EPR and pulsed ENDOR study of intermediates from reactions of aromatic azides with group 13 metal trichlorides

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Abstract

The reactions of group 13 metal trichlorides with aromatic azides were examined by CW EPR and pulsed ENDOR spectroscopies. Complex EPR spectra were obtained from reactions of aluminium, gallium and indium trichlorides with phenyl azides containing a variety of substituents. Analysis of the spectra showed that 4-methoxy-, 3-methoxy- and 2-methoxyphenyl azides all gave ‘dimer’ radical cations \([\text{ArNHC}_6H_5NH}_2\]• and trimers \([\text{ArNHC}_6H_5NHC}_6H_5NH}_2\]• followed by polymers. 4-Azidobenzonitrile, with its electron-withdrawing substituent, did not react. In general the aromatic azides appeared to react most rapidly with AlCl\(_3\) but this reagent tended to generate much polymer. InCl\(_3\) was the least reactive group 13 halide. DFT computations of the radical cations provided corroborating evidence and suggested that the unpaired electrons were accommodated in extensive π-delocalised orbitals. A mechanism to account for the reductive conversion of aromatic azides to the corresponding anilines and thence to the dimers and trimers is proposed.

Introduction

The number of applications of indium [1-6], gallium [7-11] and other group 13 metal derivatives, as promoters of radical reactions, has been increasing ever since the original work of Baba and co-workers with dichloroindium hydride [12-16]. Parallel to that, organic azides are increasingly used as sources of N-centred radicals, although most such methods also require organotin hydrides [17-23]. In seeking cleaner, less toxic and more efficient synthetic methodology – not reliant on organotin compounds [24-28] – some of us began investigating the reactions of organic azides with dichloroindium hydride [29].
allyllindium dichloride [30], and other group 13 metal derivatives. These reagents smoothly convert aromatic and aliphatic azides into the corresponding amines, γ-azidonitriles into pyrroloidin-2-imines [29], and δ-azidoesters and chlorides into allylated nitrogen heterocycles [30].

To help in elucidating the mechanisms of these reductions, we used CW EPR spectroscopy and attempted to characterise the reactive intermediates in selected reactions involving gallium trichloride. Surprisingly, we found that treatment of phenyl azide and 4-methoxyphenyl azide with gallium trichloride resulted in strong EPR spectra of long-lived paramagnetic species. By combining the results of product analyses with the results of EPR spectroscopy, we were able to show that persistent radical cations of ‘dimers’ (4-aminodiphenylamines) and ‘trimers’ (4′-phenylamino-4-aminodiphenylamines) were being formed [31]. We have now broadened the scope of this investigation to aromatic azides with a range of functionality. We report here our findings on the behaviour of aromatic azides when treated with the group 13 trichlorides of gallium, indium and aluminium.

Results and Discussion

Reaction of 4-methoxyphenyl azide (2) with group 13 metal chlorides

A set of aromatic azides, each containing an electron-releasing or an electron-withdrawing substituent in the 4-position, was chosen for this study. The position of the substituent was also varied and several other azide types were included (Scheme 1). Each organic azide was reacted with the metal halide in dichloromethane/pentane or acetonitrile solution at rt, and an aliquot (~0.1 mL) was placed in a quartz capillary tube (diam 1 mm), purged with nitrogen for 15 min and transferred to the resonant cavity of an X-band EPR spectrometer. When either AlCl₃, or GaCl₃ or InCl₃ was used, the reaction was accompanied by copious evolution of gas (probably nitrogen) and a deep blue or violet colour usually developed immediately or within a few minutes. In the case of AlCl₃ the reactions were very vigorous. Previously, we showed that the main product from the reaction of 4-methoxyphenyl azide 2 with GaCl₃ was 4-amino-4'-methoxydiphenylamine (11b, Variamine blue), together with traces of anisole, oxidised derivatives (including 4-(4-methoxyphenylamino)phenol, 4-((4-methoxyphenyl)imino)-cyclohexa-2,5-dienone) and much dark-coloured polymer [31]. The EPR spectrum showed the radical cation of Variamine blue (11b⁺) plus broad signals which we attributed to oligomer and/or polymer radical cations (Scheme 2).

When anhydrous AlCl₃ in DCM – instead of the gallium halide – was added to a solution of azide 2, a vigorous reaction took place. The resulting deep-coloured solution was transferred to the EPR spectrometer and initially the spectrum, Figure 1a, was obtained at 300 K. The broad, poorly resolved signal suggested that the mixture was dominated by polymeric material. However, when the solution was cooled down to 220 K, the well-resolved spectrum, Figure 1b, was obtained. The resolution improvement may be due to the fact that most of the polymer separates from the solution at the lower temperature.

A good computer simulation was achieved by utilising the hyperfine splitting constants (hfs) listed in Table 1. A well-resolved EPR spectrum of 11b⁺, generated from 2 with GaCl₃, is shown in Figure 1c for comparison. Figure 1d shows the experimental spectrum obtained from treatment of 2 with InCl₃, together with the corresponding computer simulation. Although the three EPR spectra appear different at first sight, the hfs derived from the simulations (Table 1) are actually quite similar. The contrasts in the spectral appearances are mainly the result of different line widths with consequently different resolutions. It is evident that the main species in each case is the radical cation 11b⁺. The acceptable agreement between the DFT-computed isotropic hfs of 11b⁺ (Table 1) and the experimental data provides additional support for this identification.

Scheme 1: Organic azides studied.
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Figure 1: EPR spectra after treatment of azide 2 with MCl₃. (a) AlCl₃ in DCM; 1st derivative spectrum at 300 K. (b) AlCl₃ in DCM; 2nd derivative spectrum at 220 K; below: computer simulation with the parameters listed in Table 1. (c) GaCl₃ in DCM/pentane at 300 K with the computer simulation below. (d) InCl₃ in DCM:CH₃CN; 4:1 at 320 K; computer simulation below.

The small differences in the hfs obtained for the different group 13 metal chlorides can probably be attributed to the different counter ions, solvents and temperatures.

