Direct syntheses of pentakis(trifluoromethyl)cyclopentadienide salts and related systems[1]

Richard D. Chambers, Alex J. Roche, and Julian F.S. Vaughan

Abstract: The well-established synthesis of heptafluorobut-2-ene **2** from hexachlorobutadiene **1** and potassium fluoride has been further investigated, and novel dienes **3** and a triene **4** have been observed. Remarkably, the potassium salt of pentakis(trifluoromethyl)cyclopentadienide **7** has been isolated from this system. Salt **7** has also been obtained directly from **2**. Cyclopentadiene **6** has been isolated from salt **7** by distillation from sulphuric acid. Bi- and tri-cyclic analogues of **7** have also been obtained, i.e., **9** and **10**, by reaction of **2** with perfluorocyclopentene.

Key words: heptafluorobut-2-ene, pentakis(trifluoromethyl)cyclopentadienide, 5*H*-pentakis(trifluoromethyl)cyclopentadiene.

Résumé : On a étudié à nouveau la synthèse bien connue de l'heptafluorobut-2-ène **2** à partir de l'hexachlorobutadiène **1** et du fluorure de potassium; on a observé la formation de nouveaux dienes **3** et d'un triène **4**. D'une façon remarquable, on a isolé de ce système le pentakis(trifluorométhyl)cyclopentadiénure de potassium **7**. Par distillation du sel **7** en présence d'acide sulfurique, on a isolé le cyclopentadiène **6** à partir du sel **7**. La réaction du composé **2** avec le perfluorocyclopentène a permis aussi d'obtenir les analogues bi- **9** et tricycliques **10** du composé **7**.

Mots clés : heptafluorobut-2-ene, pentakis(trifluorométhyl)cyclopentadiénure, 5*H*-pentakis(trifluorométhyl)cyclopentadiène.

[Traduit par la rédaction]

There is a wide interest in methodology for the introduction of trifluoromethyl and other perfluoroalkyl groups into organic compounds (2), and we are concerned with the alkene (*Z*)-2*H*-heptafluorobut-2-ene **2** as a potential "building block" for this purpose. This F-alkene is especially significant because it can be obtained directly from hexachloro-1,3-butadiene **1**, by simple displacement using potassium fluoride in an aprotic solvent. This synthesis was described in 1963 by Maynard (3), from the du Pont Co., and has subsequently been used by other workers, including this laboratory (4). However, in recent further investigation of this reaction, we have discovered some remarkable new products.

The overall procedure involves heating hexachloro-1,3-butadiene **1** with anhydrous potassium fluoride in an aprotic solvent; Maynard (3) described *N*-methyl-2-pyrrolidinone and we have found that sulpholan is very satisfactory (4). The products vary significantly with reaction conditions, and we have now identified and separated from **2** two interesting new fluorinated dienes **3a** and **3b**, and even a triene **4**. These compounds were separated by fractional distillation and the stereochemistry of the major diene isomer **3a** follows from ^{19}F NMR coupling constant data, since it is known that ^{5}J(*cis*-CF_3,CF_3) values are greater than 10 Hz, ^{5}J(*trans*-CF_3,CF_3) values are typically less than 2 Hz, and ^{4}J(*trans*-CF_3,F) coupling constants are less than for ^{4}J(*cis*-CF_3,F) (5), as shown in Fig. 1. In contrast, we were unable to deduce the structure of the minor isomer **3b** (see experimental section) because the splitting in the ^{19}F NMR spectrum was insufficiently resolved.

The mechanism of formation of the dienes **3a** and **3b**, and the triene **4** is outlined in Scheme 1, arising from fluoride ion initiated oligomerization of **2**, and other evidence for this process stems from the fact that these compounds may also be obtained directly from **2** by heating with fluoride ion in a sealed system.

