

Formation of Novel Sulfur-Containing C₆₀F₁₆ Cycloadducts between Tetrathiafulvalene and C₆₀F₁₈; A Unique Six-Electron Cycloaddition of a Fullerene Involving F₂ Loss

Adam D. Darwish,^[a] Anthony G. Avent,^[a] Olga V. Boltalina,^[b] Ilya Gol'dt,^[b] Igor Kuvytkho,^[b] Tatiana Da Ros,^[a] Joan M. Street,^[c] and Roger Taylor^{*[a]}

Abstract: Co-evaporation of solutions of C₆₀F₁₈ and tetrathiafulvalene in toluene produces an unsymmetrical C₆₀F₁₆:tetrathiafulvalene adduct through a unique six-electron cycloaddition involving displacement of two fluorine atoms by a terminal C=C double bond of the fulvalene. The adduct rearranges into two further adducts, one of which is

characterised as a new type of fullerene derivative, a thiiranofullerene, formed by elimination of a thioketene moiety from the tetrathiafulvalene adduct. The

Keywords: aromaticity • cycloaddition • elimination • fullerenes • tetrathiafulvalene

initial addition also produces a bisadduct in which the addends comprise one tetrathiafulvalene molecule and one in which carbon disulfide has been eliminated. The latter adduct involves cycloaddition of an unsaturated aromatic dithiolactone moiety.

Introduction

Use of tetrathiafulvalene as an electron donor has been in the forefront of research into photoinduced intramolecular electron transfer involving fullerenes.^[1] We intended to examine the effect of this group attached to the five-membered pyrrole-type ring of pyrrolidinofullerenes, derived from C₆₀F₁₈ since this is a better electron acceptor than C₆₀ itself. However, our preliminary experiments indicated that unplanned reactions were occurring. We therefore examined the reaction of C₆₀F₁₈^[2] with tetrathiafulvalene itself, which showed that these reagents combine to give a number of novel derivatives, here described. The nature of the combination appears to be unique, in that reaction occurs only on co-evaporation of the reagents to dryness. This results in the formation of two products **A** (major) and **D** (minor), and on standing **A** rearranges to two further products **B** and **C**, each of which was separated and purified by HPLC.

[a] Prof. R. Taylor, Dr. A. D. Darwish, Dr. A. G. Avent, Dr. T. Da Ros
The Chemistry Laboratory, CPES School
Sussex University
Brighton BN1 9QJ (UK)
Fax: (44) 1273-677-196
E-mail: R.Taylor@sussex.ac.uk

[b] Dr. O. V. Boltalina, I. Gol'dt, I. Kuvytkho
Chemistry Department
Moscow State University
Moscow 119899, (Russia)

[c] J. M. Street
Chemistry Department
The University
Southampton, SO17 1BJ (UK)

Results and Discussion

Characterisation of compound A (18.5 min HPLC retention time): The ions in the mass spectrum (Figure 1) at *m/z* 204 and 1024 show **A** to be an adduct of C₆₀F₁₆ and TTF. This is confirmed by the ¹⁹F NMR spectrum (Figure 2) which shows 16 lines together with the couplings obtained from a 2D spectrum. In general for C₆₀F₁₈ derivatives, the six peaks in the

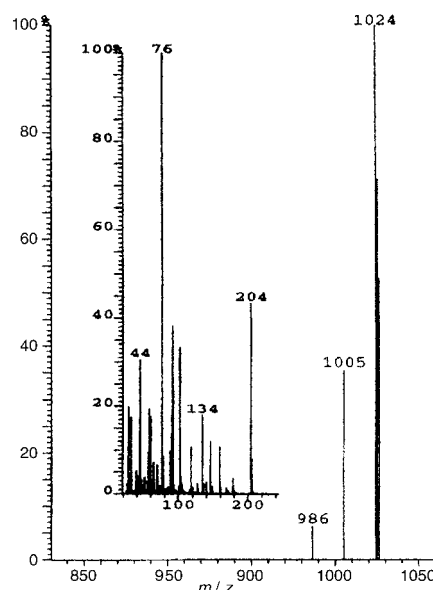


Figure 1. EI mass spectrum (70 eV) for the product **A** of 18.5 min retention time (see text).

