Muonated Radicals Formed from Phenyl- and Silyl-substituted Acetylenes

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Implantation of positive muons into samples of $PhC{\equiv}CPh$ and $PhC{\equiv}CMe$ at 298 K led to the formation of the radicals $Ph\dot{C}{=}C(Mu)Ph$ and $Ph\dot{C}{=}C(Mu)Me$; in the case of the latter compound, the alternative $Me\dot{C}{=}C(Mu)Ph$ radical was not detected. Additionally, cyclohexadienyl radicals formed by muonium atom addition to the aromatic rings were observed, in lower yield, allowing spin-delocalisation parameters (Δ_x) to be determined for the $-C{\equiv}CR$ substituents. During irradiation of $Me_3SiC{\equiv}CMe$, the $Me_3Si\dot{C}{=}C(Mu)Me$ radical was observed.

Experimental

The samples of $Ph{\equiv}CPh$, $PhC{\equiv}CMe$, and $Me_3SiC{\equiv}CMe$ were obtained from Aldrich and Fluka and were used without further purification. They were sealed either as pure liquids or in diethyl ether solution (for $PhC{\equiv}CPh$) in thin-walled 35 mm diameter glass ampoules, following deoxygenation *via* four freeze–pump–thaw cycles to a pressure of 10^{-3} mmHg. The full details of the muon spin rotation (μSR) technique have been given previously,[1] but briefly, for each experiment, the sample ampoule was maintained in a magnetic field of 3 kG applied transverse to the direction of the spin-polarised positive muon beam. The decay events were accumulated in four histograms totalling 40–60 million good events, and the muon precession frequencies were obtained preliminarily by Fourier transformation, then more precisely by fitting the appropriate lineshape function to the experimental data, which yielded additionally the radical yields, phases and relaxation rates. The muon hyperfine couplings were obtained from the muon precession frequencies. In each experiment, an intense signal was observed at the muon Larmor frequency (13.56 kHz G^{-1}) arising from muons in diamagnetic (non-radical) environments.

In order to enhance the radical signals with respect to the noise level, correlation spectra were recorded, as defined previously,[2] in which the Fourier powers $[P(\nu)]$ of the pair of lines in the transverse field μSR spectrum of each radical (see Figures 1, 2, and 3), ν_+ and ν_-, are 'combined' according to: $C(\nu_+ + \nu_-) = \{P(\nu_+)P(\nu_-)\}^{\frac{1}{2}}$. Examples are shown in Figures 1(*b*), 2(*c*), and 3(*b*).

Introduction

The transverse field muon spin rotation (μSR) technique[1] has enabled the study of a wide range of organic radicals labelled at the β-site (I) with the light hydrogen isotope, muonium (μ^+e^-) formed during irradiation of organic liquids with positive muons. By far the greatest body of data has been collected for radicals formed by overall muonium addition to double bonds, Scheme 1(*a*) (C=C,[3] C=O,[4] N=N[5] and C=S[6]); the bound muonium atom exerting a greater influence on the conformational dynamics of these radicals than a normal hydrogen (protium) atom does.[3] Our initial attempts to extend this range to 'vinyl' type radicals, by experiments in which samples of alkyl-substituted acetylenes were irradiated, met with failure: in no case were we able to observe signals other than that due to the diamagnetic fraction. We thought that this might be due to configurational inversion at the bent vinyl radical centres, Scheme 1(*b*), an effect that would modulate the muon-electron couplings between *cis* and *trans* hyperfine frequencies, which must differ appreciably from each other, thereby broadening the μSR lines beyond detectability. [EPR data for the unsubstituted vinyl radical[7] gives $A_{trans} - A_{cis} = 31$ G $= 86.8$ MHz; for a

