Reactions involving fluoride ion. Part 47.[1] Reactions of perfluorobicycloalkenes

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Electron deficient dienes **3** and **4** are obtained by defluorination of perfluorobicyclo-butylidene (**1**) and -pentylidene (**2**), using tetrakis(dimethylamino)ethene (TDAE), and these dienes are very reactive. With alkali metal fluorides, **4** gave a stable observable anion while **3** gave oligomers. The corresponding fluorinated allyl anion was however obtained *via* **3** in the presence of TDAE. Further reactions of **3** and **4** are described.

Introduction

Perfluorinated alkenes have a rich and unusual chemistry[2] but relatively little chemistry of perfluorinated dienes has been described. In previous papers, we described the synthesis of the bi(cycloalkene) systems **3** and **4**, by defluorination of the corresponding monoenes **1a,b** and **2**, with sodium amalgam (Scheme 1),[3] and some of their chemistry was included.[4] We have now developed a more convenient process, using tetrakis-(dimethylamino)ethene (TDAE), for the syntheses of **3** and **4** (see later) and consequently further chemistry of these systems has now been carried out.

Results and discussion

The dienes, **3** and **4**, are reactive towards nucleophiles and, in particular, **3** reacts vigorously with neutral methanol even at room temperature (Scheme 2).[4] By comparison, diene **4** is of lower reactivity and **5** requires the presence of base to promote the reaction. Electronically, **3**, **4** and **5** are very similar and the exceptional reactivity of **3** is, in our view, a very good illustration of the fact that angle-strain leads to enhanced reactivity. However, the very significant differences in reactivity that are exemplified in Scheme 2, help us to appreciate some of the differences in chemistry between **3** and **4**, that are described below.

Throughout this series of papers, we have been following a process of drawing 'mirror-image' analogies between familiar chemistry of carbocations, derived from unsaturated hydrocarbons, and the chemistry of carbanions, derived from perfluorinated alkenes. Significantly, it has been possible to generate and *observe* fluorinated carbanions, *e.g.* **6**, by addition of fluoride-ion to certain perfluorinated alkenes,[5] following an analogy with the spectacular observable carbocations described by Olah and co-workers.[6] In principle, we should also be able to generate allyl anions, *e.g.* **7**, by the addition of fluoride ion to fluorinated dienes. However, we are only aware of addition of fluoride ion to the allene **8** to give **9** in this context (Scheme 3).[7]
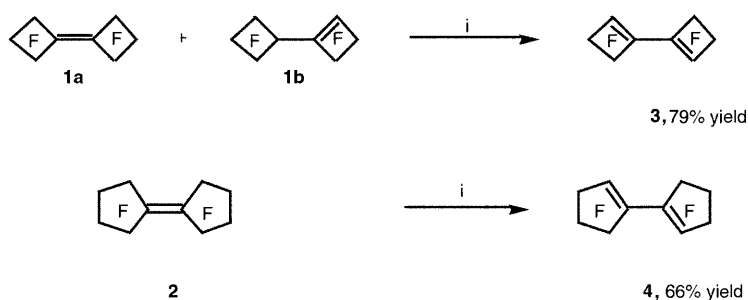
Scheme 1 Synthesis of perfluorobicyclodienes. *Reagents and conditions*: i, Na, Hg (0.5% w/w), water cooling.
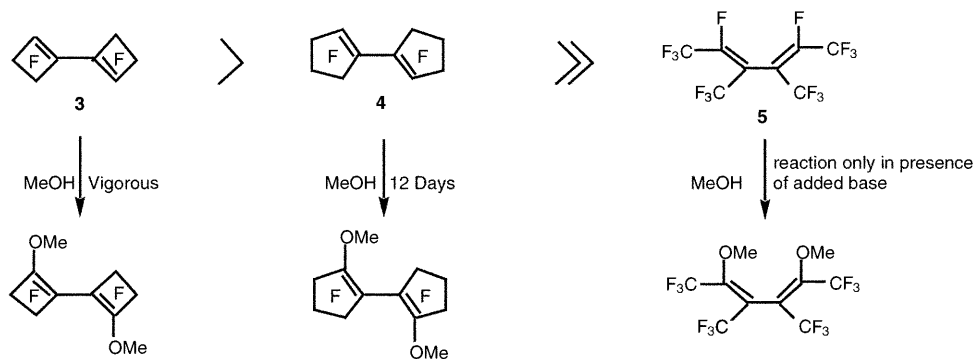
Scheme 2 Relative reactivity of perfluorinated dienes with nucleophiles.
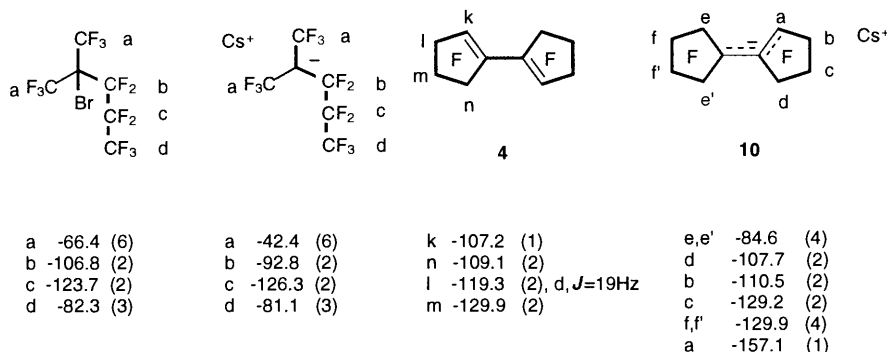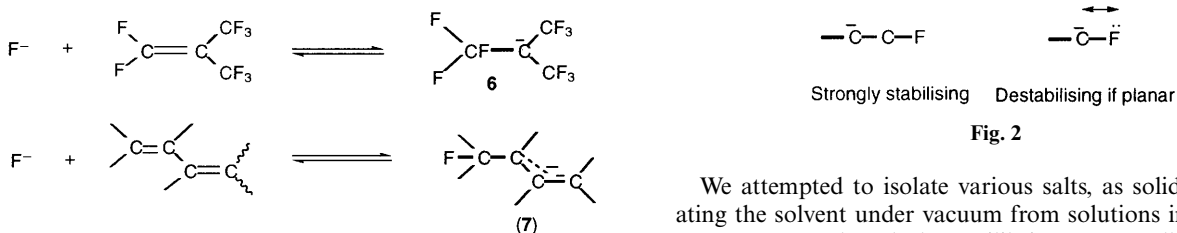
a −66.4 (6)   a −42.4 (6)   k −107.2 (1)   e,e′ −84.6 (4)

a −66.4 (6)	a −42.4 (6)	k −107.2 (1)	e,e′ −84.6 (4)	
b −106.8 (2)	b −92.8 (2)	n −109.1 (2)	d −107.7 (2)	
c −123.7 (2)	c −126.3 (2)	l −119.3 (2), d, J=19Hz	b −110.5 (2)	
d −82.3 (3)	d −81.1 (3)	m −129.9 (2)	c −129.2 (2)	
			f,f′ −129.9 (4)	
			a −157.1 (1)	

Fig. 1 [19]F Chemical shifts (ppm) and intensity of carbanions and corresponding neutral molecules.