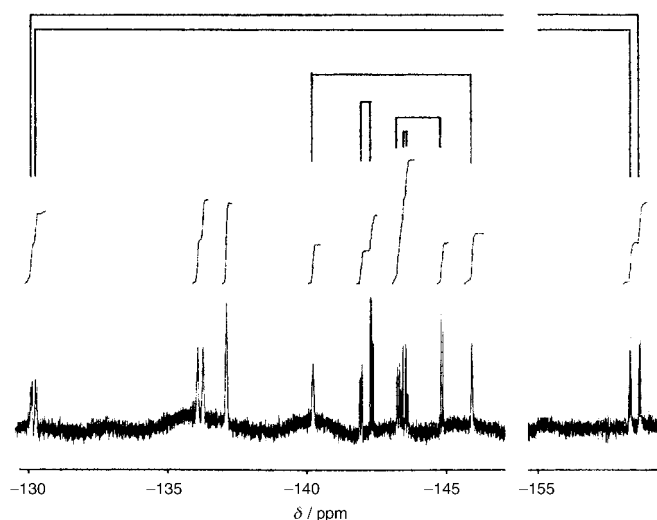


Figure 2. ^{19}F NMR spectrum of the $\text{C}_{60}\text{F}_{16}$:TTF adduct **A**.

$\delta = - (136 - 138)$ ppm region are due to fluorine atoms adjacent to the central benzenoid ring, but in the present instance two peaks (at $\delta = -140.25$ and -141.93 ppm) are shifted upfield due to the electron-releasing nature of the addend in **A** compared to $\text{C}_{60}\text{F}_{18}$ derivatives in which two fluorine atoms occupy the addend positions.

Previously we have determined the structure of $\text{C}_{60}\text{F}_{16}$ to be as shown on the Schlegel diagram in Figure 3, its formation

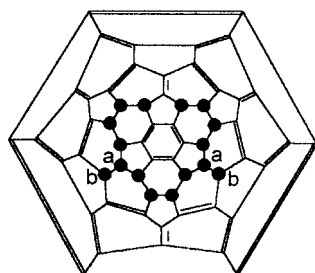


Figure 3. Schlegel diagram of the structure of $\text{C}_{60}\text{F}_{16}$.

being energetically favourable since $\text{C}_{60}\text{F}_{16}$, like $\text{C}_{60}\text{F}_{18}$, has a central fully delocalised hexagonal ring.^[3] We have confirmed that the $\text{C}_{60}\text{F}_{16}$ moiety in the adduct with TTF is that shown in Figure 3. It is characteristic of $\text{C}_{60}\text{F}_{18}$ and its derivatives, that fluorine peaks corresponding to those labelled a in Figure 3 are the most upfield in the spectrum and are coupled to b which are the most downfield; in $\text{C}_{60}\text{F}_{18}$ there are three such pairs but only two in $\text{C}_{60}\text{F}_{16}$. This pattern is evident in Figure 2, which confirms both that an a,b pair has been lost from the $\text{C}_{60}\text{F}_{18}$ precursor, and that the adduct is unsymmetrical.

The asymmetry is confirmed by the ^1H NMR spectrum (Figure 4), which shows two AB systems; one is clearly in the alkene region, $\delta = 6.46$ (d, 1H, $J = 6.6$ Hz), 6.37 (d, 1H, $J = 6.6$ Hz). Coupling constants (9.4 Hz) indicate that the other AB system is due to tertiary C–H hydrogen atoms that are exceptionally downfield due to the electron-withdrawing property of the adjacent cage: $\delta = 5.765$ (d, 1H, $J = 9.4$ Hz), 5.61 (d, 1H, $J = 9.4$ Hz). Thus addition does not take place across the central bond of TTF (analogous to addition to

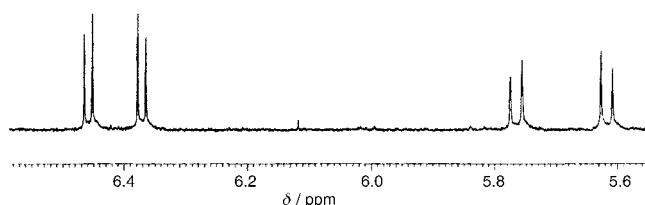


Figure 4. ^1H NMR spectrum of the $\text{C}_{60}\text{F}_{16}$:TTF adduct **A**.

tetra-alkoxyalkenes),^[4] but rather occurs at one of the 'terminal' double bonds to give the product shown in Figure 5, and the two upfield-shifted fluorine peaks noted above, are due to the fluorine atoms adjacent to the electron-supplying addend.