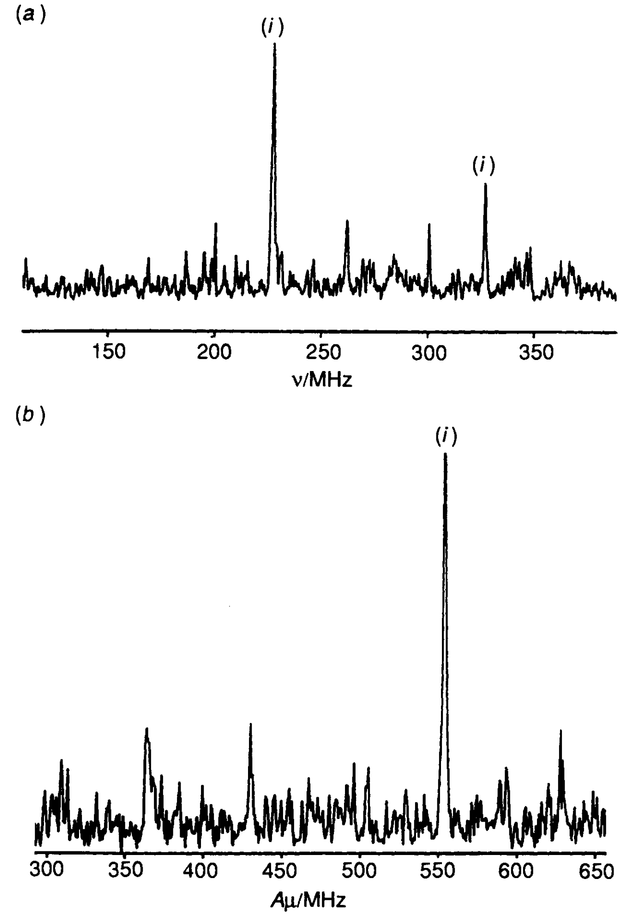


Figure 1. (*a*) The μSR spectrum recorded from $Me_3SiC{\equiv}CMe$ at 298 K. Signal marked (*i*) from $Me_3Si\dot{C}{=}C(Mu)Me$ radicals. (*b*) The correlation spectrum (see the text) confirming the presence of a single radical.