Scheme 3 (Unmarked bonds are to fluorine or a perfluoroalkyl group.)

We now find that reaction of diene **4** with excess fluoride ion, in a variety of solvents, gives solutions of anion **10** (Scheme 4).

Scheme 4 Carbanion formation.

In our earlier studies,[5,8,9] we concluded that ^{19}F resonances arising from C–F sites that are adjacent to sites of high charge density are shifted to higher frequency with respect to corresponding neutral sites. Moreover, moving to sites remote from the charge, a tendency towards alternation occurs, with the effect of charge rapidly falling off with distance (Fig. 1). Consistent with these findings, we are able to assign resonances in the spectrum of anion **10** which is also presented in Fig. 1. The surprising aspect of the ^{19}F NMR spectrum of anion **10**, is that the resonances e,e′ in the saturated ring, are equivalent; moreover, this situation did not change over a temperature range of −40 to +80 °C. However, it has been established by other workers[10] that C–C bond rotation in allyl anions occurs down to low temperatures and so we may conclude that the positions e,e′, and f,f′ in **10** are rendered equivalent by C–C bond rotation that is rapid on the NMR timescale.

We also explored the dependence of the NMR spectrum of **10** on solvent, and on counter-ion. Remarkably, the spectra were almost identical in acetonitrile, tetraglyme, DMSO and DMF; furthermore, there was little variation in the spectra when the counter-ions, potassium, caesium or $(Me_2N)_3S^+$ were used.[11–13] Caesium and potassium salts gave slightly broader lines than the $(Me_2N)_3S^+$ salt in acetonitrile which implies some exchange with fluoride ion in the former salts. These surprising similarities suggest that the anion is essentially unsolvated and unassociated, otherwise it would be difficult to imagine such small differences in the NMR spectra with both change in solvent and counter-ion.
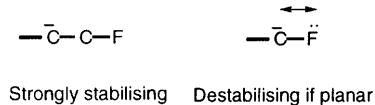

Fig. 2

We attempted to isolate various salts, as solids, by evaporating the solvent under vacuum from solutions in acetonitrile. However, even though the equilibrium was totally in favour of the anion in solution, only in the case of the salt associated with the cation, $(Me_2N)_3S^+$, was it possible to isolate a solid which could be re-dissolved to show only the presence of anion **10** in the ^{19}F NMR spectrum. Unfortunately, we were unable to grow crystals of crystallographic quality from this solid.

It is well established that fluorine adjacent to a carbanion site is strongly stabilising but that when it is attached directly to a carbanion site, inductive electron withdrawal is offset by electron-pair repulsion. Indeed, if the carbanion is planar, the latter is the dominant effect and the overall result is destabilisation (Fig. 2). The anion (**10**) is indeed planar and the fluorine atom that is directly attached to the charged centre must be destabilising, although this is clearly offset by the considerable stabilisation arising from the other fluorinated sites. To our knowledge, anions **10** and **12** (see later) are the only fluorinated anions to have been observed that have fluorine directly attached to a charged centre in a carbanion.

Reactions of the anion **10** were rather limited; *e.g.* no reaction occurred with either iodomethane or allyl bromide. Furthermore, reaction with bromine gave products **2** and **4**, *i.e.* compounds not containing bromine, and this suggests that the anion **10** may function both as a nucleophile, forming C–Br bonds, and also as a fluoride-ion donor. This fluoride ion is consumed by converting any intermediate bromo derivatives **11** to the product **2** by allylic displacement of bromine by fluorine (Scheme 5).
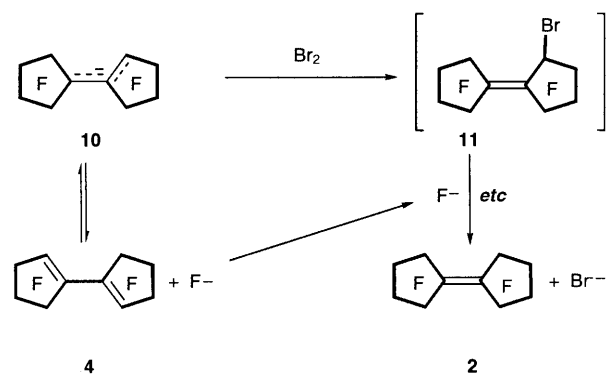
Scheme 5 Reaction of carbanion **10** with bromine.

In principle, the perfluorobicyclobutadiene (**3**) should also form a carbanion. However, when **3** was treated with Cs⁺, K⁺, Na⁺ or $(Me_2N)_3S^+$ fluorides in tetraglyme or acetonitrile, at
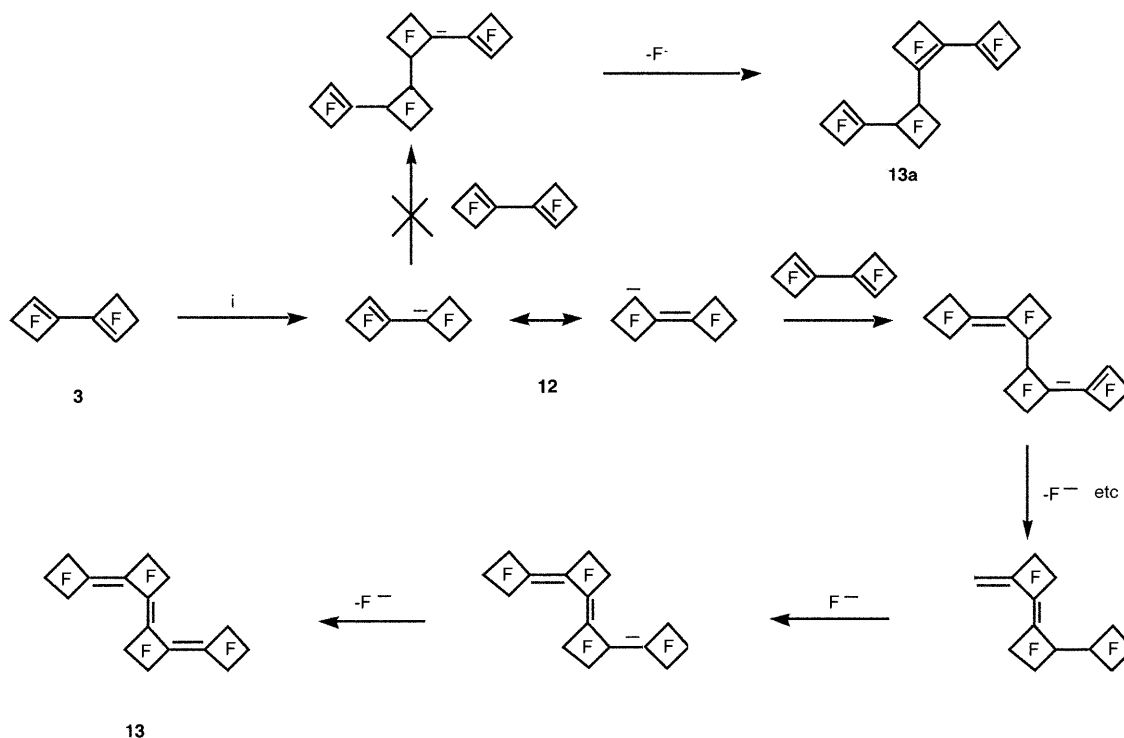
Scheme 6 Oligomerisation of **3**.

