	0.583949	
H/Mu	-1.861704	-0.587374	-1.827940	55/176
H	-2.827889	1.272157	2.119482	108
H	-1.236548	0.511171	1.999723	12
H	-2.627277	-0.412524	2.577256	47
H	-4.757298	0.247192	0.273841	102
H	-4.136131	-0.997272	-0.811805	9
H	-4.322182	-1.330398	0.914783	50
H	2.358886	-2.349036	0.131846	
H	2.966606	1.872821	0.284059	
H	-1.129465	-2.345754	0.060134	
H	0.334316	-3.287885	-0.262738	
H	-0.518488	-2.484446	-1.580069	
H	0.073928	2.884036	-1.332221	
H	1.344256	3.369363	-0.202276	
H	-0.253759	2.918437	0.388555	
H	4.421374	-1.390484	1.181667	
H	4.699292	0.354826	1.141979	
H	4.887413	-0.604509	-0.323326	



Sum of electronic and zero-point Energies = -809.326536 a.u.

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