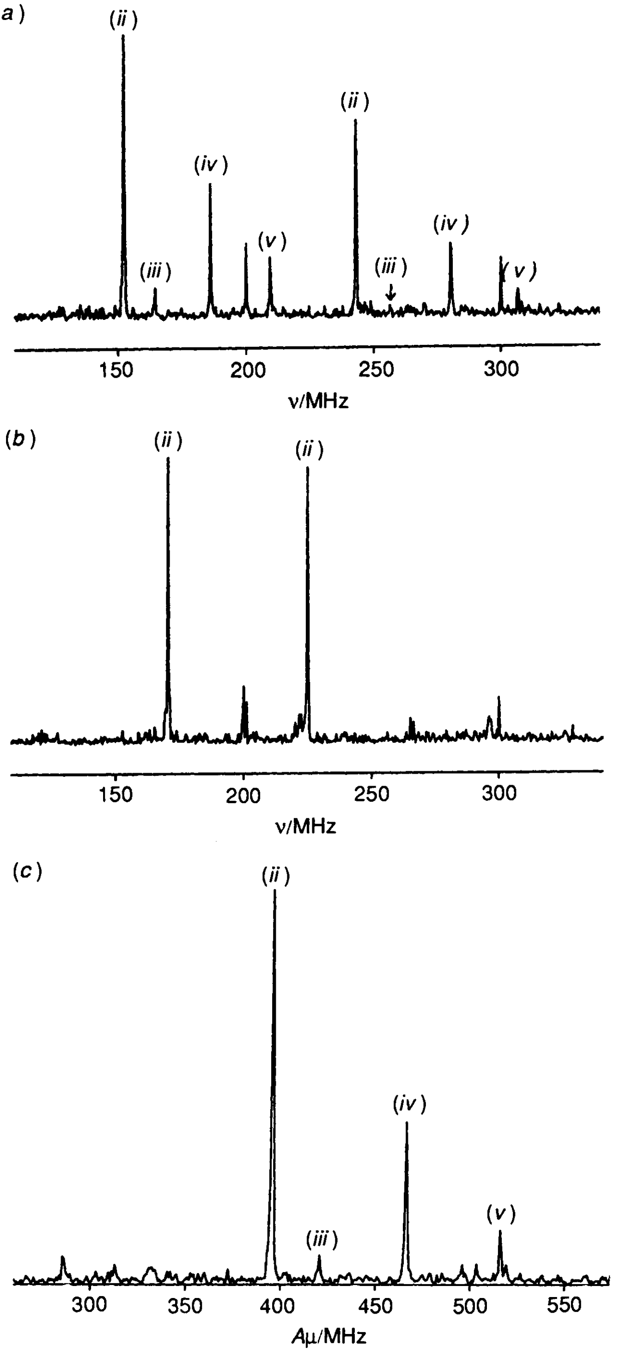


Figure 2. (*a*) The μSR spectrum recorded from $\mathrm{PhC{\equiv}CMe}$ at 298 K, in a magnetic field of 3 kG, showing (*ii*) $\mathrm{Ph\dot{C}{=}C(Mu)Me}$ radicals, and cyclohexadienyl radicals: (*iii*) *para* isomer, (*iv*) *ortho* isomer, (*v*) *meta* isomer. (*b*) The same sample as in (*a*), but with the magnetic field reduced to 1 kG, showing reduction in intensity and splitting of lines from radicals (*iii*)–(*v*); intensity of lines from $\mathrm{Ph\dot{C}{=}C(Mu)Ph}$ (*ii*) unaffected. (*c*) The correlation spectrum from the $\mathrm{PhC{\equiv}CMe}$ sample, recorded at 3 kG, confirming the presence of four radicals as indicated in (*b*).

similar structure of a muonated radical, this difference would be increased by 3.1833 (γ_μ/γ_p) and so even more pronounced relaxation effects are anticipated.] Therefore, either a linear radical centre, or, at least, a structurally rigid vinyl radical is required. We discovered that this could be accomplished by either phenyl[8] or trimethylsilyl[9,10] substitution, and the present work reports our continued efforts in this area.

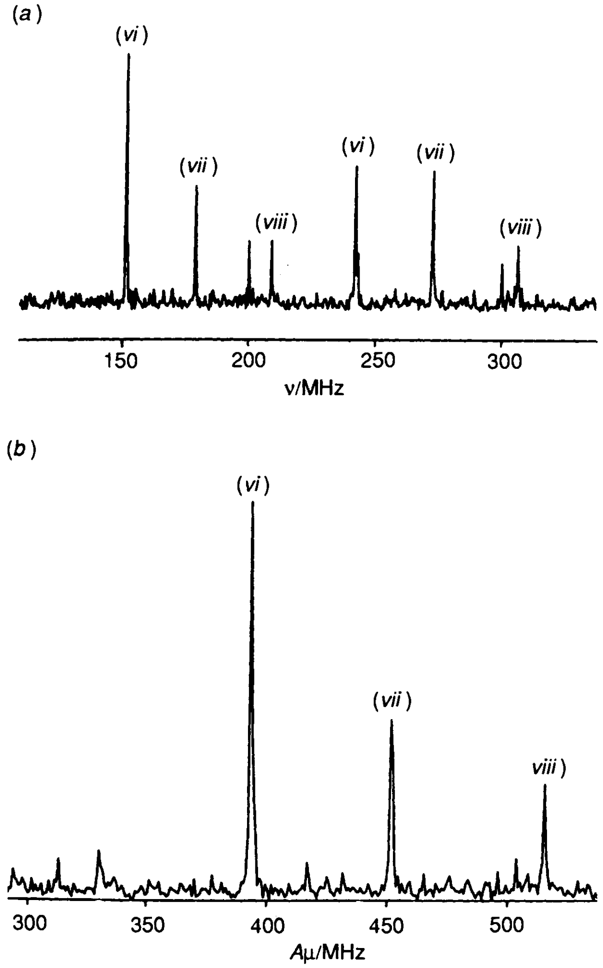
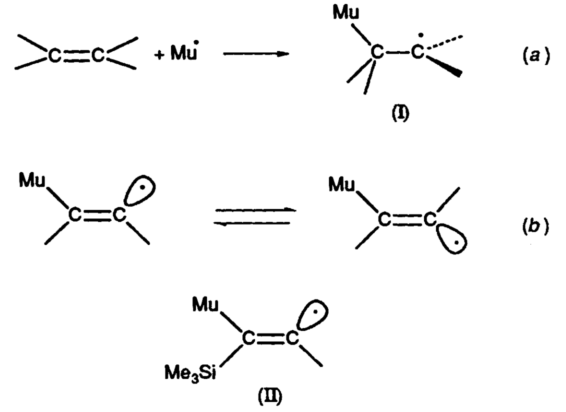