room temperature, only products of oligomerisation were observed (Scheme 6, Tables 1 and 2, see Experimental section).

Considering the mechanism of oligomerisation, there are two potential structures for the dimer, *i.e.* **13** and **13a**. However, these two possibilities are readily distinguished by the fact that structure **13a** would show two resonances in the ^{19}F NMR spectrum corresponding to vinylic sites whereas, in fact, only resonances corresponding to CF_2 positions were observed and this is only consistent with the structure **13**. Mass-spectral data showed that the remainder of the product consisted of higher oligomers (up to a pentamer) of **3** but these were not characterised.

In a previous paper,[3] we demonstrated that tetrakis-(dimethylamino)ethene (TDAE) could be used to defluorinate perfluoro-3,4-dimethylhex-3-ene (**14**) to give diene **5** (Scheme 7). When we applied this convenient process, for the defluorin-
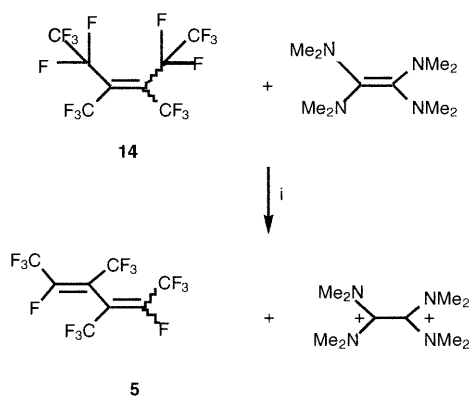
Scheme 7 Reaction of perfluoro-3,4-dimethylhex-3-ene with TDAE. *Reagents and conditions*: i, TDAE, with or without solvent (dichloromethane).

ation of **2**, to the synthesis of the diene **4**, a high yield of the required product **4** was obtained. However, in view of the interaction of fluoride with diene **3** outlined above, it was understandable that when **1** was treated with TDAE in a similar manner, the dimer of **3**, *i.e.* **13**, was the main product. Nevertheless, in contrast to these findings, when the reaction of **1** with


Fig. 3 ^{19}F Chemical shifts (ppm) and intensity of **3** and **12**.

| 3			12		
k	-95.7	(1)	d,d'	-88.5	(4)
l	-117.2	(2)	e,	-121.7	(2)
m	-115.7	(2)	c	-113.0	(2)
			b	-107.0	(2)
			a	-142.2	(1)

TDAE was carried out in the absence of a solvent, an orange solid was obtained which was soluble in acetonitrile, and the ^{19}F NMR spectrum of this solution showed the presence of carbanion **12**. The spectral data are summarised in Fig. 3, together with those of the precursor, **3**. The relationship between the two spectra parallels those already recorded in Fig. 1 for the anion **10** and its precursor **4**. It is noteworthy that the equivalent signals were observed for d and d', again illustrating C–C bond rotation in the allyl system.

The fact that the anion **12** is generated during the reaction of TDAE with **1** is at first sight puzzling because, as we explained above, the diene **3**, which is formed in the presence of TDAE, reacts rapidly with alkali metal fluorides to give oligomers of **3**. It follows, therefore, that the diene **3** must be trapped immediately by the powerful fluoride-ion source derived from TDAE during the defluorination process. Furthermore, fluoride from this source must be sufficiently reactive to force the equilibrium towards the anion, otherwise reaction of the anion **12** with diene **3** would occur as illustrated in Scheme 6. Addition of boron trifluoride–diethyl ether to the solution of **12** yielded **3** and reactions of these systems are summarised in Scheme 8.