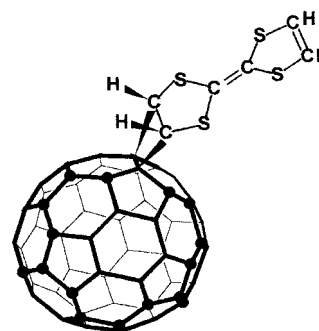
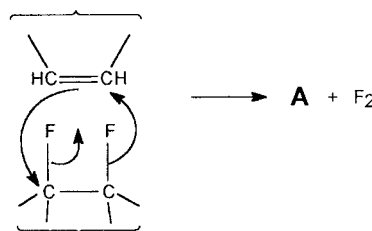


Figure 5. Structure of the $\text{C}_{60}\text{F}_{16}$:TTF adduct **A** (● = F).

This formation mechanism is unique and involves displacement of fluorine by the π electrons of one of the terminal double bonds in a six-electron process as shown in Scheme 1. Halogen loss from either C_{60}Cl_6 , C_{60}Br_6 or C_{60}Br_8 in the presence of TTF has been reported^[5] but derivatives were neither isolated nor characterised; both bromine and chlorine attached to fullerenes are much more labile than fluorine.



Scheme 1. Mechanism of formation of **A** from $\text{C}_{60}\text{F}_{18}$ and TTF.

Rearrangement of A into compounds B and C (retention times 30.3 and 48.6 min, respectively): A remarkable rearrangement of **A** occurred, but only when it was subjected to NMR spectroscopy. We were very puzzled by this observation but find now that it is triggered by the presence of CDCl_3 . Thus a sample left standing in toluene shows no rearrangement, but one to which CDCl_3 has been added does rearrange, the effect of this solvent being possibly to provide increased polarity necessary for the process. Additional peaks very slowly grow into the spectrum during acquisition of the signals

for **A** (which correspondingly diminish). The process was allowed to go to completion, the sample being then reprocessed by HPLC, which gave two new components **B** and **C**.

Both of the new derivatives, (**B**, minor, retention time 30.3 min) and (**C**, major, retention time 48.6 min) gave parent ions of 1082 amu in their identical mass spectra (e.g. Figure 6; inset shows the low mass region). This corresponds to

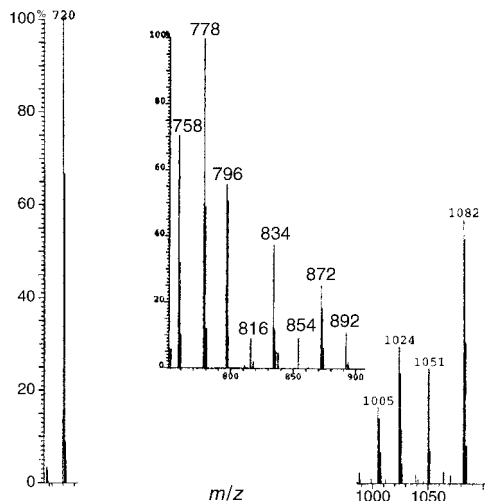


Figure 6. Mass spectrum (70 eV) for the products of **C** obtained from decomposition of the $C_{60}F_{16}$:TTF adduct **A**; **B** gave a similar spectrum.

$C_{60}F_{16}:[(CH)_2-S]$, and the spectrum shows fragment ions at m/z 1050 (loss of S), 1024 (loss of CH–CH), and in the low mass region a peak at 778 amu [$C_{60}:(SCH-CH)$] (loss of all of the fluorine atoms).