The 4-methoxy-tetradecuterio-azide 3 was also treated with AlCl₃ in DCM, and the resulting spectrum and simulation are shown in Figure 2.

The unpaired electron interacts with two non-equivalent N-atoms, a single comparatively large H-atom and a pair of equivalent H-atoms. The spectrum obtained previously on treatment of 3 with GaCl₃ was better resolved (Table 1) [31]. However, it is clear that the same ‘dimer’ species was formed with AlCl₃, probably having picked up the NH and NH₂ hydrogen atoms from the solvent. The line width of the spectrum with AlCl₃ was ca. 0.7 G. Therefore, it is not surprising that hfs from aromatic ring D-atoms were not resolved. Again, differences in the hfs of the spectra from AlCl₃ and GaCl₃ can be attributed to the different counter ions.

Reactions of phenyl azide and 4-substituted-phenyl azides with group 13 metal chlorides

Azides 1, 6 and 7 were chosen to vary the electronic properties and leaving group abilities of 4-substituents. We showed previously that treatment of phenyl azide 1 with GaCl₃ gave well-resolved spectra of 4-aminodiphenylamine radical cation (11a⁺⁺, the dimer) and of the trimer under different reaction conditions [31]. On treatment with InCl₃, 1 gave little sign of reaction. No colour developed and no EPR spectra were obtained. However, a vigorous reaction took place between 1 and AlCl₃ with nitrogen evolution and development of a deep blue colour. The EPR spectrum, Figure 3a, was dominated by a broad component, probably due to polyaniline type material, together with some fine structure. The second derivative spectrum at low modulation amplitude discriminated against the broad signal, and spectrum, Figure 3b, was obtained after digitally removing the residual broad component.

Figure 2: EPR spectrum after treatment of tetra-deuterated azide 3 with AlCl₃. Top: 2nd derivative spectrum at 290 K in DCM. Bottom: computer simulation using the hfs from Table 1.

Figure 3: EPR spectra after treatment of azide 1 with AlCl₃. (a) 1st derivative spectrum in DCM at 280 K. (b) 2nd derivative spectrum after digital removal of residual broad central component. (c) computer simulation.
The hfs were similar to those of 11a$^{17}$ (Table 1, entry for I with GaCl$_3$) except that the smaller hfs were not resolved. Minor differences in the magnitudes of the hfs can be attributed to the different counter ions. The trimer radical cation was not observed, but clearly a contribution from this species could be hidden under the broad component.

No reaction of 4-azidobenzonitrile 7 with InCl$_3$, GaCl$_3$ or AlCl$_3$ was observed and no paramagnetic species were detected by EPR spectroscopy. It appears the electron-accepting property of the CN group inhibited the coupling process at some stage. It is also worth mentioning that, as expected, aliphatic azides such as the CN group inhibited the coupling process at some stage. It is also worth mentioning that, as expected, aliphatic azides such as $\text{CH}_3\text{CN}$, was used to promote the reaction, a beautifully resolved spectrum resulted, Figure 4c.

Very interesting results were obtained from reactions of 1-azido-4-fluorobenzene (6). When 6 was treated with GaCl$_3$ in DCM, a deep blue-violet colour developed and the spectrum was dominated by a broad feature, Figure 4a, although underlying fine structure was evident. When dichlorogallium hydride, prepared from GaCl$_3$ and Et$_3$SiH in CH$_2$CN, was used to promote the reaction, a beautifully resolved spectrum resulted, Figure 4b.

The good simulation of this spectrum, Figure 4c, enabled the hfs shown in Table 1 to be determined. Comparison of these hfs

| Precursor | MCl$_3$/solvent | Radical cation species | 1N | 1N | (N)H | (N)H$_2$ | 2H | 2H | 2H | 2H | Other |
|-----------|-----------------|-----------------------|----|----|------|----------|----|----|----|----|-------|
| Ph$_3$N$_3$ | GaCl$_3$/DCM | 11a$^{**}$ | 4.9 | 4.9 | 6.8 | 5.6 | 3.1 | 2.0 | 1.0 | 0.6 | 1H, 1.0 |
| Ph$_3$N$_3$ | AlCl$_3$/DCM, ACN | 11a$^{**}$ | 4.5 | 4.5 | 6.3 | 5.0 | 2.2 |
| Ph$_3$N$_3$ | DFT | 11a$^{**}$ | 4.3 | 2.2 | −8.4 | −4.8 | −2.0 | −1.8 | −1.1 | 1.0 | 1H, −2.3 |
| 4-MeOC$_6$H$_4$N$_3$ | AlCl$_3$/DCM | 11b$^{**}$ | 4.9 | 4.3 | 7.3 | 3.7 | 1.2 | 1.2 |
| 4-MeOC$_6$H$_4$N$_3$ | GaCl$_3$/DCM | 11b$^{**}$ | 5.2 | 4.4 | 7.3 | 3.8 | 3.1 | 2.2 | 0.8 | 0.4 |
| 4-MeOC$_6$H$_4$N$_3$ | InCl$_3$/DCM 4, ACN 1 | 11b$^{**}$ | 5.2 | 4.0 | 7.8 | 3.2 | 3.2 | 3.2 | 1.8 |
| 4-MeOC$_6$H$_4$N$_3$ | DFT | 11b$^{**}$ | 4.2 | 2.0 | −8.1 | −4.4 | −2.0, −1.6, −1.6, −1.4 | −0.8 | 0.2 | MeO, 1.2 |
| 4-MeOC$_6$H$_4$N$_3$ | AlCl$_3$/DCM | 11b$^{**}$ | 5.9 | 4.8 | 6.7 | 4.9 | − | − | − | − |
| 4-MeOC$_6$H$_4$N$_3$ | GaCl$_3$/DCM | 5.2 | 4.4 | 7.1 | 3.5 | 0.8, 0.7 | 5.7, 5.7 | 5.2, 5.7 | − | − |
| 3-MeOPh$_3$N$_3$ | GaCl$_3$/ACN | 17a$^{**}$ | 4.3 | − | − | − | − | − | − | − | MeO, −0.1 |
| 3-MeOPh$_3$N$_3$ | DFT | 17a$^{**}$ | 3.8 | 1.1 | −7.6 | −2.3, −2.0, −7.2, −7.3, 2.6, −3.4 | −2.3, 1.3, −0.9, −0.2 |
| 2-MeOC$_6$H$_4$N$_3$ | GaCl$_3$/DCM | 17b$^{**}$ | 4.1 | 4.1 | 5.5 | 5.5 |
| 2-MeOC$_6$H$_4$N$_3$ | DFT | 17b$^{**}$ | 4.0 | 1.5 | −8.1 | −3.9 | −1.6, −1.5, −1.6 | 0.8, 0.7, 2D | −0.3, 0.1 |
| 4-FC$_6$H$_4$N$_3$ | HGaCl$_2$/ACN, TES$^a$ | 11c$^{**}$ | 4.4 | 3.9 | 4.0 | 4.0 | 2.0 | 2.0 | 1.0 | 0.5 |
| 4-FC$_6$H$_4$N$_3$ | DFT | 11c$^{**}$ | 4.0 | 2.5 | −7.9 | −5.5 | −1.7 | −1.4 | −1.4 | 0.5 |
| 2-Nap$_3$ | InCl$_3$/DCM 4, ACN 1 | 17b$^{**}$ | 3.4 | 3.4 | 5.6 | 2.8 | 2.8 (1H) |