Oligomerisation of perfluorocyclobutene (**15**) with pyridine, has been described previously, and reactions *via* the ylide **16** have been proposed (Scheme 9).[14] Indeed, Burton and co-workers isolated and characterised stable ylides derived from perfluorinated alkenes in reactions with trialkylamines,[15] phosphines[16,17] and arsines.[18] We have now established that stable ylides may be obtained by reaction of pyridine, triethylamine or triphenylphosphine with either **3** or **4** (Scheme 10).
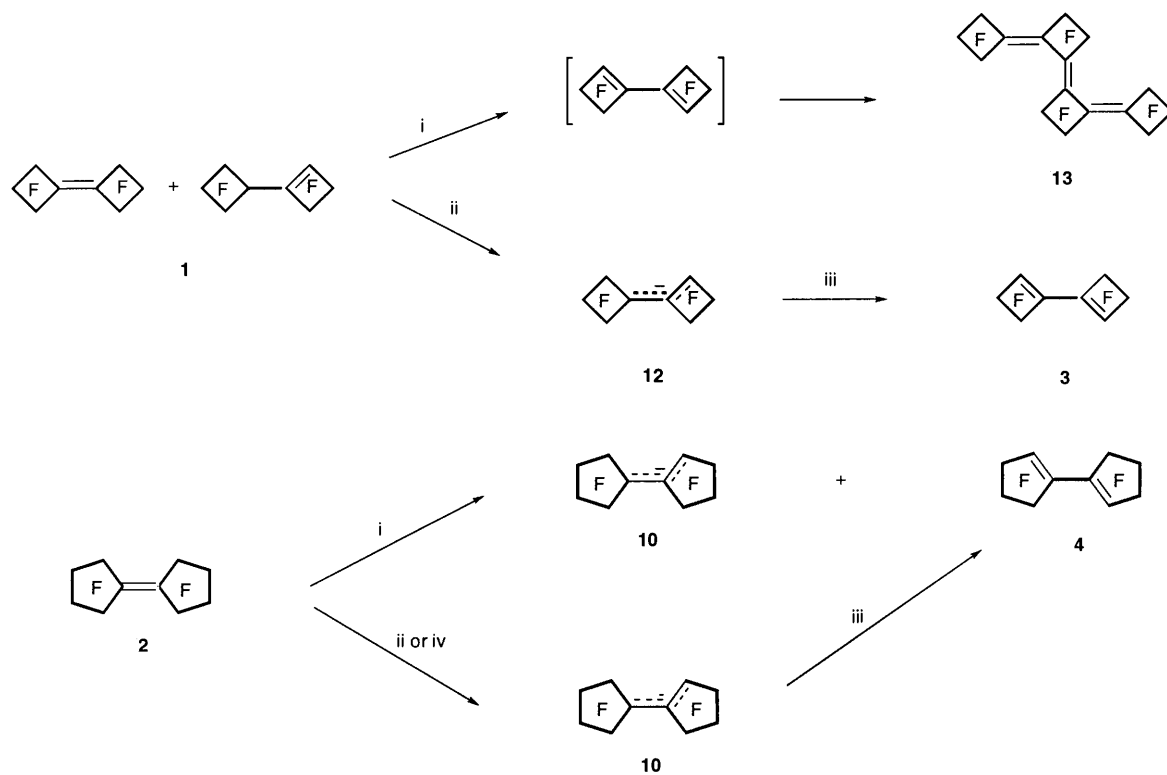
Scheme 8 Synthesis of perfluorobicyclodienes. *Reagents and conditions*: i, TDAE–CH$_2$Cl$_2$; ii, TDAE; iii, CH$_3$CN–BF$_3$·Et$_2$O; iv, TDAE–CH$_3$CN.
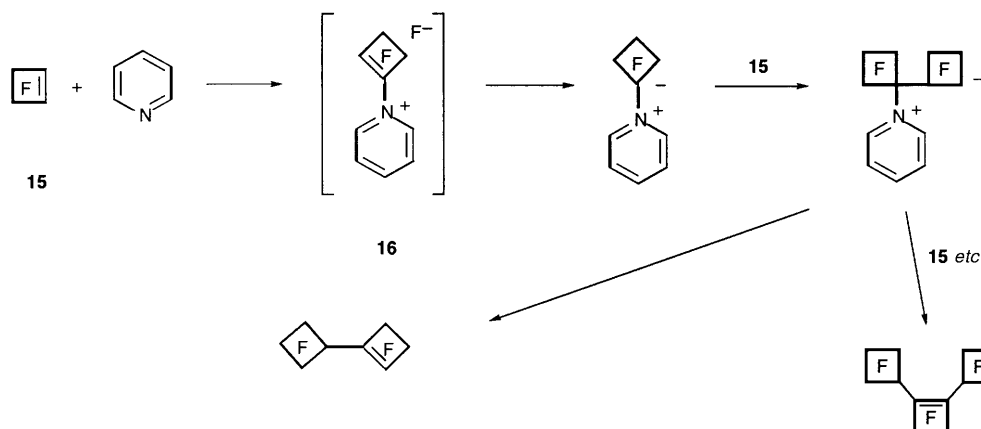
Scheme 9 Oligomerisation of perfluorocyclobutane.

Whereas in carbanions **10** and **12** we had equivalence of signals for e and e′ and d and d′ repectively (Figs. 1 and 3), in ylide **20** we observed separate signals for d and g. The analogous situations are common to all the ylides mentioned in Scheme 10 (see also Experimental section) and it indicates that any rotation about the C–C bond which joins the two rings is very slow on the NMR timescale. The most obvious explanation of this situation is that the charge in ylides **17–20** is essentially localised at the positions adjacent to the charged nitrogen or phosphorus, **19**, thus giving much greater double-bond character to the carbon–carbon bonds that link the rings.

We have sought to convert **3** and **4** into other functional derivatives by replacing vinylic-fluorine by iodine, using alkalimetal iodides. Clearly, a factor that must be borne in mind is that a metal fluoride is formed in the reaction and this could promote oligomerisation of **3** or the formation of carbanion **10**. Indeed, reaction of **3** with potassium iodide in tetraglyme gave mainly oligomers but reaction with lithium or sodium iodide in acetonitrile, diethyl ether, or tetraglyme, gave the diiodo derivative **21**. In the corresponding reactions of **4**, the use of potas-

sium iodide gave a mixture of the diiodo compound **22** and the carbanion **10**, but sodium and lithium iodides gave only **22** (Scheme 11).

We had anticipated the possibility of ring formation by reaction of the diiodides, **21** or **22**, with copper but these reactions gave only high molecular weight material that we were unable to characterise.

Clearly, these electron-deficient dienes have an unusual chemistry with considerable scope for further study as efficient difunctional electrophiles, and reaction of **3** and **4** with aniline and pyrrole demonstrates a very high level of reactivity towards potential nucleophiles (Scheme 12).

Experimental

Unless indicated otherwise, ^{1}H and ^{19}F NMR spectra were recorded at room temperature on a Bruker AC 250 spectrometer operating at 250.13 or 235.34 MHz respectively. Samples were dissolved in CDCl$_3$, and tetramethylsilane and fluorotrichloromethane were used as internal references.