Figure 3. (*a*) The μSR spectrum recorded from $\mathrm{PhC{\equiv}CPh}$, in diethyl ether solution, at 298 K and 3 kG, showing (*vi*) $\mathrm{Ph\dot{C}{=}C(Mu)Ph}$ radicals, and cyclohexadienyl radicals: (*vii*) *ortho* isomer, (*viii*) *meta* isomer. (*b*) The correlation spectrum from $\mathrm{PhC{\equiv}CPh}$, confirming the presence of three radicals, as indicated in (*a*).



Scheme 1.

Results and Discussion

1-Trimethylsilylprop-1-yne: $\mathrm{Me_3SiC{\equiv}CMe}$.—Figure 1 shows a μSR spectrum obtained during radiolysis of $\mathrm{Me_3SiC{\equiv}CMe}$ with positive muons. The two high-frequency lines are due to the formation of a single radical, which we assign to $\mathrm{Me_3Si\dot{C}{=}C(Mu)Me}$ on the basis of our prior experience that an α-$\mathrm{Me_3Si}$ group is required to render muonated vinyl radicals

Table 1. Hyperfine data for vinyl radicals.[a]

Radical	$(A\mu')$[b]	(Ap)[c]	$A\mu'/Ap$
$Me_3Si\dot{C}{=}C(Mu)H$	66.4[d]	58.3[d]	1.14
$Me_3Si\dot{C}{=}C(Mu)Me$	62.1[e]	—	—
$Me_3Si\dot{C}{=}C(Mu)SiMe_3$	82.2[d]	76.7[f]	1.07
		72.4[g]	1.14
$Ph\dot{C}{=}C(Mu)H$	47.1[h]	41.5[i]	1.13
$Ph\dot{C}{=}C(Mu)Me$	44.4[e]	—	—
$Ph\dot{C}{=}C(Mu)Ph$	44.1[e]	—	—

[a] 1 G = 10^{-4} T. [b] Couplings measured at 298 K and reduced by γ_μ/γ_p. [c] Proton coupling in the corresponding protic radical. [d] From ref. 10. [e] This work. [f] Value obtained in solid matrix at 77 K, from ref. 10. [g] Liquid-phase value from ref. 32. [h] From ref. 8. [i] Ref. 12.

detectable by causing the radical centre to be linear and thus preventing the inversion in Scheme 1(*b*).[10] The coupling is also very similar to that found in the $Me_3Si\dot{C}{=}C(Mu)H$ radical.[9,10]

It is important to note that the signals are very weak, particularly by comparison with the intense spectrum obtained from $Me_3SiC{\equiv}CSiMe_3$[9,10] (where only one radical is possible), even at much lower statistics. Since the overall radical yield (P_R) is likely to be similar for both acetylenes, we suggest that the alternative $Me_3Si(Mu)C{=}\dot{C}Me$ radical is also formed, accounting for much of P_R, but is undetectable due to the inversion of the =C–Me centre. This implies that the latter is the more stable of the two radicals, probably because of hyperconjugation between the radical centre and the β-C–Si bonding electrons.[11] Although the greatest hyperconjugative interaction occurs when the silyl group is *trans* with respect to the free radical, this is clearly insufficient to lock the radical into the *trans* configuration (**II**). We propose a similar effect to explain the fact that only weak signals were observed in $Me_3SiC{\equiv}CH$, from the radical $Me_3Si\dot{C}{=}C(Mu)H$; the alternative, $Me_3SiC(Mu){=}\dot{C}H$, being undetectable.

Phenyl-substituted Acetylenes.—The observation of two equivalent β-protons in the $Ph\dot{C}{=}CH_2$ radical by EPR spectroscopy[12] confirms that the radical centre is linear. This is almost certainly due to 'benzylic' delocalisation of the unpaired electron, given the observation of couplings to the ring protons and the reduction in the magnitude of the methylene proton coupling (41.5 G) from that in the linear $Me_3Si\dot{C}{=}CH_2$ radical (58 G).[10] The muonated analogue, $Ph\dot{C}{=}C(Me)H$, was the first 'triple-bond' muonium adduct to be detected.[8] We now discuss results for triple-bond (vinyl) and also ring-adduct (cyclohexadienyl) radicals, formed in $PhC{\equiv}CPh$ and $PhC{\equiv}CMe$. Figures 2 and 3 show μSR spectra recorded from samples of $PhC{\equiv}CMe$ and $PhC{\equiv}CPh$, respectively.