$^a$All g-factors were 2.0032 ± 0.0005. Assignments of hfs to specific atoms are tentative and are based on the DFT computations. Note that only the magnitudes and not the signs of hfs can be derived from the EPR spectra.

$^b$Treatment of Ph$_3$N$_3$ and 3-MeOC$_6$H$_4$N$_3$ with InCl$_3$ gave only very weak and broad unresolved spectra.

$^c$DFT computations: geometries optimised to UB3LYP/6-31+G(d,p) then single point calculations with 6-311++G(d,p) basis.

$^d$Data from ref [31].

$^e$HGaCl$_2$ prepared from GaCl$_3$ and Et$_3$SiH (TES), $^f$The computed a(F) varied from 4.3 G, with the 6-311+G(d,p) basis set, to 9.5 G with the DGDZVP basis set.

Table 1: EPR parameters of ‘dimers’ [ArNHC$_6$H$_4$NH$_2$]$^{2+}$ from treatment of aryl azides with group 13 metal chlorides.$^a$
Figure 4: EPR spectra after GaCl$_3$ and InCl$_3$ reactions of azide 6. (a) 1st derivative spectrum from 6 and GaCl$_3$ in DCM at 300 K. (b) 1st derivative spectrum of dimer ($11c^{+\ast}$) from 6 and HGaCl$_2$ in CH$_3$CN at 300 K. (c) computer simulation of (b) with hfs of Table 1. (d) 1st derivative spectrum of trimer ($19^{+\ast}$) from 6 and InCl$_3$ in DCM at 300 K. (e) computer simulation of (d) with hfs of Table 2.

Treatment of 6 with InCl$_3$ in DCM led to the usual broad signal from oligomeric and polymeric species superimposed on a spectrum with much narrower lines. On recording the spectrum with a smaller modulation amplitude, and digitally removing the residual broad feature, the spectrum shown in Figure 4d resulted. This is obviously a different species from that of Figure 4b and, after many trials, a satisfactory simulation was obtained, Figure 4e. The derived hfs are presented in Table 2 and they clearly correspond to a trimer, also probably containing a single F-atom, i.e. $19b^{+\ast}$.

It seems clear that the MCl$_3$ reactions with aromatic azides entail a progression from the aniline $X_6H_4NH_2$, to the dimer $X_6H_4NH_6H_4NH-C_6H_4NH_2$, thence to oligomers and eventually polyaniline type polymers $X[X_6H_4NH]_nX_6H_4NH_2$. Some polymer radical cation was always observed by EPR spectroscopy, but whether dimer or trimer or oligomer dominated the spectrum depended on a delicate balance between solvent, metal halide and other factors.

Reactions of 2-methoxy- and 3-methoxyphenyl azides with group 13 metal chlorides

Aromatic azides 4 and 5 were chosen to investigate how the position of the MeO substituent influenced the reaction. Treatment of the 3-methoxy precursor 4 with InCl$_3$ or HInCl$_2$ gave only very weak and broad EPR spectra. However, reaction of 4 with GaCl$_3$ in CH$_3$CN gave a strong EPR spectrum and the hfs derived from the computer simulation are presented in Table 1. The comparatively large line width (~0.9 G) did not permit the resolution of small hfs from aromatic ring H-atoms. For the same reason, the hfs from the second N-atom were not resolved. However, it is clear that this species is probably a ‘dimer’ although the connectivity of the angular structure $17a^{+\ast}$ is somewhat different from that of the 4-aminodiphenylamines derived from the 4-substituted phenyl azides (Scheme 3).

Treatment of 6 with GaCl$_3$ in CH$_3$CN at 300 K. (b) 1st derivative spectrum of dimer ($11c^{+\ast}$) from 6 and HGaCl$_2$ in CH$_3$CN at 300 K. (c) computer simulation of (b) with hfs of Table 1. (d) 1st derivative spectrum of trimer ($19^{+\ast}$) from 6 and InCl$_3$ in DCM at 300 K. (e) computer simulation of (d) with hfs of Table 2.

Scheme 3: Dimer and trimer radical cations.