17

18

3 + Et₃N →

3 + Ph₃P →

**19**

4 + [pyridine] →

20
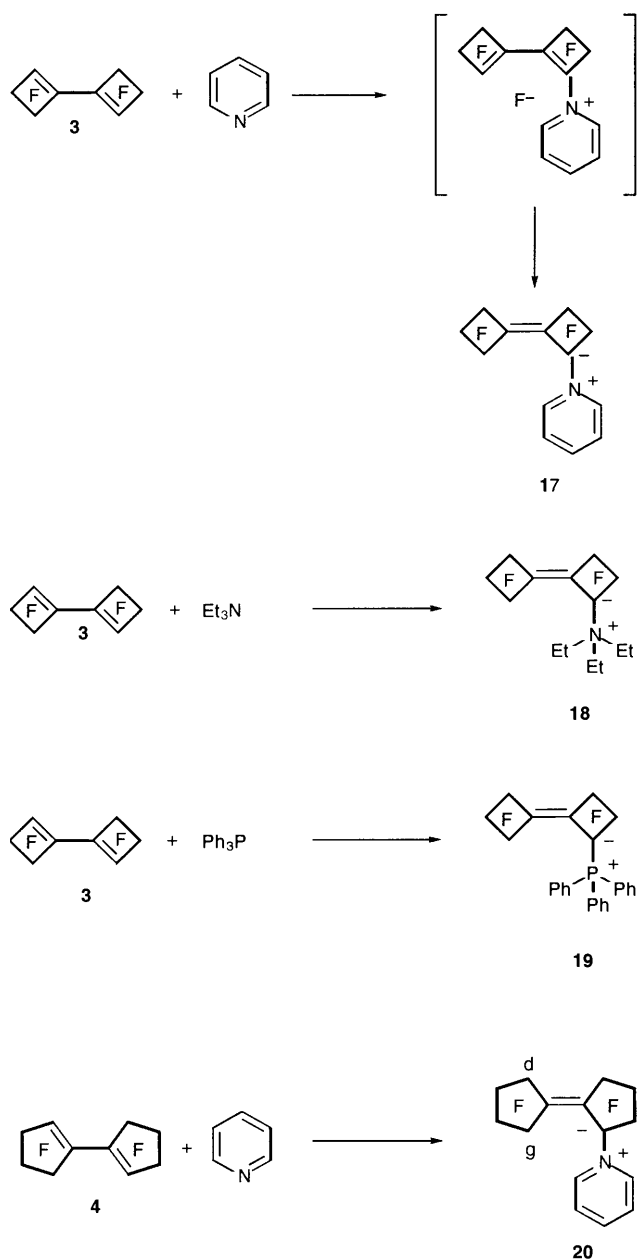
Scheme 10 Ylide formation.

Coupling constants are given in Hz. GLC Mass spectra were recorded on a VG 7070E spectrometer linked to a Hewlett Packard 5790A gas chromatograph fitted with a 25 m cross-linked methyl silicone capillary column. Mass spectra were generated by electron impact. Anhydrous acetonitrile was purchased from the Aldrich Chemical Co. and glymes were dried by distillation (early fractions discarded) and then stored over molecular sieve (4 Å). **CAUTION** *It should be assumed that the dienes discussed in this paper are toxic, and they should be handled accordingly.*

Reactions of 3 and 4 with fluoride ion

Perfluoro-1,1′-bicyclopent-1-enyl 4—formation of carbanions. Perfluoro-1,1′-bicyclopent-1-enyl **4** (1.2 g) was added to caesium fluoride (0.5 g, 3.3 mmol) in tetraglyme (5 ml). A violet colouration formed immediately and after 2 hours the solution was homogeneous. The NMR spectrum of a sample of this solution (see Results and discussion section) was measured and a slight excess of BF₃·Et₂O (3.3 mmol) was added to the remainder to produce two layers, the lower of which was shown by NMR to be starting material **4**.

21

22 + **10**

4

22
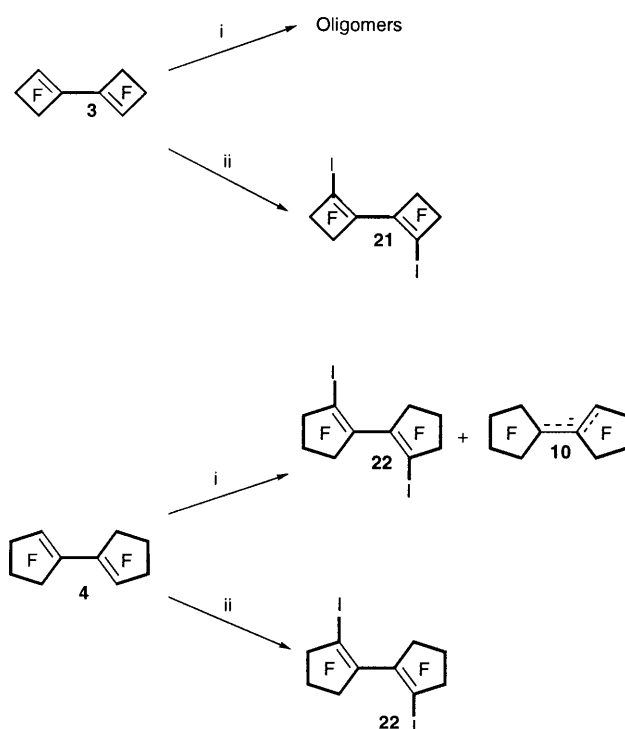
Scheme 11 Halogen exchange. *Reagents and conditions*: i, KI–solvent; ii, NaI or LiI–solvent.

Oligomerisation of perfluoro-1,1′-bicyclobut-1-enyl 3. Perfluoro-1,1′-bicyclobut-1-enyl **3** and an excess of dry fluoride in dry solvent were stirred for a specified time before being poured into water (see Tables 1 and 2 for details). This produced a precipitate which was filtered, dried and sublimed under reduced pressure (<1 mm) to give the dimer, *perfluoro-1,1′:2′,1″:2″:1‴-quatercyclobutylidene* **13**; mp 127–128 °C

13
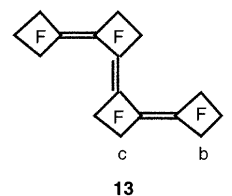
(Found: C, 33.4; F, 66.9. $C_{10}F_{20}$ requires C, 33.6; F, 66.4%); δ_F −110.1 (2F, s, F_c), −117.9 (2F, s, F_b), −130.6 (1F, s, F_a); m/z 572, (M⁺, 7%). Higher oligomers were identified by mass spectroscopy.

Defluorination of mono-enes 1 and 2 using TDAE

Perfluorobicyclobutylidene 1. *i) In a solvent.* TDAE (2.0 g, 10 mmol) in dichloromethane (5 ml) was slowly added under dry nitrogen to a stirred solution of perfluorobicyclobutylidene **1** (3.5 g, 10.8 mmol) in dichloromethane (5 ml) at 0 °C and a yellow solid precipitate was immediately formed. Filtration under nitrogen afforded a yellowish solid and an orange solution. The solid was washed with water (10 ml) and sublimed under vacuum (<1 mm) to give a white solid (1.1 g) which was identified as dimer **13**.

ii) In the absence of a solvent. TDAE (1.9 g, 9.5 mmol) was added to perfluorobicyclobutylidene **1** (4.06 g, 12.6 mmol) slowly at 0 °C under dry nitrogen and an orange solid was immediately formed. Remaining alkene **1** was removed from the system under reduced pressure and dry acetonitrile (10 ml) was added. The solution was then filtered under nitrogen to give a white solid and a brown solution which was shown by NMR to contain carbanion **12**. Addition of BF₃·Et₂O (2.0 g, 14 mmol)