We have also examined the filtered sulpholan residue from the preparation of **2**, and, remarkably, the ^{19}F NMR spectrum showed only one sharp resonance at $\delta_F = -50$ ppm! It is unlikely that we would have been able to identify this component from this unusual signal, except for the fact that we had already synthesized various salts of the pentakis(trifluoromethyl)cyclopentadienide (6), and these had given similar ^{19}F NMR signals. FAB mass spectroscopy confirmed the presence of potassium (*m/z* 39 (100%), in the positive ion spectrum), and showed only a *m/z* 405 (100%) peak in the negative ion spectrum, which is consistent with **7**. Thus we had obtained potassium pentakis(trifluoromethyl)cyclopentadienide **7** in one step from hexachloro-1,3-butadiene and potassium fluoride! This is amusing to those of us who were seeking syntheses of **7** because, in our own laboratory, it is clear that we have been disposing of samples of **7** with the residue, following the synthesis of **2**!

5*H*-Pentakis(trifluoromethyl)cyclopentadiene (**6**) has been

Received November 14, 1995.

This paper is dedicated to Professor Howard C. Clark in recognition of his contributions to Canadian chemistry.

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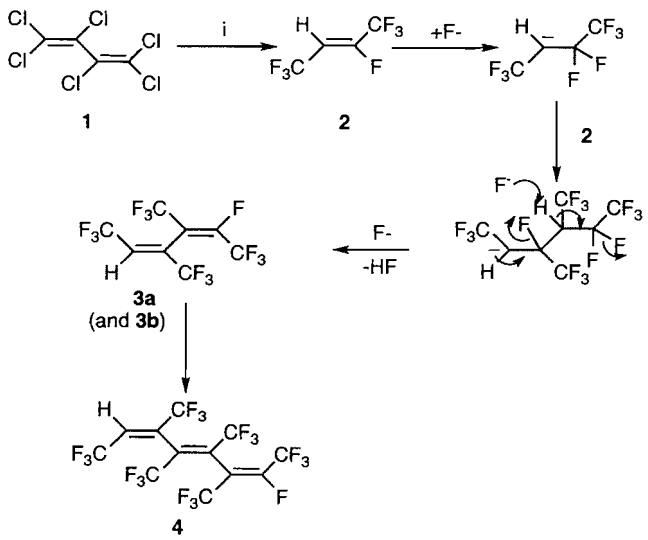
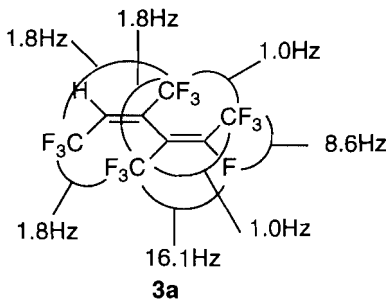
Scheme 1.

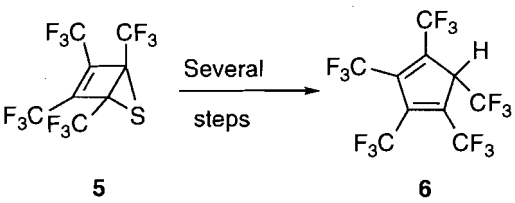


Reagents and conditions: i, KF, sulpholan, 190°C.

Fig. 1. ^{19}F NMR coupling constant data.



Scheme 2.



described by Laganis and Lemal (7) in several steps, starting with a valence isomer of tetrakis(trifluoromethyl)thiophene (**5**) (Scheme 2), and they also showed that **6** is a very strong acid ($pK_a \leq -2$). However, we have now been able to isolate and characterize the acidic diene **6** by distillation from the sulpholan residue, after the addition of concentrated sulphuric acid.

The mechanism of formation of **7** is probably that outlined in Scheme 3, essentially derived from **2**. The cyclization step to give **6** is extremely interesting because, as a *5-endo-trig* process, it is formally "disallowed" by the Baldwin rules (8). It seems more appropriate, therefore, to regard the process as an initial electrocyclic ring closure, to give **6**, followed by elimination of the acidic proton by fluoride ion, now acting as a base. In confirmation of this mechanism, we have also shown that **7** can be obtained by reaction of **2** with caesium fluoride in sulpholan in a sealed tube. Again this is a direct route to **7** from easily accessible starting materials.