Treatment of the 2-methoxy precursor 5 with GaCl$_3$ in DCM, or with HGaCl$_2$ in CH$_3$CN, gave essentially the same strong spectrum, see Figure 5a and Supporting Information. The hfs derived from the simulations (Table 1) suggest that this is also a dimer type radical cation $17b^{+\ast}$. However, with the passage of time a central peak began to appear in this spectrum. When 5 was treated with HGaCl$_2$, prepared from GaCl$_3$ and Et$_3$SiH, the species with a central peak dominated the spectrum, Figure 5b. Treatment of 5 with InCl$_3$ in DCM or with HInCl$_2$ in THF (prepared from InCl$_3$ and DIBAL-H) also gave rise to a spectrum of this same species, Figure 5c. A well-resolved spectrum of this species was obtained by treatment of 5 with...
Table 2: EPR hfs of ‘trimer’ species \([\text{[ArNH}]_2 \text{C}_6 \text{H}_4 \text{NH}_2]^+\) from treatment of aryl azides with group 13 metal chlorides.\(^a\)

| Precursor | MCl\(_3\)/solvent or DFT | Trimer radical cation | N  | N  | N(H\(_2\)) | (N)H\(_2\) | (N)H | (N)H | H-rings | Other |
|-----------|--------------------------|-----------------------|----|----|------------|-----------|------|------|---------|-------|
| \(\text{PhN}_3\)\(^b\) | GaCl\(_3\)/DCM | 19a** | 5.0 | 4.9 | 3.0 | 6.5 | 4.9 | 2.1 | 2.1 (3H) | 1.0 (3H) |
| \(\text{PhN}_3\)\(^b\) | DFT\(^c\) | 19a** | 5.4 | 3.4 | 2.0 | -3.0 | -7.8 | -4.8 | -1.6 (4H) | -1.0 (3H) |
| 4-FC\(_6\)H\(_4\)N\(_3\)\(^6\) | InCl\(_3\)/DCM | 19b** | 5.5 | 5.5 | 2.6 | 6.2 | 7.2 | 4.5 | 2.2 (1H) | 1.5 (2H) | 0.5 (6H) | 2.2 (1F) |
| 4-FC\(_6\)H\(_4\)N\(_3\)\(^6\) | DFT\(^d\) | 19b** | 3.7 | 2.1 | 1.5 | -3.2 | -7.2 | -4.2 | -1.3 (4H) | -0.6 (4H) | <0.6 (4H) |
| 2-MeOC\(_6\)H\(_4\)N\(_3\)\(^5\) | InCl\(_3\)/DCM | 18** | 4.8 | 4.8 | 4.8 | 5.1 | 5.1 | 5.1 | – |
| 2-MeOC\(_6\)H\(_4\)N\(_3\)\(^5\) | HGaCl\(_2\)/CN | 18** | 4.5 | 4.5 | 3.0 | 4.1 | 1.7 | 5.5 | 5.5 | 1.7 (1H) | 0.5 (4H) |
| 2-MeOC\(_6\)H\(_4\)N\(_3\)\(^5\) | DFT\(^c\) | 18** | 4.4 | 3.9 | 1.5 | -2.0 | -1.6 | -6.6 | -5.1 | -2.0 (1H) | -1.7 (2H) | -1.1 (1H) | <0.7 (8H) |

\(^a\)All \(g\)-factors 2.0032 ± 0.0005, assignments of hfs to specific atoms are tentative and are based on the DFT computations. Note that only the magnitudes and not the signs of hfs can be derived from the EPR spectra. \(^b\)Data from ref [31]. \(^c\)DFT: UB3LYP/6-31G(d). \(^d\)DFT computations: UB3LYP/6-31+G(d,p) then single point calculation with 6-311++G(d,p) basis. \(^e\)HGaCl\(_2\) prepared from GaCl\(_3\) and Et\(_3\)SiH (TES).

HGaCl\(_2\) prepared with Et\(_3\)SiH in CH\(_3\)CN, Figure 5d. The hfs derived from the computer simulation, Figure 5c and Table 2 show the presence of three N-atoms and of four H-atoms with sizeable hfs that can probably be attributed to NH or NH\(_2\) groups. Thus, this species is almost certainly a ‘trimer’ although this will necessarily have an angular structure 18** rather than the linear type structure of the trimers from 4-substituted azides such as 19** (Scheme 3).

The results from azides 4 and 5 showed that the position of the MeO substituent in the phenyl azides was not critical. The reactions with gallium and indium promoters proceeded along similar lines to that of phenyl and 4-substituted phenyl azides to give dimers, trimers and polymers.

The spectra obtained on treatment of 2-azidonaphthalene 8 with InCl\(_3\), GaCl\(_3\) and AlCl\(_3\) are shown in Figure 6a, Figure 6b and Figure 6c, respectively.

The broad signal in Figure 6c shows that polymerisation dominated the reaction with AlCl\(_3\). Similarly, the main broad feature in Figure 6b suggests that polymerisation was again dominant in the reaction with GaCl\(_3\). The comparatively well-resolved species observed in the InCl\(_3\)-promoted reaction, Figure 6a, was well simulated on using the parameters shown in Table 1. The data show that the unpaired electron interacted with two

Figure 5: EPR spectra after GaCl\(_3\)- and InCl\(_3\)-promoted reactions of 2-methoxyphenyl azide 5. (a) 1st derivative spectrum of 17b** from 5 with GaCl\(_3\) in DCM. (b) 1st derivative spectrum of 17b** from 5 with HInCl\(_2\) in THF at 300 K. (c) 1st derivative spectrum of 18** from 5 with HGaCl\(_2\) in CH\(_3\)CN at 300 K. (d) 1st derivative spectrum of 18** from 5 with HGaCl\(_2\) in CH\(_3\)CN at 300 K. (e) computer simulation of (d).
Figure 6: EPR spectra after In-, Ga- and Al-promoted reactions of azide 8. (a) intermediate from InCl₃ treatment of 8 at 260 K in DCM and CH₃CN (4:1). (b) spectrum from GaCl₃ treatment of 8 at 300 K in DCM/pentane. (c) spectrum from AlCl₃ treatment of 8 at 300 K in DCM.