Table 1 Perfluoro-1,1′-bicyclobut-1-enyl (**3**) with excess fluoride

Diene (**3**)			F⁻ source				
g	mmol	Solvent		g	mmol	Time/day	Yield **13** (%)
1.6	5.6	Tetraglyme	CsF	0.86	5.7	1	76
2.3	8.0	Tetraglyme	KF	0.58	10.0	1	65
1.3	4.5	Tetraglyme	NaF	0.85	20.0	7	68
3.2	11.2	Acetonitrile	CsF	1.10	7.2	2	82
2.1	7.3	Acetonitrile	TAS-F	2.20	8.0	1	65

Table 2 Perfluoro-1,1′-bicyclobut-1-enyl (**3**) with fluoride using excess diene

Diene (**3**)		F⁻ source				Yield (%)[a]	
g	mmol		g	mmol	Time/day	**13**	Higher oligomers
0.9	3.2	CsF	0.02	0.13	5	43	39
0.8	2.8	CsF	0.05	0.31	5	34	24
1.3	4.5	KF	0.11	1.9	5	26	45
2.2	7.7	NaF	0.11	2.6	5	26	47

[a] Estimated by GLC.
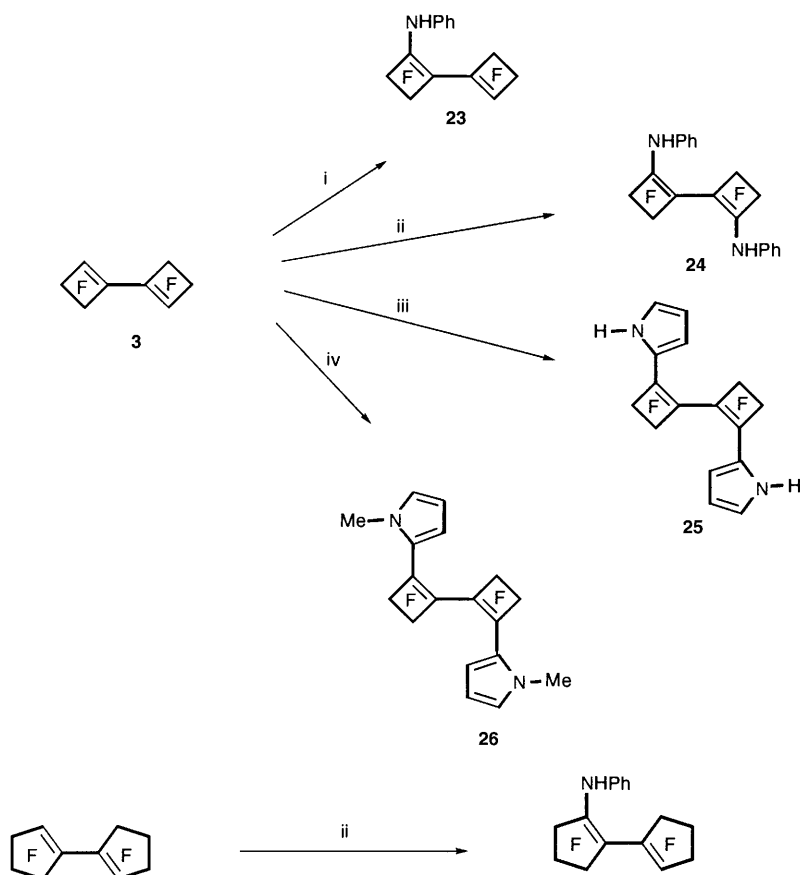
Scheme 12 Reactions with amines. *Reagents*: i, aniline (equimolar); ii, aniline (excess); iii, pyrrole; iv, *N*-methylpyrrole.

gave a solution which was shown by GCMS and NMR to have diene **3**[3] as the main perfluorinated component, accompanied by the dimer **13**.

Reaction of perfluorobicyclopentylidene 2 with TDAE. *i) In dichloromethane.* TDAE (1.41 g, 7.1 mmol) in dichloromethane (20 ml) was slowly added under dry nitrogen to a stirred solution of perfluorobicyclopentylidene **2** (3.1 g, 7.3 mmol) in dichloromethane (20 ml) at 0 °C to give an orange solution. The mixture was allowed to warm to room temperature during which time a solid was precipitated. Filtration under nitrogen

afforded a white solid and an orange solution and the ¹⁹F NMR spectrum of the solution showed it to contain perfluoro-1,1′-bicyclopent-1-enyl **4** and the carbanion **10** in a ratio of 3:2 but no **2**. Addition of BF₃·Et₂O (1.05 g, 7.4 mmol) to the solution converted the carbanion into diene **4**[3] (1.66 g, 59%).

ii) In acetonitrile. TDAE (0.97 g, 4.9 mmol) in acetonitrile (3 ml) was slowly added under dry nitrogen to a stirred solution of perfluorobicyclopentylidene **2** (2.02 g, 4.8 mmol) in acetonitrile (3 ml) at room temperature to give a yellow solution with a white precipitate. Filtration under nitrogen afforded a white solid and a yellow solution. The ¹⁹F NMR spectrum of the

Table 3 Perfluoro-1,1′-bicyclobut-1-enyl (**3**) with KCl and KI

Diene **3**		Halide source				Yield (%)	
g	mmol		g	mmol	Time/day	**13**	Higher oligomers
1.9	6.6	KCl	0.5	6.7	2	12	36
1.5	5.2	KI	0.91	5.5	14	68	—

solution showed only the presence of carbanion **10**. Addition of BF$_3$·Et$_2$O (0.7 g, 5.0 mmol) gave two layers, the lower one of which was identified as diene **4** (1.5 g, 81%).

iii) In the absence of solvent. TDAE (1.33 g, 6.7 mmol) was added to perfluorobicyclopentylidene **2** (3.07 g, 7.2 mmol) slowly at 0 °C under dry nitrogen. A brown solid was immediately formed. Remaining alkene **2** was removed from the system under reduced pressure and dry acetonitrile (10 ml) was added. The solution was then filtered under nitrogen to give a white solid and a brown solution. The solution was shown by NMR to contain the carbanion **10**. Addition of BF$_3$·Et$_2$O (1.1 g, 7.8 mmol) to the solution gave a lower layer which was identified by GCMS and NMR as diene **4** (1.9 g, 62%).

Reaction of perfluoro-1,1′-bicyclobut-1-enyl 3 with halides other than fluoride

Perfluoro-1,1′-bicyclobut-1-enyl **3** was treated with potassium iodide and with potassium chloride as described above for potassium fluoride and again, oligomerisation took place. Results are given in Table 3.