Furthermore, a variety of salts may be obtained by reaction of an aqueous solution of the appropriate halide with the acidic diene **6** (Scheme 4). Single crystal X-ray structural analyses of tetraalkylammonium salts of **7** confirmed the product structure. However, rotation within the crystal, even at low temperatures, prevents a precise determination of bond lengths and angles.

The results described above pointed the way to a synthesis of a variety of more complex fluorocarbon salts. For example, we have shown that reaction of fluoride ion with **2** in the presence of perfluorocyclopentene **8** gave a mixture of two novel salts **9** and **10**, while the diene **3** in the presence of **8** with fluoride ion gave only **9**. These compounds were characterized by ^{19}F NMR and FAB mass spectrometry, which is a particularly valuable tool with these and related systems. However, attempts to obtain the corresponding dienes from **9** and **10**, by distillation from concentrated sulphuric acid, has, so far, led to products too complex to separate, although GLCMS revealed the presence of the desired dienes, but accompanied by other unidentified products.

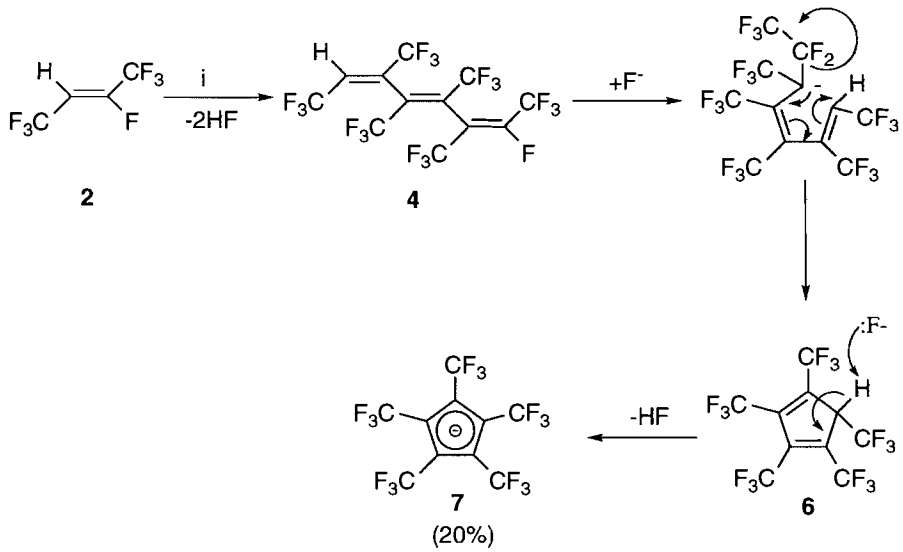
Experimental

^1H NMR spectra were recorded on a Bruker AC250 spectrometer operating at 250.13 MHz, a Varian Gemini VXR200 spectrometer operating at 199.98 MHz, or a Varian VXR400S spectrometer operating at 399.96 MHz. ^{19}F NMR spectra were recorded on the Bruker AC250 spectrometer operating at 235.34 MHz or on the Varian VXR400S spectrometer operating at 376.29 MHz. ^{13}C spectra were recorded on the Varian VXR400S spectrometer operating at 100.58 MHz, or the Varian Gemini VXR200 spectrometer operating at 50.29 MHz. All spectra were recorded with TMS and fluorotrichloromethane as internal references. The *J* values are given in Hz. GLCMS mass spectra were recorded on a Fisons Trio 1000 spectrometer linked to a Hewlett Packard 5890 series II gas chromatograph fitted with a 20 m cross-linked methyl silicone capillary column. All GLCMS mass spectra were generated by electron impact. FAB mass spectra were recorded using a VG7070E spectrometer, and glycerol as a solvent. FTIR spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer. Solid samples were run as KBr discs, liquid samples were run as thin films between KBr plates, and volatile samples were run in a gas cell fitted with KBr plates.