Vinyl Radicals.—In Table 1, we have collated all the available data for muonated vinyl radicals, along with those for their protic analogues, where available. The hyperfine isotope ratios [$A\mu'/Ap$] are all close to 1.14, which is within the range established previously for conformationally rigid radicals, and termed the 'residual isotope effect.'[3] The existence of this effect has now been confirmed by avoided level crossing (ALC) results for muonated ethyl radicals in the gas phase,[13] and so all of the hyperfine isotope ratio for this radical cannot be explained purely by conformational averaging, in contrast with arguments based on previously obtained data.[14]

It is clear that the muon hyperfine couplings in the $Ph\dot{C}{=}C(Mu)Ph$ and $Ph\dot{C}{=}C(Mu)Me$ radicals are substantially reduced from the values found in the silyl analogues, because of the 'benzylic' delocalisation referred to above. In experiments with $PhC{\equiv}CMe$, the radical $Ph\dot{C}{=}C(Mu)Me$ was the only one detected, and although the conformational inversion in Scheme 1(*b*) is expected to operate in the alternative $Ph(Mu)C{=}\dot{C}Me$ radical, we feel that the absence of signals from the latter species is due to the expected much lower rate constant for its formation, than that for the delocalised radical which is observed. It is of interest to assess the extent of this delocalisation with respect to a 'localised' linear vinyl radical. The couplings in the trimethylsilyl analogues are unlikely to represent 'upper-limits' since we believe that these are partially delocalised, hence their linearity. Recent EPR results for $(Me_3Si)_nNR_{(3-n)}^{+\bullet}$ radical cations[15] make it clear that the unpaired electron is partially delocalised onto the silyl groups, as shown by a fall in the anisotropic ^{14}N couplings from the values found in $Me_nNH_{(3-n)}^{+\bullet}$ radicals; by analogy, delocalisation is therefore expected from the carbon radical centres in the vinyl radicals.

There exist various theoretical estimates[16] for the spin density at the exocyclic carbon atom in the benzyl radical which depend on the model and method of calculation chosen, but most lie within the range 0.57–0.77. In a previous study of benzyl and pyridylmethyl radicals,[17] an 'experimental' value of 0.68 was obtained by assuming that the 'negative' spin density at the *ipso* carbon atom was equal to that at one of the *meta* positions; however, the spin correlation effect that leads to these negative spin densities is approximately proportional to the sum of the (positive) spin densities at the adjacent carbon atoms,[18] and on this basis a value of *ca.* 2.34 ρ (*meta*) is obtained. Thus a McConnell *Q*-value[19] of −25.3 G and an exocyclic spin density of 0.65 is obtained. Since the ring proton couplings in $Ph\dot{C}H_2$ and $Ph\dot{C}{=}CH_2$ are almost identical with each other,[12] it can reasonably be assumed that the extent of spin delocalisation onto the phenyl groups is the same for both radicals (35%); therefore, a $\dot{C}{=}CH_2$ coupling of 63.5 G is predicted for a hypothetical, localised, linear vinyl radical. This value is slightly lower than that obtained from an INDO calculation for a similar, spin-localised radical,[20] but is greater than that estimated previously using a spin density of 0.7 for $Ph\dot{C}{=}CH_2$ (58.3 G):[12] a value that would suggest that the $Me_3Si{-}\dot{C}{=}CH(R)$ radicals are not delocalised at all. Our estimate suggests spin-delocalisation of *ca.* 8% onto the silyl group, which is evidently sufficient to render their configurations linear.