Reactions of carbanion 10 with bromine

Bromine (0.35 g, 3.2 mmol) was added to carbanion **10**, which had been formed by the interaction of diene **4** (1.1 g, 2.8 mmol) with caesium fluoride (0.6 g, 3.9 mmol) in tetraglyme (5 ml) as described above. After stirring the mixture for about one week, two layers formed of which the lower layer was shown by NMR and GCMS to be a mixture of diene **4** (44%) and perfluorobicyclopentylidene **2** (56%).

Perfluoro-1,1′-bicyclobut-1-enyl 3 with lithium iodide

A mixture of diene **3** (1.24 g, 4.33 mmol) and excess lithium iodide (2.48 g, 18.5 mmol) in tetraglyme (10 ml) was stirred at room temperature for two days. After this treatment, water was added to the mixture and a yellow solid precipitated. Following filtration, the solid was washed with water, dried and then sublimed under reduced pressure (<1 mm) to yield *2,2′-diiodo-octafluoro-1,1′-bicyclobut-1-enyl* **21** (1.34 g, 68%) (Found: C, 19.0; I, 50.2. C$_8$F$_8$I$_2$ requires C, 19.1; I, 50.6%); δ_F −108.3 (1F, m, F$_a$ or F$_b$), −112.0 (1F, m, F$_a$ or F$_b$); *m/z* 502 (M$^+$, 56%).

Reactions using sodium iodide as the source of iodide, and ether or acetonitrile as solvents gave a similar result.

Perfluoro-1,1′-bicyclopent-1-enyl 4 with sodium iodide

A mixture of diene **4** (2.22 g, 5.8 mmol) and excess sodium iodide (4.13 g, 27.7 mmol) in tetraglyme (30 ml) was stirred at room temperature for one day. Then, removal of solvent under reduced pressure gave a residual oil which on distillation under reduced pressure afforded *2,2′-diiododododecafluoro-1,1′-bicyclopent-1,1′-enyl* **22** (1.57 g, 45%) (Found: C, 20.2; I, 41.7.


22
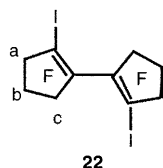
C$_{10}$F$_{12}$I$_2$ requires C, 19.9; I, 42.2%); δ_F −109 (2F, F$_a$ and F$_c$), −132 (1F, F$_b$); δ_F (measured at 233 K in (CD$_3$)CO) −106.5 and −110.1 (1F, AB J_{FF} 260.8, F$_a$ or F$_c$), −106.3 and −112.3 (1F, AB J_{FF} 259.8, F$_a$ or F$_c$), −129.1 and −131.8 (1F, AB J_{FF} 237.7, F$_b$); *m/z* 602 (M$^+$, 100%).

Reactions using lithium iodide as the source of iodide, and ether or acetonitrile as solvents gave a similar result.

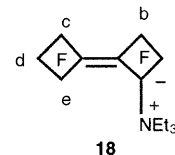### Perfluoro-1,1′-bicyclobut-1-enyl 3 with pyridine

A mixture of perfluoro-1,1′-bicyclobut-1-enyl (**3**) (1.96 g, 6.9 mmol) and pyridine (0.67 g, 8.5 mmol) in acetonitrile (10 ml) was stirred at room temperature for 5 days to give a yellow solution. Removal of solvent under reduced pressure gave a brown solid which was thoroughly washed with dry ether. After removal of solvent under vacuum, the remaining white solid was identified as *perfluoro(bicyclobutyliden-2-id-2-yl)-pyridinium* **17** (1.19 g, 47% yield); δ_F −91.0 (1F, br, F$_a$), −96.2

17
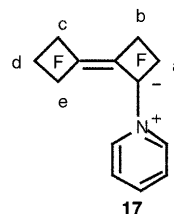
(1F, br, c or e), −107.0 (1F, br, e or c), −114.6 (1F, br, F$_b$), −125.8 (1F, br, F$_d$); δ_H 8.1 (2H, t, *J* 7.1, H$_3$ and $_5$), 8.4 (1H, t, *J* 7.7, H$_4$), 8.6 (2H, d, *J* 6.1, H$_2$ and $_6$).

Perfluoro-1,1′-bicyclobut-1-enyl 3 with triethylamine

A Carius tube charged, by vacuum transfer, with a mixture of perfluoro-1,1′-bicyclobut-1-enyl **3** (1.7 g, 6 mmol) and triethylamine (0.4 g, 4 mmol) was rotated at room temperature for 24 h to give a brown solid. The tube was opened under dry nitrogen and then the solid was thoroughly washed with dry ether. Removal of solvent under vacuum gave (perfluoro-bicyclobutyliden-2-id-2-yl)triethylammonium **18** (1.43 g, 62%


18

yield) (Found: C, 43.1; H, 3.7; N, 3.4. C$_{14}$H$_{15}$F$_{10}$N requires C, 43.3; H, 3.9; N, 3.6%); δ_F −92.1 (1F, br, F$_a$), −95.1 (1F, br, c or e), −99.5 (1F, br, e or c), −115.0 (1F, br, F$_b$), −126.0 (1F, m, F$_d$); δ_H 1.3 (3H, t, *J* 6.1, CH$_3$), 3.6 (2H, q, *J* 6.3, CH$_2$).

Perfluoro-1,1′-bicyclopent-1-enyl 4 with pyridine

A mixture of perfluoro-1,1′-bicyclopent-1-enyl **4** (1.34 g, 3.5 mmol) and pyridine (0.45 g, 5.7 mmol) in acetonitrile (5 ml) was stirred at room temperature for 5 days to give a yellow solution. Removal of solvent under reduced pressure gave a brown solid which was thoroughly washed with dry ether. After removal of

solvent under vacuum, the remaining white solid was identified as (perfluorobicyclopentyliden-2-id-2-yl)pyridinium **20** (1.12 g,

20
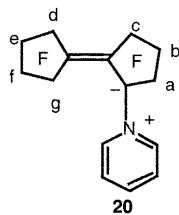
69% yield); δ_F −89.0 (1F, br, F_a), −90.9 (1F, br, $F_{d \text{ or } g}$), −102.6 (1F, br, $F_{g \text{ or } d}$), −109.2 (1F, br, F_c), −129.7 (1F, br, $F_{b, e \text{ or } f}$), −131.6 (1F, br, $F_{b, e \text{ or } f}$), −131.9 (1F, br, $F_{b, e \text{ or } f}$); δ_H 8.1 (2H, t, J 7.2, $H_{3 \text{ and } 5}$), 8.4 (1H, t, J 7.4, H_4), 8.6 (2H, d, J 6.3, $H_{2 \text{ and } 6}$).