Reaction of 1 with potassium fluoride

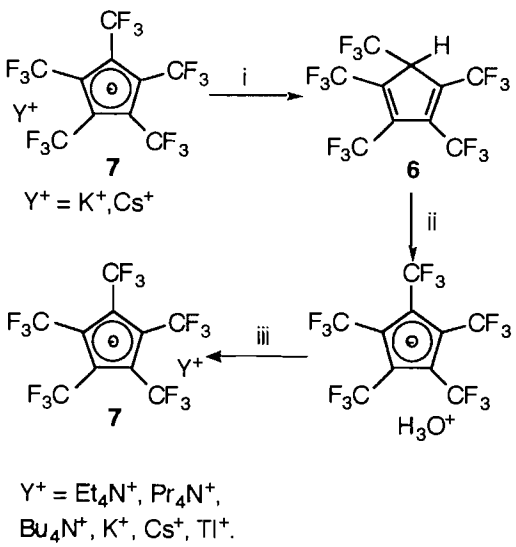
The method used was essentially that used by Maynard (3), using hexachlorobuta-1,3-diene **1** (334 g, 1.3 mol), potassium fluoride (600 g, 10.2 mol), and sulpholan (2 L). The volatile products were collected at liquid air temperatures, and fractional distillation gave (Z)-2H-*heptafluorobut-2-ene* **2** (105.1 g, 45%); bp 7–8°C (lit. (3) bp, 7–10°C); ν_{max}/cm^{-1}: 1220, 1310; δ_H(250 MHz; $CDCl_3$): 5.45 (dq, *J* 28.3 and 5.3, C*H*); δ_F(235 MHz; $CDCl_3$): −61.6 (3 F, s, CF_3CH), −76.2 (3 F, s, CF_3CF), −119.9 (1 F, s, C*F*); δ_C(100 MHz; $CDCl_3$):

Scheme 3.



Reagents and conditions: i, CsF, sulpholan, 190 °C.

Scheme 4.



Reagents and conditions: i, 98% H_2SO_4; ii, H_2O; iii, Y-Hal.

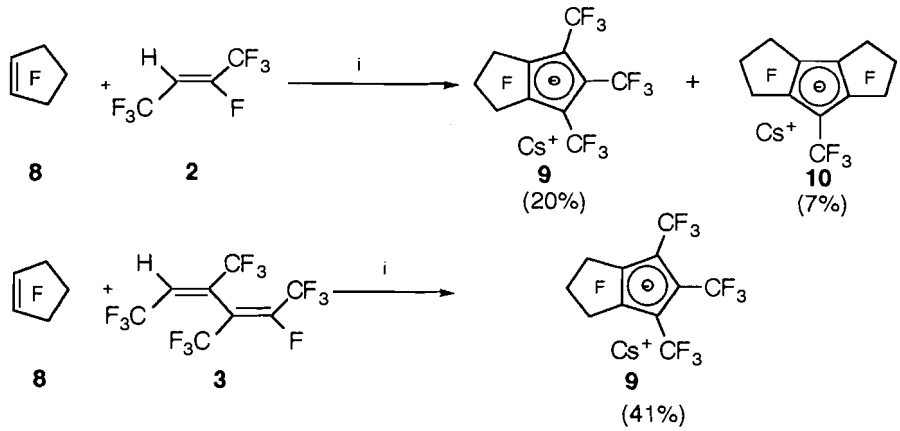
101.3 (q, *J* 39.1, *C*H), 116.2 (qd, *J* 272.5 and 38.3, CF_3CF), 119.5 (q, *J* 269.5, CF_3CH), 150.8 (dqq, *J* 283.3, 41.2 and 5.9, $CFCF_3$); *m/z* 182 (M^+, 23%), 163 (54), 113 (90), 69 (100).