N-atoms, two (N)H₂ atoms, one (N)H-atom and one other H-atom; other splittings were not resolved. The magnitudes of the hfs are somewhat smaller than those of analogous atoms in the dimer from 1. This is exactly as would be expected from the greater extent of aromatic delocalisation in a dimer from 8. Clearly, however, more than one isomer is possible.

Pulse ENDOR spectrum of the intermediate from 4-fluorophenyl azide 6

Pulsed ENDOR experiments, based on the ESE effect, were carried out on the frozen solution from azide 6 at 50 K. The echo signal was created by the microwave pulse sequence, and an rf pulse was applied during the ‘mixing period’, which corresponded to the time T in the Davies ENDOR sequence [32]. The rf pulse drove the nuclear spin transitions, which led to a change in the ESE intensity. The ENDOR signal was therefore measured by monitoring the ESE intensity while the rf frequency was varied. In the case of an $S = \frac{1}{2}$ system coupled with a nucleus with nuclear spin $I = \frac{1}{2}$, the Davies ENDOR spectrum consists of two lines at the nuclear resonance frequencies $\nu_a$ and $\nu_b$, which correspond to the transitions associated with the electron spin manifolds $M_S = +\frac{1}{2}$ and $M_S = -\frac{1}{2}$, respectively. If the Larmor frequency ($\nu_n$) of the nucleus in question is larger than the hyperfine interaction, then the resonance frequencies are given by:

$$\nu_{ap} = |\nu_n \pm \frac{1}{2}a_{\text{iso}}|.$$  \hspace{1cm} (1)

If $\nu_n$ is less than $\frac{1}{2}a_{\text{iso}}$, the frequencies are then given by:

$$\nu_{ap} = |\frac{1}{2}a_{\text{iso}} \pm \nu_n|.$$  \hspace{1cm} (2)

An additional complication arises if the nuclear spin is $>\frac{1}{2}$, which adds another term describing the nuclear quadrupole interaction in the above equations [33]. In frozen solution all orientations of the paramagnetic species are observed and therefore an anisotropic ENDOR spectrum is expected. The latter is more complex and requires a detailed understanding of the anisotropy of the system. The above equations are not suitable for such a situation and a more complete resonance condition that considers all the orientations is needed. In the case of a system with $I = \frac{1}{2}$ the parameter $a_{\text{iso}}$ in Equation 1 and Equation 2 is replaced by $A_i$ (i.e. one of the principal components of the hyperfine tensor).

The Davies ENDOR spectrum from the species derived from the 4-fluoroazide 6 sample at 50 K is shown in Figure 7. The inset shows the ESE-EPR spectrum, with an arrow indicating the magnetic field position at which the ENDOR experiment was performed. The ENDOR spectrum shows powder pattern lineshapes, as expected for frozen solutions, due to the anisotropic hyperfine interactions. Two main features cover the whole spectrum; a powder pattern centred about the $^1$H Larmor frequency and a second broad signal located at lower frequency and spread over 8 MHz width.

![Figure 7: Experimental and simulated Davies ENDOR spectrum after the Ga-promoted reaction of azide 6 recorded at 50 K. The inset shows the field-swept EPR spectrum with an arrow indicating the magnetic field position of the ENDOR experiment.](image)

The lack of resolution encountered in the ENDOR spectrum makes an unequivocal analysis difficult. Therefore, our ENDOR simulation was based mainly on the CW EPR results. A simulated spectrum is displayed in Figure 7, and a deconvoluted version is in the Supporting Information together with one chosen set of ENDOR hyperfine tensor parameters. Almost all the $^1$H hyperfine splittings fit well within the ENDOR spectra,
but it is worth noting, as mentioned above, that a satisfactory
simulation was only achieved by assuming an anisotropic line-
shape of the hyperfine couplings. Extra weak hyperfine
couplings, unresolved in the CW EPR, were also included in the
simulation. These probably correspond to hyperfine coupling in
polymer which was undoubtedly present. The broad feature at
low frequency is related to a mixture of fluorine (19F) and
nitrogen (14N) contributions. The anisotropy and the unre-
solved nuclear quadrupole of the nitrogen couplings make the
spectra difficult to interpret. Each 1H contributes three sets of
peaks to the spectrum times the number of 1H’s present. This
represents an enormous number of lines in one spectrum. Obvi-
ously, they cannot all be assigned from this broad unresolved
powder pattern. Almost axial tensors were assumed (see
Supporting Information). However, it should be noted that it
may well be possible to simulate these spectra with other param-
eter sets. The experimental Davies ENDOR data support the
CW EPR data in confirming the magnitudes of the hyperfine
couplings and the nitrogen interactions. Further pulse tech-
niques such as electron spin echo envelope modulation
(ESEEM) and its multidimensional extension Hyscore would be
required to get more insight into the nitrogen contribution.
Regarding the 19F contribution; only the low-frequency part of
the 19F coupling fits well with the experimental data. The 19F
high-frequency line in our simulation is not consistent with the
experimental spectrum, which suggests that the latter might be
highly asymmetric. Such situations have been previously
reported in other studies where it was shown that this could be
related to the relaxation time. Sometimes relaxation processes
can lead to a partial saturation in the nuclear transitions such
that the observed signal is the result of a transition in one mani-
fold only [34]. Partial saturation may explain the absence of the
19F high-frequency line in our spectrum.

DFT computations of radical cation properties
Quantum chemical calculations were carried out with the
Gaussian 03 programme package [35,36]. Density functional
theory with the UB3LYP functional was employed. The equi-
librium geometries were fully optimised with respect to all
geometric variables, no symmetry being assumed either with
the 6-31+G(d,p) basis set (dimers) or with the 6-31G(d) basis
set (trimers). Isotropic EPR hfs were derived from computed
Fermi contact integrals evaluated at the H- and N-nuclei. The
hfs were taken directly from the Gaussian output files and are
shown in Table 1 and Table 2.

The optimum structures of the radical cations 17a++ and 17b++
their associated SOMOs are shown in Figure 8.