Compound **B** was too unstable for further analysis but **C** was shown to be structurally similar to **A** in being both an asymmetric compound and giving a 16-line ^{19}F NMR spectrum (Figure 7). The 2D spectrum showed that the two most

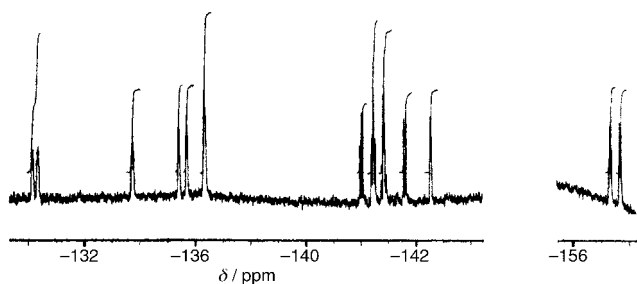
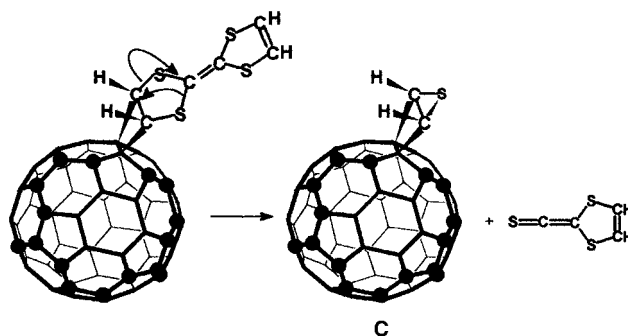


Figure 7. ^{19}F NMR spectrum of **C**.

upfield lines are coupled with the two most downfield lines, confirming the $C_{60}F_{16}$ motif, and the absence of one a and b type fluorine atom locates the sulfur-containing addend. The peaks were each about $\delta = 3$ ppm downfield from corresponding peaks in the precursor (except for the peak at $\delta_F = -140.25$ ppm which is shifted downfield by 6.4 ppm), and this confirms further the similar location of the addends in **A** and **C** (see Scheme 2). The large downfield shift of one of the peaks is consistent with a reduced interaction between one of



Scheme 2. Conjectured mechanism for the elimination of a thioketene moiety from $C_{60}F_{16}$: TTF **A** to give derivative **C**.

the fluorine atoms and the sulfur atom that was adjacent to it in **A**.

The 1H NMR spectrum shows two doublets at $\delta = 5.99$ and 5.82 ppm ($J = 11.1$ Hz), consistent with the proposed structure (Scheme 2); these peaks are slightly downfield from those for the corresponding hydrogen atoms in **A**.

The elimination is driven presumably by reduction in the eclipsing strain between S and F in the cycloaddend. Alternative structures can be conjectured, but all are unsatisfactory, for example formation of the isomeric thiophenofullerene is ruled out because it would have C_s symmetry, and the frontside substitution of C on the cage by S, required for its formation, should not be possible. Likewise, a mechanism involving attack of a (remote) sulfur atom on the localised double bond in the tetra-addended hexagonal ring may also be ruled out; it would lead to 1,4-addition of $-CH=CH-S-$, producing a very strained structure and location of a double bond in an unaddended pentagonal ring, which is energetically unfavourable.

We rule out also a process in which either one or two fluorine atoms undergo consecutive 1,3-shifts (discovered recently in $C_{10}C_{60}F_{36}$).^[6] This would lead to structures (Figure 8) with either two or three fluorine atoms having only one

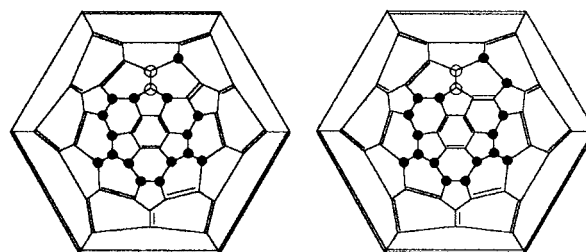
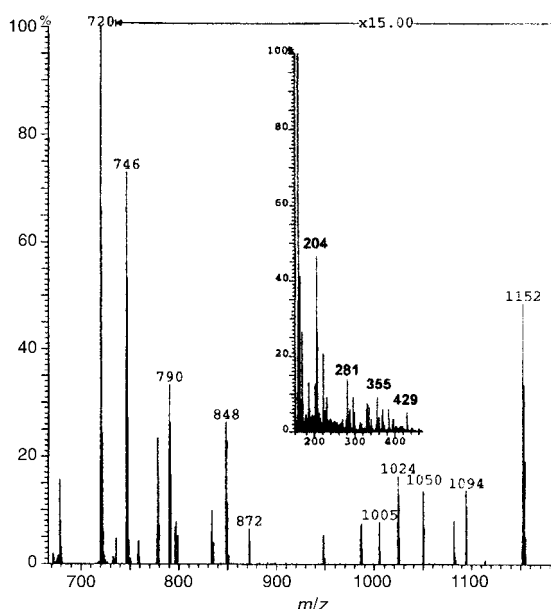