A higher boiling fraction (bp 78–80°C) was shown by GLCMS to contain three components, and preparative scale GLC (SE30/40°C) produced a 4:1 mixture of two isomers of *5H-perfluoro-3,4-bis(trifluoromethyl)hexa-2,4-diene* ***3a*** and ***b*** (13.2 g, 6%). For the diene mixture (Anal. calcd. for C_8HF_{13}: C 28.0, H 0.3%; found: C 28.0, H 0.2%); $\lambda_{max}(CH_3CN)$/nm: 295; ε/dm^3 mol^{-1} nm^{-1}: 1148; ν_{max}/cm^{-1}: 1400, 1300–1200. The major isomer was confirmed as the (*Z, E*) isomer (**3a**). δ_H(250 MHz; $CDCl_3$): 6.68 (q, *J* 6.3, C*H*); δ_F(235 MHz; $CDCl_3$): −60.8 (3 F, dqq, *J* 16.1, 1.8, 1.0, CF_3C-3), −62.3 (3 F, sept, *J* 1.8, CF_3C-4), −68.7 (3 F, m, *J* 1.8, 6-CF_3), −70.4 (3 F, dsept, *J* 8.6 and 1.0, 1-CF_3), −105.0 (1 F, qq, *J* 16.1 and 8.6, C*F*); *m/z*: 343 (M^+ − 1, 21%), 293 (100), 243 (98), 69 (50). The stereochemistry of the minor isomer **3b** has not been confirmed as yet; δ_H(250 MHz; $CDCl_3$): 6.41 (q, *J* 6.7, C*H*); δ_F(235 MHz; $CDCl_3$): −56.7 (3 F, s, CF_3C-3), −62.1 (3 F, s, CF_3C-4), −64.6 (3 F, s, 1-CF_3), −68.3 (3 F, s, 6-CF_3), −101.8 (1 F, s, C*F*); *m/z*: 343 (M^+ − 1, 20%), 293 (50), 69 (100). In the original diene distillate there was a component (1% by GLCMS) identified as *7H-perfluoro-3,4,5,6-tetra(trifluoromethyl)octa-2,4,6-triene* ***4***; *m/z*: 505 (M^+ − 1, 2%), 467 (33), 321 (66), 69 (100). The residual sulpholan solution was shown to contain *potassium pentakis(trifluoromethyl)cyclopentadienide* (***7***) (12.9 mmol, 3%) (by ^{19}F NMR integrated against an internal standard of 1,1,1-trifluorotoluene); δ_F(235 MHz; $CDCl_3$): −49.8 (s, CF_3); FAB+ *m/z*: 39 (M^+, 100%), FAB− *m/z*: 405 (M^+, 100%).

The residual sulpholan solution was filtered and 98% sulphuric acid (750 mL, 14.1 mol) was added dropwise under reduced pressure. Volatile products were collected at liquid air temperatures, and were shown by GLCMS to contain one compound identified as *5H-pentakis(trifluoromethyl)cyclopentadiene* (***6***) (4.5 g, 86%); ν_{max}/cm^{-1}: 2977, 1664, 1450–1000; δ_H(250 MHz; $CDCl_3$): 4.80 (q, *J* 5.6, C*H*); δ_F(235 MHz; $CDCl_3$): −57.1 (6 F, s, 2-CCF_3), −60.2 (3 F, s, 5-CCF_3), −60.9 (6 F, s, 1-CCF_3); δ_C(100 MHz; $CDCl_3$): 58.4 (q, *J* 32.1, C-5), 119.2 (q, *J* 275.1, CF_3C-5), 120.2 (q, *J* 272.4, CF_3C-1), 122.6 (q, *J* 284.1, CF_3C-1) 139.7 (q, *J* 40.4, C-1), 139.8 (q, *J* 40.3, C-2); *m/z*: 406 (M^+, 2%), 69 (100).