The C—NH bond lengths in radical cation 17a++ (1.40 and 1.38
Å) and 17b++ (1.38, 1.39 Å) indicated significant double bond
character. The CNC angles in 17a+++ and 17b+++ were 128.9 and
131.6°, showing significant widening from trigonal. The
aromatic rings in all the structures were twisted significantly out
of co-planarity. As might be expected on steric grounds, this
increased in the dimers as the substitution site moved from the
4- to the 3- to 2-position. For example, the computed dihedral
angles between the rings increased from 26.8 to 30.7 to 39.0 in
the series 4-MeO-11b++, 3-MeO-17a++ and 2-MeO-17b++,
respectively. It seems that a compromise was reached in which
the repulsive steric interaction between substituents of neigh-
bouring rings was balanced against the stabilising effect from
conjugation of the π-systems. The SOMOs depicted in Figure 8
show that there was still sufficient orbital overlap in the linear
and angular dimer and trimer radical cations to support lengthy
π-systems extending over all the rings and N-atoms. This is in
accordance with the EPR spectroscopic data, that show exhaus-
tive delocalisation of the unpaired electron in dimer and trimer
radical cations. The computed hfs in Table 1 and Table 2 show
reasonable correspondence with the experimentally observed
values.

Conclusion

Literature reports show that anilines can easily be oxidised
to the corresponding resonance-stabilised radical cations,
which can couple with more aniline to afford very persistent
radical cation dimers [37,38]. The generation of these
radical cations depends critically on the reaction conditions, in
particular on the degree of protonation, which can facilitate
electron transfer (ET) [39,40]. It has also been reported that
electrochemical oxidation of aromatic amines can generate the
same radical cations which can polymerise giving oligo- and
poly-anilines [41]. In view of the fact that product analyses [31]
identified aniline amongst the products from 1 and anisole
amongst the products from 2, it seems probable that the
aromatic amines are the precursors of the dimer and trimer
species.

A possible mechanism for production of anilines from the
aromatic azides is set out in Scheme 4. Coordination of the
metal halide to the starting azide should produce the Lewis
base–acid adduct 12 that could undergo reduction by ET from
more azide to afford, after nitrogen loss, the metal-coordinated
aminyl radical 13 together with the ArN=N=N=Ar.
Aminyl radical 13 could then abstract an H-atom from solvent
RH (or from HMC12 when the metal hydrides were used) with
the production of metal-coordinated amine 14. The latter can
then pick up a proton to produce an aromatic amine and
regenerate the metal halide. The reason 4-azidobenzoanitrile 7
did not react with any of the group 13 metal chlorides may well
be that the ET step 12 → 13 was inhibited by the presence of
the electron acceptor CN group.
Several mechanisms have been proposed in the literature for the formation of ‘dimers’ from anilines. These include [42-44]: (i) initial formation of the radical cation ArNH$_2$$^+$ which then couples with more aniline and forms the 4-aminodiaryl amine radical cation after loss of HX and (ii) formation of the aniline radical ArNH$^•$, which couples with ArNH$_3^+$, ArNH$_2$ or ArNH$_2$$^+$.$^+$. A plausible mechanism for formation of the dimer and trimer radical cations we observed is shown in Scheme 5 for the case of 2-methoxyaniline.

Ips$^o$ attack by radical 13a on the aniline would lead to the production of delocalised radical 15. Elimination of MeOMCl$_3^-$ would then yield radical 16, which, on protonation, would afford the observed long-lived dimer radical cations 17.$^+$. Of
course, proton transfer could occur earlier in the reaction, such that coupling takes place with the anilinium cation instead. Trimer $18^{**}$ could be produced by coupling of $17^{**}$ with more $13a$ followed by a similar sequence of steps. The trimer could then grow into oligomer and polymer by a succession of such coupling reactions.

In general, the aromatic azides appeared to react most rapidly with AlCl$_3$ but this reagent tended to generate much polymer. InCl$_3$ was the least reactive group 13 halide such that no reaction was observed with PhN$_3$ and very little reaction occurred with the 3-methoxyazide 4. GaCl$_3$ and HGaCl$_2$ were the best promoters. The dimers were the main products from reactions of excess 1 and 2 with GaCl$_3$ such that the process could have synthetic potential. In general, the GaCl$_3$- and HGaCl$_2$-promoted reactions were also best for spectroscopic studies because they gave the most intense and well-resolved spectra of $[\text{ArNHArNH}_2]^{**}$ and/or $\{[\text{ArNH}]_2\text{ArNH}_2\}^{**}$ with the narrowest line widths.

### Experimental

**EPR and ENDOR spectroscopy.** EPR spectra were obtained with a Bruker EMX X-Band 10/12 spectrometer fitted with a rectangular ER4122 SP resonant cavity and operating at 9.4 GHz with 100 kHz modulation. An aliquot (~0.1 mL) of the reaction mixture from each aromatic azide and the metal chloride in CH$_2$Cl$_2$/pentane or CH$_3$CN solution was placed in a 1 mm o.d. quartz capillary tube, de-aerated by bubbling nitrogen for 20 min and transferred to the resonant cavity. Spectra were examined at several temperatures but generally best resolution and signal intensity were obtained at around 300 K. Most of the EPR spectra were recorded with 2.0 mW power, 1.0–0.2 G$_{pp}$ modulation intensity and a gain of ~10$^6$. In all cases where spectra were obtained, hfs were assigned with the aid of computer simulations using the Bruker SimFonia and NIEHS Winsim2002 software packages.

Pulsed EPR and ENDOR were performed using a pulsed EPR X-band spectrometer (Bruker Elexsys E580) equipped with a Dice-ENDOR accessory, a radio frequency (rf) amplifier and a dielectric-ring ENDOR resonator (Bruker EN4118X-MD-4-W1). Samples were maintained at 50 K using liquid helium in an Oxford CF-935 cryostat. Field-swept electron spin echo (ESE) spectra were recorded using a two-pulse ESE sequence while ESE-ENDOR experiments were carried out using Davies three-pulse sequence $\pi$-$T$-$\pi$/2-$\pi$-$\pi$-echo with a selective rf pulse of variable frequency applied during time $T$. The pulse lengths used were 128 and 256 ns for $\pi$/2 and $\pi$ respectively, and 10 $\mu$s for the $\pi$-rf pulse. ENDOR data were processed and simulated using the EasySpin package (freeware from http://www.easyspin.org/).