Figure 8. Structure that would result from consecutive 1,3-shifts of fluorine; ● = F, ○ = sites of $-CH=CH-S-$ addend

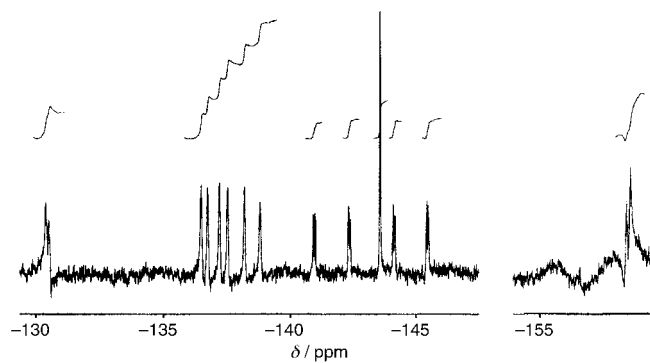
sp^3 -carbon atom neighbour, which would then appear well downfield, as for b-type fluorine atoms. The second migration would lose the aromaticity of the central ring since it would then lack the sextet of surrounding sp^3 -carbon atoms.

Characterisation of compound D (retention time 21 min): The mass spectrum (Figure 9) for this compound shows a parent ion at 1152 amu with fragmentation ions at 1094, 1050 and 1024 amu, the latter again being $C_{60}F_{16}$. These correspond to

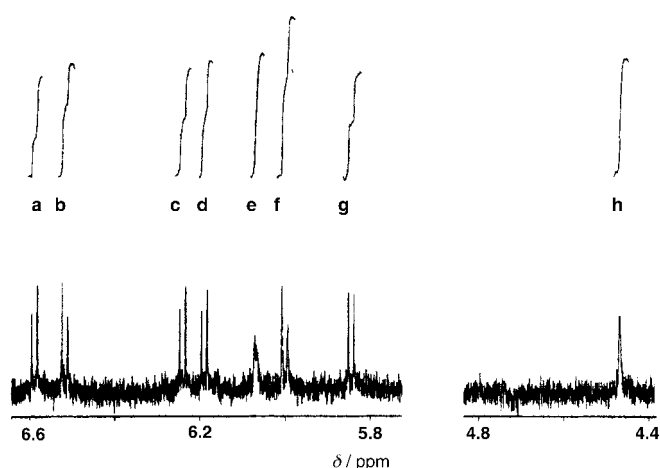
Figure 9. EI mass spectrum (70 eV) for **D**.

loss of fragments of 58, 44 and 26 amu (128 amu total). The identical fragmentation pattern (ions at 848, 790, 746 and 720 amu) is seen in the spectrum after total fluorine loss. The fragments can only be $-S-CH-CH-$, $-C(S)-$, and $-CH-CH-$. Thus in order to produce this derivative, the TTF adduct has eliminated carbon disulfide. The spectrum also shows a peak of 204 amu (TTF) indicating (confirmed below) that a second TTF molecule has also cycloadded to the cage, and is cleaved under EI mass spectrometry conditions.

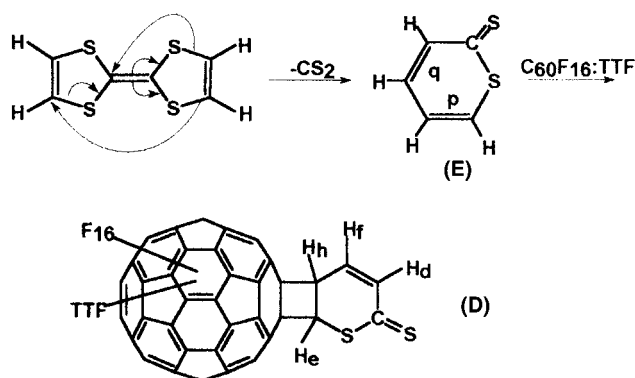
The ^{19}F NMR spectrum (Figure 10) shows sixteen fluorine atoms, and has the usual pattern of the two most downfield peaks being coupled to the two most upfield ones (confirmed by a 2D ^{19}F NMR spectrum), and thus addition again involves loss of an a- and b-type fluorine atom.