H_2O (100 mL) was added to **6**, producing *hydronium pentakis(trifluoromethyl)cyclopentadienide* (11.1 mmol, quant.); δ_F(235 MHz; D_2O): −51.4 (s, CF_3). On addition of aqueous tetraethylammonium iodide (15.9 g, 64.4 mmol), a precipitate formed, which was recrystallized (diethyl ether – hexane), giving colourless crystals identified as *tetraethylammonium pentakis(trifluoromethyl)cyclopentadienide* (5.7 g, 83% from

Scheme 5.



Reagents and conditions: i, sulpholan, CsF, 110°C.

Table 1. Formation of salts of anion **7**.

Salt used	Product	Yield (%)
Et_4NI	Et_4N^+ $C_5(CF_3)_5^-$	83
Et_4NBr	Et_4N^+ $C_5(CF_3)_5^-$	80
Pr_4NI	Pr_4N^+ $C_5(CF_3)_5^-$	80
Bu_4NI	Bu_4N^+ $C_5(CF_3)_5^-$	86
KI	K^+ $C_5(CF_3)_5^-$	15[a]
CsF	Cs^+ $C_5(CF_3)_5^-$	12[a]
$Tl(CH_3CO_2)$	Tl^+ $C_5(CF_3)_5^-$	15[a]

[a]Products were continuously extracted (dichloromethane) due to some solubility of these products in water, and this resulted in lower yields.

potassium pentakis(trifluoromethyl)cyclopentadienide); mp 241°C (dec.); ν_{max}/cm^{-1}: 3050, 1200, 1150; δ_H(250 MHz; $CDCl_3$): 1.42 (3 H, tt, *J* 7.2 and 1.9, CH_3), 3.51 (2 H, q, *J* 7.2, CH_2); δ_C(100 MHz; $CDCl_3$): 15.7 (s, CH_3), 53.1 (t, *J* 2.6, CH_2), 110.2 (q, *J* 19.2, CCF_3), 124.7 (q, *J* 271.3, CF_3); δ_F(235 MHz; $CDCl_3$): −50.9 (s, CF_3); FAB+ *m/z*: 130 (M^+, 100%); FAB− *m/z*: 405 (M^+, 100%). Anal. calcd. for $C_{18}H_{20}F_{15}N$: C 40.4, H 3.7, N 2.6%; found: C 40.1, H 3.9, N 2.9%.

General procedure for salt formation

As above, an aqueous solution of the desired halide salt (typically 500% excess) was added to the aqueous hydronium pentakis(trifluoromethyl)cyclopentadienide solution. This mixture was stirred for 1 h, before extraction (dichloromethane) and recrystallization (ether–hexane).

Tetrapropylammonium pentakis(trifluoromethyl)cyclopentadienide: mp 141–142°C; ν_{max}/cm^{-1}: 3100, 1350, 1225; δ_H(250 MHz; $CDCl_3$): 0.96 (3 H, t, *J* 7.2, CH_3), 1.70 (2 H, sext, *J* 7.2, CH_3CH_2), 3.01 (2 H, m, NCH_2); δ_C(100 MHz; $CDCl_3$): 15.3 (s, CH_3), 31.0 (s, CH_3CH_2), 55.2 (s, NCH_2), 110.1 (q, *J* 19.0, CCF_3), 123.3 (q, *J* 270.5, CF_3); δ_F(235 MHz; $CDCl_3$): −50.9 (s, CF_3); FAB+ *m/z*: 186 (M^+, 100%); FAB− *m/z*: 405 (M^+, 75%), 91 (solvent, 100). Anal. calcd. for $C_{22}H_{28}F_{15}N$: C 44.7, H 4.7, N 2.4%; found: C 44.8, H 4.6, N 2.4%.