**DFT calculations.** All computations were done with the Gaussian 03W programme package (Version 6.1.0.0) [35]. Geometries were optimised at the UB3LYP/6-31+G(d,p) level [45] (dimers) and the UB3LYP/6-31G(d) level (trimers) and single point calculations at these geometries with a triple zeta quality basis set (6-311++G(d,p)) were used to predict isotropic EPR hfs. The DGTZVP basis set, similar to that recommended by Schäfer et al. [46], was also employed for some computations.
General procedure for the reaction of aryl azides with indium trichloride. The starting azide (1 mmol) was added at 0 °C to an acetonitrile solution of indium trichloride (1.1 mmol) in DCM (4 mL) and stirred for 5 min at 0 °C. Gas was evolved and the solutions took on a dark blue or violet colour. The resulting solutions were rapidly transferred into a quartz capillary tube and purged with nitrogen for few minutes. The tube was sealed and placed in the EPR resonant cavity. Spectra were recorded at several different temperatures. Some samples were photolysed with a 500 W super pressure Hg arc.

General procedure for the reaction of aryl azides with dichloroiridium hydride. The starting azide (1 mmol) was added at 0 °C to an acetonitrile solution of dichloroiridium hydride (1.1 mmol), generated in situ by stirring under an argon atmosphere anhydrous indium trichloride (243 mg, 1.1 mmol, previously dried by heating at 130 °C under argon for 1 h) and triethylsilane (177 μL, 1.1 mmol) in ACN (4 mL) for 5 min at 0 °C [47]. The resulting solution was rapidly transferred into a quartz capillary tube and nitrogen was bubbled inside for few minutes. The tube was sealed and placed in the EPR cavity. Spectra were recorded at several different temperatures. Some samples were photolysed with a 500 W super pressure Hg arc. Selected samples were given an aqueous work-up with NaHCO₃ followed by extraction with diethyl ether. In each case the corresponding aromatic amine was identified by comparison with literature data.

General procedure for the reaction of aryl azides with AlCl₃. Aluminium trichloride (1.1 mmol) was dried under reduced pressure at 25 °C for 1 h. Then DCM (3 mL) was added and a DCM solution of the azide (1 mmol in 1 mL) was introduced at rt. Gas was evolved, sometimes violently, and dark blue or violet colours developed. The resulting solution was then transferred to a capillary quartz tube and purged with nitrogen. The capillary was sealed and several EPR spectra were run at different temperatures. Product analysis was performed by quenching the reaction with an aqueous solution of NaOH and extracting with DCM. The mixtures were analysed by GC–MS and, when possible, by ¹H NMR and ¹³C NMR spectroscopy.

General procedure for the reaction of aryl azides with GaCl₃. A pentane solution of gallium trichloride (0.55 mL of 0.5 M; 0.28 mmol) was added under a nitrogen atmosphere to a DCM solution of the azide (0.25 mmol in 4 mL) at rt. Gas was evolved and an intense blue or violet colour developed. The resulting solution was then transferred into a capillary quartz tube and purged with nitrogen. The capillary was sealed, and the sample was analysed by EPR spectroscopy at several different temperatures. Products analysis was performed as above.

Ethyl 5-azidopentanoate (9) [48] was prepared by treatment of the corresponding alkyl bromide with sodium azide in DMSO [49]; IR (νmax, CHCl₃), 1718 (CO) and 2092 (N≡) cm⁻¹; ¹H NMR (400 MHz) δ 1.24 (t, J = 7.2 Hz, 3H), 1.54–1.77 (m, 4H), 2.32 (t, J = 6.9 Hz, 2H), 3.28 (t, J = 6.6 Hz, 2H), 4.13 (q, J = 7.2 Hz, 2H).

Aromatic azides 1–8 were prepared by standard diazotisation of the corresponding anilines followed by treatment with sodium azide, and were identified by comparison with literature data: phenyl azide (1) [50], 1-azido-4-methoxybenzene (2) [48], 1-azido-3-methoxybenzene (4) [51], 1-azido-2-methoxybenzene (5) [48], 1-azido-4-fluorobenzene (6) [48], 4-azidobenzonitrile (7) [52] and 2-azidonaphthalene (8) [53]. 2,3,5,6-Tetradecuero-4-methoxyphenyl azide (3) was prepared by diazotisation of 2,3,5,6-tetradecuero-4-methoxyaniline, derived in turn from the reaction of 3,5-dideuero-4-methoxyaniline hydrochloride with boiling D₂O for 4 days in a sealed tube [31].

Supporting Information
Supporting information features general procedures, EPR spectra from azides 4 and 5, deconvolution of ENDOR spectrum from azide 6, Cartesian coordinates for DFT-computed structures of dimer and trimer radical cations.

Supporting Information File 1
EPR and pulsed ENDOR study of intermediates from reactions of aromatic azides with group 13 metal trichlorides
[http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-6-84-S1.pdf]

