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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 = $\mu^+ + e^-$). 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

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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=CHPh (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 ($\mu^+ + e^-$ gives Mu). The transverse-field muon spin rotation (TF- μ SR) spectrum (Figure 1) shows two radical precession signals (v_1 and v_2) in addition to the diamagnetic signal (v_D). This observation suggests that the reaction of **2** with Mu affords a single radical product. The muon

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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 phosphaalkene **1** and the isomeric alkene **2**. Information on the radical geometries can be found in the Supporting Information.



Figure 1. Transverse field μ SR (TF- μ SR) 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 (μ ALCR), was employed to determine other hfcs, as explained in the Supporting Information. The μ ALCR 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 ³¹P ($I = \frac{1}{2}$) and three associated with the inequivalent protons: PH, CH₂, and CH₃. The signal at 4.8 kG (Figure 2a) is readily assigned to phosphorus with hfc $A_P = 140$ MHz. The alternative assignment to one of the protons is unfeasible, because it would give $A_H = 164$ 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 (μ ALCR) 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) ³¹P; (b) three unique ¹H environments (i.e. CH₂, CH₃ and PH).

Assignment of the three resonances attributed to protons is more complicated, and ultimately relies on comparison with computational prediction of the hfcs. However, some qualitative arguments can be made on the basis of isotope effects in the -CH₂Mu group and the observed temperature dependence of the hfcs. A freely rotating -CH3 group has three equivalent protons and averaging of the $C_{\alpha}(2p_z)\text{-}CH_3$ dihedral angles φ results in $<\cos^2\phi>$ = 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 -CH2Mu results in wellestablished 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 $-CH_3$ group should be greater than those in the -CH₂Mu 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 hfcs 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 $A_{\rm H} = 71.4$ 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- μ SR spectrum shown in Figure 3 that two different radicals ensue from the reaction of Mu with the phosphaalkene **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_{μ} = 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</i> -H
9.778 ± 0.004	71.40 ± 0.08	P- <i>H</i>
10.481 ± 0.002	58.37 ± 0.04	CH ₃
10.772 ± 0.002	52.98 ± 0.04	C <i>H</i> ₂Mu

[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 ³¹P 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) ³¹P (one signal each from **1a** and **1b**); (b) six equivalent protons in **1b** (i.e. two CH₃ groups).

In principle, there is ambiguity in the translation of μ ALCR resonance fields to hfcs 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_{μ}) 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** ($A_{\rm H}$ = 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 hfcs lead to the conclusion that the major radical is **1b**. The limited literature data on comparable ³¹P hfcs of α -phosphinoalkyl radicals supports this conclusion (178 MHz for Et₂P-CHCH₂CMe₃ 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_{μ} = 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 ³¹P 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>P</i> Mu (1b)
6.407±0.008	285.1±0.6	<i>P</i> -CMu(1a)
13.173±0.003	57.8±0.1	-C(CH ₃) 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 hfcs 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 hfcs and those determined by experiment. The apparent discrepancy for $-CH_2Mu$ 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:

$$\overline{A}(CH_2Mu) = \left\lceil 2A_H + A_L' \right\rceil / 3 \tag{1}$$

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 hfcs 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 hfcs. 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.

 $\ensuremath{\text{Table 3.}}$ Comparison of experimental and computed hyperfine constants (MHz).

Radical	Site ^[a]	Exp. ^[b]	Calc. ^[c]
	CH ₂ Mu	254	391
	C <i>H</i> ₂Mu	53	35
2a	C <i>H</i> ₃	58	57
	PH	71	58
	PH	140	136
	C <i>H</i> ₃	58	58
1b	<i>P</i> Mu	160	159
	P <i>Mu</i>	304	241
10	<i>P</i> -CMu	285	220
Ia	P-CMu	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 phosphaalkene 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 µSR spectroscopy to gain additional insight into the propagation mechanism of phosphaalkenes.

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COMMUNICATION

Entry for the Table of Contents

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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 ³¹P hyperfine coupling constants are reported for these radicals and an isotopologue generated from an alkene.



Lalangi Chandrasena, Dr. Kerim Samedov, Dr. lain 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