Allowing for the residual ($A\mu'/Ap$) isotope ratio, a muon coupling of 72.5 G is predicted for a localised (linear) muonated vinyl radical: therefore, the respective spin densities are 0.65, 0.61, and 0.61 at the vinyl carbon atoms in the radicals $Ph\dot{C}{=}C(Mu)H$, $Ph\dot{C}{=}C(Mu)Me$ and $Ph\dot{C}{=}C(Mu)Ph$. This suggests that more spin density is withdrawn when a β-hydrogen is replaced by a methyl or a phenyl group, which contrasts with the EPR results for $MeCO^{+\bullet}$[21] and $H_2CO^{+\bullet}$[22,23] radical cations; the former apparently showing less delocalisation than the latter.

Ring-adduct (*Cyclohexadienyl*) *Radicals.*—The cyclohexadienyl radical may be regarded as (π-) isoelectronic with the benzyl radical if these are considered to be formed from a combination of the pentadienyl system and, respectively, a doubly occupied CH_2 group orbital with π-symmetry or a C=C π-bonding orbital; it therefore appears reasonable that there might be a relationship between the effect of substituents in both. The linear plot shown in Figure 4 demonstrates that there is such a relationship for *meta* and *para* substituents.

Recently, Arnold and coworkers[24–27] have derived a set of radical substituent constants ($\sigma^\bullet$) from the methylene proton coupling constants in *meta*- and *para*-substituted benzyl radicals, and shown that they correlate very well with the rate constants of a number of reactions with transition states in which there is substantial radical character. Arnold has defined his $\sigma^\bullet$ values according to an equation of the form (1),[24]

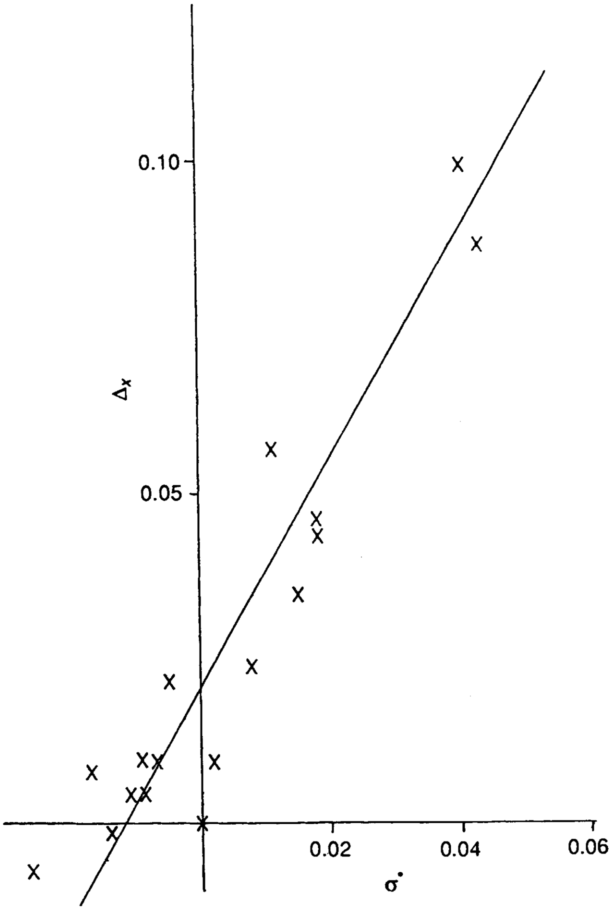


Figure 4. Plot of Δ_x values derived from equation (2) and data from ref. 30 *vs.* $\sigma^{\bullet}$ values, defined by equation (1) from refs. 24–27. Linear regression of the data leads to equation (3). $r = 0.94$.

where x is the coupling for the substituted and x_0 that for the unsubstituted benzyl radical; therefore, these parameters measure the spin-delocalising ability of the substituents, and similarly, delocalisation parameters [Δ_x, from equation (2)] may be determined for the wide range of cyclohexadienyl radicals studied by the μSR method.[1]