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References
1. Takami, K.; Yorimitsu, H.; Oshima, K. Org. Lett. 2002, 4, 2993–2995. doi:10.1021/ol026401w
26. Darmceny, V.; Renaud, P. Top. Curr. Chem. 2006, 263, 71–106. doi:10.1007/128_030
27. Walton, J. C. Top. Curr. Chem. 2006, 264, 163–200. doi:10.1007/128_021
28. Walton, J. C.; Studer, A. Acc. Chem. Res. 2005, 38, 794–802. doi:10.1021/ar050089j
29. Benati, L.; Bencivenni, G.; Leardini, R.; Nanni, D.; Minozzi, M.; Spagnolo, P.; Scilapi, R.; Zanardi, G. Org. Lett. 2006, 8, 2499–2502. doi:10.1021/ol0608637
30. Bencivenni, G.; Lanza, T.; Minozzi, M.; Nanni, D.; Spagnolo, P.; Zanardi, G. Org. Biomol. Chem. 2010, 8, 3444–3450. doi:10.1039/c001848a
31. Bencivenni, G.; Cesari, R.; Nanni, D.; El Mikami, H.; Walton, J. C. Org. Biomol. Chem. 2010. doi:10.1039/C0OB00084A
32. Davies, E. R. Phys. Lett. A 1974, 47, 1–2. doi:10.1016/0375-9601(74)90778-4
33. Van Doorslaer, S.; Vinck, E. Phys. Chem. Chem. Phys. 2007, 9, 4620–4638. doi:10.1039/b701566b
34. Epel, B.; Manikandan, P.; Kronick, P. M. H.; Goldfarb, D. Appl. Magn. Reson. 2001, 21, 287–297. doi:10.1007/s002310100482
35. Gaussian 03 Revision A.1; Gaussian, Inc.: Pittsburgh, PA, 2003.
36. Barone, V. In Recent Advances in Density Functional Theory; Chong, D. P., Ed.; World Scientific Publishing Co.: Singapore, 1996. [for the basis set B3LYP/6-31G(d)].
37. Forrester, A. R.; Hay, J. M.; Thomson, R. H. Organic Chemistry of Stable Free Radicals; Academic Press: New York, 1968; pp 247–268. Chapter 6.
38. Male, R.; Allenderforfer, R. D. J. Phys. Chem. 1988, 92, 6237–6240. doi:10.1021/j100333a014
39. Wolf, J. F.; Forbes, C. E.; Gould, S.; Shacklette, L. W. J. Electrochem. Soc. 1989, 136, 2887–2891. doi:10.1149/1.2096307
40. Wienk, M. M.; Janssen, R. A. J. Am. Chem. Soc. 1996, 118, 10626–10628. doi:10.1021/ja9616591
41. Petr, A.; Dunsch, L. J. Phys. Chem. 1996, 100, 4867–4872. doi:10.1021/jp9529650
42. Petr, A.; Dunsch, L. J. Electroanal. Chem. 1996, 419, 55–59. doi:10.1016/S0022-0728(96)80050-1
43. Simon, P.; Farsang, G.; Amatore, C. J. Electroanal. Chem. 1997, 435, 165–171. doi:10.1016/S0022-0728(97)00284-2
44. Goto, M.; Otsuka, K.; Chen, X.; Tao, Y.; Oyama, M. J. Phys. Chem. A 2004, 108, 3980–3986. doi:10.1021/jp035579c
45. Becke, A. D. J. Phys. Chem. 1993, 98, 5646–5652. doi:10.1063/1.464913
46. Schäfer, A.; Horn, H.; Ahrlik, R. J. Chem. Phys. 1992, 97, 2571–2577. doi:10.1063/1.463096
47. Hayashi, N.; Shibata, I.; Baba, A. Org. Lett. 2004, 6, 4981–4983. doi:10.1021/ol0404784v
48. Bencivenni, G.; Lanza, T.; Leardini, R.; Minozzi, M.; Nanni, D.; Scilapi, R.; Spagnolo, P.; Zanardi, G. Org. Lett. 2006, 8, 417–420. doi:10.1021/ol050628n
49. Benati, L.; Bencivenni, G.; Leardini, R.; Minozzi, M.; Nanni, D.; Scilapi, R.; Spagnolo, P.; Zanardi, G. Org. Lett. 2006, 9, 3046–3053. doi:10.1021/ol0507839
50. Benati, L.; Bencivenni, G.; Leardini, R.; Minozzi, M.; Nanni, D.; Scilapi, R.; Spagnolo, P.; Zanardi, G. Org. Chem. 2006, 71, 434–437. doi:10.1021/ol0521697
51. Benati, L.; Bencivenni, G.; Leardini, R.; Minozzi, M.; Nanni, D.; Scilapi, R.; Spagnolo, P.; Zanardi, G. Org. Chem. 2006, 71, 5822–5825. doi:10.1021/ol060824k
52. Bencivenni, G.; Lanza, T.; Leardini, R.; Minozzi, M.; Nanni, D.; Spagnolo, P.; Zanardi, G. J. Org. Chem. 2006, 73, 4721–4724. doi:10.1021/jo060453z
53. Lanza, T.; Leardini, R.; Minozzi, M.; Nanni, D.; Spagnolo, P.; Zanardi, G. Angew. Chem., Int. Ed. 2008, 47, 9439–9442. doi:10.1002/anie.200804333
54. Minozzi, M.; Nanni, D.; Spagnolo, P. Chem.– Eur. J. 2009, 15, 7830–7840. doi:10.1002/chem.201002710
55. Baguley, P. A.; Walton, J. C. Angew. Chem., Int. Ed. 1998, 37, 3072–3082. doi:10.1002/(SICI)1521-3773(19981204)37:23<3072::AID-AnIE3072>3.0.CO;2-N
56. Studer, A.; Amrein, S. Synthesis 2002, 7, 835–849. doi:10.1055/s-2002-28507
57. Bencivenni, G.; Lanza, T.; Minozzi, M.; Nanni, D.; Scilapi, R.; Spagnolo, P.; Zanardi, G. Angew. Chem., Int. Ed. 2008, 47, 9439–9442. doi:10.1002/anie.200804333
58. Minozzi, M.; Nanni, D.; Spagnolo, P. Chem.– Eur. J. 2009, 15, 7830–7840. doi:10.1002/chem.201002710
59. Baguley, P. A.; Walton, J. C. Angew. Chem., Int. Ed. 1998, 37, 3072–3082. doi:10.1002/(SICI)1521-3773(19981204)37:23<3072::AID-AnIE3072>3.0.CO;2-N
60. Studer, A.; Amrein, S. Synthesis 2002, 7, 835–849. doi:10.1055/s-2002-28507
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