Tetrabutylammonium pentakis(trifluoromethyl)cyclopentadienide: mp 118–119°C; ν_{max}/cm^{-1}: 3050, 1500, 1225, 1150; δ_H(250 MHz; $CDCl_3$): 0.95 (3 H, t, *J* 7.2, CH_3), 1.33 (2 H, sext, *J* 7.2, CH_3CH_2), 1.60 (2 H, pent, *J* 7.2, NCH_2CH_2), 3.11 (2 H, m, NCH_2); δ_C(100 MHz; $CDCl_3$): 13.1 (s, CH_3), 19.2 (s, CH_3CH_2), 23.4 (s, NCH_2CH_2), 58.5 (s, NCH_2), 109.6 (q, *J* 18.5, CCF_3), 123.7 (q, *J* 269.9, CF_3); δ_F(235 MHz; $CDCl_3$): −50.1 (s, CF_3); FAB+ *m/z*: 242 (M^+, 100%); FAB− *m/z*: 405 (M^+, 100%). Anal. calcd. for $C_{26}H_{36}F_{15}N$: C 48.2, H 5.6, N 2.2%; found: C 48.2, H 5.7, N 2.0%.

Potassium pentakis(trifluoromethyl)cyclopentadienide: mp >330°C; ν_{max}/cm^{-1}: 1500, 1200, 1050; δ_F(235 MHz; $CDCl_3$): −49.8 (s, CF_3); FAB+ *m/z*: 39 (M^+, 100%); FAB− *m/z*: 405 (M^+, 100%). Anal. calcd. for $KC_{10}F_{15}$: C 27.0%; found: C 27.1%.

Caesium pentakis(trifluoromethyl)cyclopentadienide: mp >330°C; ν_{max}/cm^{-1}: 1500, 1250, 1100; δ_F(235 MHz; $CDCl_3$): −49.9 (s, CF_3); FAB+ *m/z*: 133 (M^+, 100%); FAB− *m/z*: 405 (M^+, 100%). Anal. calcd. for $CsC_{10}F_{15}$: C 22.3%; found: C 22.3%.

Thallium pentakis(trifluoromethyl)cyclopentadienide: mp >330°C; ν_{max}/cm^{-1}: 1450, 1200, 1100; δ_F(235 MHz; $CDCl_3$): −49.8(s, CF_3); FAB+ *m/z*: 93 (solvent, 100%), 205 (M^+, 41%); FAB− *m/z*: 405 (M^+, 100%). Anal. calcd. for $TlC_{10}F_{15}$: C 19.7%; found: C 19.6%.

CsF and ***2*** *in a sealed system*

A Carius tube containing **2** (1.18 g, 4.68 mmol), caesium fluoride (6.00 g, 39.47 mmol), and sulpholan (10 mL) was heated and rotated at 190°C for 3 days. Volatiles were removed under reduced pressure, and the sulpholan residue was shown by ^{19}F NMR (integrated against an internal standard of 1,1,1-trifluorotoluene) and FAB mass spectrometry to contain *caesium pentakis(trifluoromethyl)cyclopentadienide* (0.28 mmol, 13%), as above.

Synthesis of ***9*** *and* ***10***

A Carius tube containing **2** (0.7 g, 3.8 mmol), perfluorocyclohexene **8** (1.04 g, 4.9 mmol), caesium fluoride (2.00 g, 13.2

mmol), and sulpholan (20 mL) was heated and rotated at 110°C for 5 days. Volatiles were removed under reduced pressure, and the sulpholan residue was shown by ^{19}F NMR (integrated against an internal standard of 1,1,1 trifluorotoluene) and FAB mass spectrometry to contain *caesium perfluoro-1,2,3-trihydro-4,5,6-trimethylpentalenide* **9** (0.4 mmol, 20%); δ_F(235 MHz; $CDCl_3$): −49.7 (3 F, s, 5-CCF_3), −52.5 (6 F, s, 4-CCF_3), −97.7 (4 F, s, 1-CF_2), −121.1 (2 F, s, 2-CF_2); FAB+ *m/z*: 133 (M^+, 100%); FAB− *m/z*: 417 (M^+, 100%); and *caesium perfluoro-1-methyl-2,3,4,5,6,7-hexahydrodicyclopenta[*b,d*]cyclopentadienide* **10** (0.2 mmol, 7%); δ_F(235 MHz; $CDCl_3$): −54.4 (3 F, s, CF_3), −98.4 (4 F, s, 2-CF_2), −100.1 (4 F, s, 4-CF_2), −122.2 (4 F, s, 3-CF_2); FAB+ *m/z*: 133 (M^+, 100%), FAB− *m/z*: 429 (M^+, 29%), 395 (100).