$$\sigma^{\bullet} = 1 - x/x_0 \qquad (1)$$

$$\Delta_x = 1 - A\mu/A\mu_0 \qquad (2)$$

In Arnold's work, the most greatly rate-accelerating (*para*) substituents are those that are strongly conjugating: particularly C≡N and C=O, as reflected by their relatively large, positive, $\sigma^{\bullet}$ values. The large Δ_x values for these substituents are also in accord with this. However, there are no published experimental data for benzyl radicals with vinyl or ethynyl substituents, which are potentially even more strongly spin-delocalising than C≡N, given the $-CH_2$ couplings which fall in the order: $N{\equiv}C{-}CH_2$[28] > $HC{\equiv}C{-}CH_2$[20] > $H_2C{=}CH{-}CH_2$[29] (21.2, 18.92, 14.35 G). Data for the effect of RC≡C– substituents on the cyclohexadienyl radical are provided by the present work, since, in addition to the triple-bond vinyl adducts, *ortho*, *meta*, and *para* ring adducts were observed (Figures 2 and 3). Distinction between these and the vinyl radicals was achieved by reducing the strength of the applied transverse magnetic field from 3 kG to 1 kG, whereupon doublet splittings of the spectral lines associated with the cyclohexadienyl radicals were observed [Figure 2(*b*)], while those from $Ph\dot{C}{=}C(Mu)Ph$ and $Ph\dot{C}{=}C(Mu)Me$ remained as sharp singlets. In each case, the doublet splitting for the ring adduct arises from the large (*ca.* 48 G) hyperfine coupling to the interacting CHMu group proton. This is because in intermediate magnetic fields, the transitions corresponding to different proton spin states are no longer all degenerate, as they are in high fields, and the two high-field lines split into patterns characteristic of the proton hyperfine multiplicities.[1] At 1 kG, the ring proton couplings are too small to give an observable splitting, and so only the dominant doublet splittings are apparent.

Table 2. Hyperfine couplings ($A\mu'$/G) for aromatic ring adducts of muonium.[a]

X	*ortho*	*meta*	*para*	Δ_x[b]	$\sigma^{\bullet}$[c]
–H[d]	57.7	57.7	57.7	0	0
$-CO_2Me$[d]	56.0	57.8	52.7	0.088	0.039
–C≡N[d]	54.5	58.1	52.0	0.100	0.045
–Ph[d]	52.0	57.7	47.3	0.180	0.091
–C≡CH[e]	52.6	57.9	47.8	0.172	0.087
–C≡CMe[f]	52.3	57.9	47.5	0.177	0.090
–C≡CPh[f]	50.7	57.8	—[g]	—	—
$-CH{=}CH_2$[h]	47.7	—	42.5	0.263	0.139

[a] 1 G = 10^{-4} T. [b] Spin-delocalisation parameters for *para* substituents, Δ_x, derived using equation (2). [c] $\sigma^{\bullet}$ values, according to Arnold [equation (1)] calculated from $A\mu'$ couplings for cyclohexadienyl radicals using equation (3). [d] From ref. 30. [e] From ref. 8. [f] This work. [g] The *para* adduct was note detected. [h] From ref. 31.

The muon hyperfine couplings for the ethynyl-substituted cyclohexadienyl radicals are given in Table 2. The values for the *ortho* and *para* adducts are even lower than those for the corresponding adducts of benzonitrile (PhCN)[30] and methyl benzoate ($PhCO_2Me$),[30] and so it appears that the ethynyl substituents should be even more rate accelerating in reactions with non-polar transition states with a high degree of radical character (homolytic bond breaking); the order being PhC≡C– > MeC≡C– > HC≡C–, in line with their expected, and apparent, increase in spin-delocalising power. Since Arnold did not include results from phenyl- and vinyl-substituted benzyl radicals (which, to our knowledge, are unknown species) in his series, we have included results for the cyclohexadienyl adduct of biphenyl[30] and styrene[31] in our present data, and used the least-squares fit to the data in Figure 4 [equation (3)] to

$$\Delta_x = 1.742\,\sigma^{\bullet} + 0.021 \qquad (3)$$

estimate $\sigma^{\bullet}$ (Arnold) values for these and the ethynyl substituents (Table 2). We are aware that it is not strictly justified to derive one set of σ-values from another, but feel that this exercise serves well usefully to compare the two sets of data, which *are* certainly comparable. The Δ_x values for *ortho*- and *para*-phenyl substituents are similar to those derived for the RC≡C– substituents, but those for $H_2C{=}CH-$ are largest of all and so we predict that a vinyl group should have the most strongly rate-enhancing effect of all the substituents considered so far.

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