Figure 10. ^{19}F NMR spectrum of **D**.

The ^1H NMR spectrum (Figure 11) shows eight lines a–h. Decoupling experiments showed that H_a is coupled to H_b , and H_c is coupled to H_e but these pairs are neither coupled to each other nor to any other hydrogen atoms. They are assigned to the TTF addend, and show similar shift characteristics to those of the four hydrogen atoms in $\text{C}_{60}\text{F}_{16}:\text{TTF}$ (**A**). 'Roofing' showed H_d to be coupled with H_f , and decoupling showed also

Figure 11. ^1H NMR spectrum of **D**.

that H_h is coupled to both H_f and to H_e . Together with the MS fragmentation data, these data show that the second addend is an unsaturated dithiolactone, **E** (Scheme 3), produced by elimination of CS_2 from TTF. The ready formation of **E** is due to it having substantial aromaticity. In **E**, the π density of one

Scheme 3. Cycloaddition of a dithiolactone intermediate **E**, formed through loss of carbon disulfide from tetrathiofulvalene.

of the double bonds (p ; in Scheme 3) is enhanced through coordination with sulfur, whilst in the other (q) it is reduced through conjugation with the $>\text{C}=\text{S}$ group; the former double bond is thus the one which undergoes [2+2] cycloaddition with the fullerene cage. In the ^1H NMR spectrum, H_e is shifted downfield compared to H_h due to electronegativity of the adjacent sulfur atom, and H_d is likewise downfield relative to H_f due to the adjacent $\text{C}=\text{S}$ group.

One addend, presumably the TTF moiety, has occupied the a and b positions in the $\text{C}_{60}\text{F}_{18}$ precursor, and the dithiolactone **E** has added onto the curved non-fluorinated surface of **A**. Although the MS fragmentation pattern is different from that observed with **A** in that the TTF addend cannot be seen, it is evident as a fragment ion (204 amu) in the low mass region of the spectrum (inset to Figure 9). However, we cannot totally discount the alternative possibility that **E** has, through addition, displaced the a- and b-type fluorine atoms, whilst TTF has added elsewhere to the cage.

Conclusion

Overall this work provides yet further examples of the unusual structures that are produced on reaction with fullerene cages, exacerbated in the present case by the presence of fluorine atoms.

Experimental Section

Reagents: Tetrathiofulvalene was supplied by Aldrich, and C₆₀F₁₈ preparation has been described.^[2] Mass spectra (EI) were run at 70 eV, ¹H and ¹⁹F NMR spectra at 500 and 376.4 MHz, respectively.

Reaction of C₆₀F₁₈ with tetrathiofulvalene: An initial experiment was performed by heating a mixture of C₆₀F₁₈ (3.0 mg, 2.8 × 10⁻³ mmol) and tetrathiofulvalene (TTF, 1.2 mg, 5.6 × 10⁻³ mmol) in toluene (5 mL, HPLC grade), which was then evaporated to dryness on a rotavapor (reduced pressure, 40 °C) to give a deep brown solid. Monitoring of the reaction by HPLC, using a 10 × 250 mm Cosmosil Buckyprep column with elution by toluene at 4.7 mL min⁻¹, showed that the reaction occurred almost entirely during this evaporation procedure. HPLC purification of this material gave, apart from recovered reagents, peaks with retention times (Cosmosil 5 PYE column, toluene elution at 4 mL min⁻¹) of 18.5 min (**A**, major) and 21 min (**D**, minor). The result was replicated a number of times, with recovered unreacted C₆₀F₁₈ being recycled. Increasing the amount of TTF did not reduce the amount of unused C₆₀F₁₈, and the yield was not altered if the mixture was heated under reflux for 5 h before evaporation to dryness, probably because this induced a retro-addition. A solution of **A** in toluene, in the presence of CDCl₃, slowly rearranged; HPLC of the product obtained after about four days yielded two components **B** (minor) and **C** (major) with retention times of 30.3 and 48.6 min, respectively.