Synthesis of ***9***

A Carius tube containing perfluorocyclohexene **8** (1.04 g, 4.9 mmol), caesium fluoride (2.00 g,13.2 mmol), (*Z,E*) and (*Z,Z*)-5*H*-perfluoro-3,4-dimethyl-2,4-diene **3** (1.6 g, 4.7 mmol), and sulpholan (20 mL) was heated and rotated at 110°C for 5 days. The volatiles were removed under reduced pressure, and the sulpholan residue was shown by ^{19}F NMR (integrated against an internal standard of 1,1,1 trifluorotoluene) and FAB mass spectrometry to contain *caesium perfluoro-1-methyl-2,3,4,5,6,7-hexahydrodicyclopenta*[b,d]*cyclo-pentadienide* **9** (1.9 mmol, 41%), as above.

Attempted protonation of ***9*** *and* ***10***

Sulphuric acid (98%, 50 mL) was added dropwise to a sulpholan (20 mL) solution containing caesium perfluoro-1,2,3-trihydro-4,5,6-trimethylpentalenide **9** (0.98 mmol) and caesium perfluoro-1-methyl-2,3,4,5,6,7-hexahydrodicyclopenta-[*b,d*]cyclopentadienide **10** (0.34 mmol) under reduced pressure. Volatile products were collected in a trap maintained at liquid air temperatures, and were shown by GLCMS to contain greater than 10 different compounds, two of which have been proposed on the basis of their GLCMS data as *5H-perfluoro-1,2,3-trihydro-4,5,6-trimethylpentalena-4,6-diene*, *m/z*: 368 ($M^+ - CF_2$, 86%), 349 ($M^+ - CF_3$, 54), 318 ($M^+ - CF_2CF_2$, 100), and *1H-perfluoro-1-methyl-2,3,4,5,6,7-hexahydrodicyclopenta*[b,d]*cyclopenta-8,9-diene*, *m/z*: 380 ($M^+ - CF_2$, 34%), 361 ($M^+ - CF_3$ 16), 330 ($M^+ - CF_2CF_2$, 49).

Acknowledgements

We thank the Engineering and Physical Sciences Research Council (EPSRC) and EA Technology for financial support (to A.J.R. and J.F.S.V.), and J.A.K Howard and A.S. Batsanov for the X-ray structure analyses.

References

1. R.D. Chambers, J.F.S. Vaughan, S.J. Mullins, T. Nakamura, and A.J. Roche. J. Fluorine Chem. **72**, 231 (1995).
2. (*a*) M.A. McClinton and D.A. McClinton. Tetrahedron, **48**, 189 (1992); (*b*) J.P. Begue and D. Bonnet-Delphon. Tetrahedron, **47**, 3207 (1991); (*c*) D.J. Burton and Z.Y. Yang. Tetrahedron, **48**, 189 (1992).
3. J.T. Maynard. J. Org. Chem. **28**, 112 (1963).
4. R.D. Chambers and A.J. Palmer. Tetrahedron, **31**, 3293 (1969).
5. (*a*) R.D. Chambers, S. Partington, and D.B. Speight. J. Chem. Soc. Perkin Trans. 1, 2673 (1974); (*b*) J.W. Emsley, L. Phillips, and V. Wray. Fluorine coupling constants. Pergamon, Oxford. 1977.
6. R.D. Chambers, S.J. Mullins, A.J. Roche, and J.F.S. Vaughan. J. Chem. Soc. Chem. Commun. 841 (1995).
7. E.D. Laganis and D.M. Lemal. J. Am. Chem. Soc. **102**, 6633 (1980).
8. J.E. Baldwin. J. Chem. Soc. Chem. Commun. 734 (1976).