NMR spectroscopy

¹⁹F NMR spectrum of A: δ_F = -130.11 (d, 1F, J = 18.6 Hz), -130.30 (d, 1F, J = 18.7 Hz), -136.11 (d, 1F, J = 9.2 Hz), -136.28 (d, 1F, J = 8.4 Hz), -137.12 (m, 2F), -140.25 (m, 1F), -141.93 (dd, 1F, J = 17.3 and 29.4 Hz), -142.32 (dd, 1F, J = 16.1 and 29.4 Hz), -143.3 (dd, 1F, J = 4.7 and 21 Hz), -143.44 (dd, 1F, J = 4.2 and 7.6 Hz), -143.55 (dd, 1F, J = 4.0 and 7.4 Hz), -144.87 (dd, 1F, J = 6.4 and 21.3 Hz), -145.93 (m, 1F, J = 6.2 and 12.9 Hz), -158.34 (m, 1F, J = 9.6 and 18.7 Hz), -158.68 (m, 1F, J = 9.4 and 18.9 Hz).

¹⁹F NMR spectrum of C: δ_F = -130.2, (d, 1F, J = 19 Hz), -130.4 (d, 1F, J = 19 Hz), -133.8 (m, 1F, J = 7 Hz), -135.47 (m, 1F), -135.76 (m, 1F), -136.4 (m, 2F), -142.08 (dd, 1F, J = 10 and 19 Hz), -142.5 (m, 2F), -142.9 (m, 2F), -143.66 (dd, 1F, J = 6 and 27 Hz), -144.6 (m, 1F, J = 6 Hz), -157.4, (df, 1F, J = 10 Hz), -157.7 (dt, 1F, J = 10 Hz).

¹⁹F NMR spectrum of D: δ_F = -130.38 (d, 1F), -130.51 (d, 1F), -136.49 (br s, 1F), -136.74 (br s, 1F), -137.21 (br s, 1F), -137.54 (br s, 1F), -138.21 (br s, 1F), -138.82 (br s, 1F), -140.93 (dd, 1F, J = 28.0 and 15.9 Hz), -142.38 (d, 1F, J = 24 Hz), -143.61 (coincident, 2F), -144.17 (d, J = 28 Hz), -145.48 (dd, 1F, J = 27.4 and 10.5 Hz), -158.36 (m, 1F, J = 9.3 Hz), -158.52 (m, 1F, J = 9.5 Hz).

¹H NMR spectrum of D: δ = 6.590 (d, 1H, J = 6.54 Hz; H_a), 6.519 (d, 1H, J = 6.51 Hz; H_b), 6.242 (d, 1H, J = 6.66 Hz; H_c), 6.190 (d, 1H, J = 6.57 Hz; H_d), 6.07 (m, 1H; H_e), 6.002 (dd, 1H, J = 6.64 and 0.9 Hz; H_f), 5.845 (d, 1H, J = 6.68 Hz; H_g), 4.47 (m, 1H; H_h).

Acknowledgement

This work was supported by a Joint Project Grant from the Royal Society, the EPSRC, and the EU TMR USEFULL contract (FMRX-CT970126).

- [1] K. B. Simonsen, V. K. Konovalov, T. A. Konovalova, T. Kawai, M. P. Cava, L. D. Kispert, R. M. Metzger, J. Becher, *J. Chem. Soc. Perkin Trans. 2* **1999**, 657–665; D. M. Guldi, S. González, N. Martin, A. Antón, J. Garín, J. Orduna, *J. Org. Chem.* **2000**, 65, 1978–1983; J. L. Segura, E. M. Priego, N. Martin, *Tetrahedron Lett.* **2000**, 41, 7737–7741; R. Lipiec, A. Graja, P. Hudhomme, S.-G. Liu, A. Gorgues, *Synth. Metals* **2000**, 109, 67–72.
- [2] O. V. Boltalina, V. Yu. Markov, R. Taylor, M. P. Waugh, *Chem. Commun.* **1996**, 2549–2551.
- [3] A. G. Avent, O. V. Boltalina, A. Yu. Lukonin, J. M. Street, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **2000**, 1359–1363.
- [4] X. Zhang, A. Fan, C. S. Foote, *J. Org. Chem.* **1996**, 61, 5456–5461.
- [5] Y. Yoshida, A. Otsuka, O. O. Drozdova, G. Saito, *J. Am. Chem. Soc.* **2000**, 122, 7244–7251.
- [6] A. G. Avent, R. Taylor, *Chem. Commun.* **2002**, 2726–2727.

Received: November 4, 2002 [F4549]