Reaction with triphenylphosphine

Reaction of perfluoro-1,1′-bicyclobut-1-enyl 3 with triphenylphosphine. A mixture of perfluoro-1,1′-bicyclobut-1-enyl **3** (1.50 g, 5.2 mmol) and triphenylphosphine (1.17 g, 4.5 mmol) in acetonitrile (35 ml) was stirred at room temperature for 24 h to give a red–brown solution. Removal of solvent under reduced pressure gave a solid which was thoroughly washed with dry ether and, after removal of solvent, was identified as (*perfluorobicyclobutyliden-2-id-2-yl*)*triphenylphosphonium* **19**


19
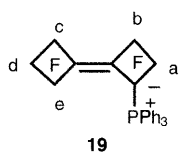
(2.05 g, 72% yield) (Found: C, 57.2; H, 2.8; F, 35.0; P, 5.5. $C_{26}H_{15}F_{10}P$ requires C, 56.9; H, 2.7; F, 34.7; P, 5.7%); δ_F −98.0 (1F, br, F_a), −100.3 (1F, br, $F_{c \text{ or } e}$), −102.2 (1F, br, $F_{c \text{ or } e}$), −113.3 (1F, d J_{FF} 15.3, F_b), −128.6 (1F, br, F_d); *m/z* 548 (M⁺ 6%).

Under similar reaction conditions, perfluoro-1,1′-bicyclopent-1-enyl **4** failed to react with triphenylphosphine.

Reactions of dienes with other nitrogen-containing compounds

Perfluoro-1,1′-bicyclobut-1-enyl 3 with aniline. *i) Equimolar amounts.* A mixture of aniline (0.58 g, 6.3 mmol) and diene **3** (1.79 g, 6.3 mmol) in acetonitrile (7 ml) was stirred for 24 h at room temperature. Evaporation of the solvent gave a brown viscous liquid which on sublimation at reduced pressure (<1 mm) yielded *2-(phenylamino)nonafluoro-1,1′-bicyclobut-1-enyl* **23** (0.35 g, 15% yield) (Found: C, 47.0; H, 1.7; F, 47.2; N, 3.8.


23
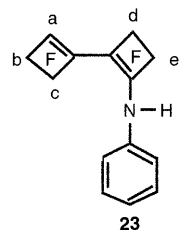
$C_{14}H_6F_9N$ requires C, 46.8; H, 1.4; F, 47.6; N, 3.9%); δ_H 7.2 (2H, d, J 7.6, *ortho* H), 7.3 (1H, t, J 7.3, *para* H), 7.4 (2H, t, J 7.6, *meta* H), 8.5 (1H, br, NH); δ_F −107.3 (2F, m, F_e), −109.5 (1F, br, F_a), −114.4 (2F, br, F_d), −115 (2F, m, F_b or F_c), −116.6 (2F, m, F_c or F_b); *m/z* 359 (M⁺, 100%).

Perfluoro-1,1′-bicyclobut-1-enyl 3 with aniline. *ii) Excess aniline.* When aniline (0.89 g, 9.6 mmol) was added to diene **3** (1.12 g, 3.9 mmol) in acetonitrile (10 ml), an exothermic reaction occurred. Stirring was continued for 1 hour at room temperature and this yielded a yellow liquid. Evaporation of the solvent and unreacted aniline gave a yellow solid which was washed with cold pentane to give *2,2′-bis(phenylamino)-octafluoro-1,1′-bicyclobut-1-enyl* **24** (0.89 g, 53% yield) (Found: C, 55.5; H, 2.6; F, 34.8; N, 6.2. $C_{20}H_{10}F_8N_2$ requires C, 55.8; H, 2.3; F, 35.4; N, 6.5%); δ_H 6.7 (2H, d, J 7.5, *ortho* H), 7.1 (1H, t, J 6.7, *para* H), 7.2 (2H, t, J 6.8, *meta* H), 9.0 (1H, br, NH); δ_F −106.3 (1F, m, F_a or F_b), −114.8 (1F, br, F_a or F_b); *m/z* 432 (M⁺, 6%).


24
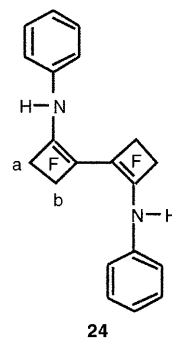
Perfluoro-1,1′-bicyclobut-1-enyl 3 with pyrrole. When pyrrole (0.33 g, 5.2 mmol) was added to diene **3** (0.68 g, 2.5 mmol) in acetonitrile (5 ml), an exothermic reaction occurred. Stirring was continued for 24 hours at room temperature and this yielded a red–brown liquid. Evaporation of the solvent gave a brown solid which on sublimation under reduced pressure (<1 mm) gave *2,2′-dipyrrol-2-yloctafluoro-1,1′-bicyclobut-1-enyl* **25** (0.55 g, 63% yield) (Found: C, 50.1; H, 2.1; F, 40.4; N,


25
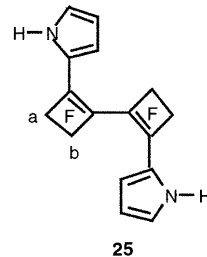
7.4. $C_{16}H_8F_8N_2$ requires C, 50.5; H, 2.1; F, 40.0; N, 7.4%); δ_H 6.4 (2H, m, ring H), 6.7 (2H, ring H), 7.3 (2H, ring H); δ_F −106.5 (1F, m, F_a or F_b), −113.6 (1F, br, F_a or F_b); *m/z* 380, (M⁺, 3%); IR 3400 cm⁻¹, N–H.

Perfluoro-1,1′-bicyclobut-1-enyl 3 with N-methylpyrrole. A mixture of *N*-methylpyrrole (0.52 g, 6.4 mmol) and diene **3** (0.62 g, 2.2 mmol) in acetonitrile (10 ml) was gently refluxed for 3 days, and this yielded a red–brown liquid. Evaporation of the solvent gave a brown solid which on sublimation under reduced pressure (<1 mm) gave *2,2′-bis(N-methypyrrol-2-yl)octafluoro-1,1′-bicyclobut-1-enyl* **26** (0.51 g, 57% yield) (Found: C, 52.6;

26
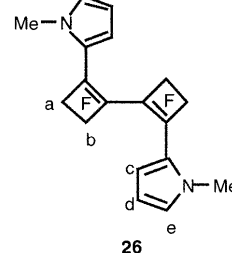
H, 2.9; F, 37.1; N, 6.8. $C_{18}H_{12}F_8N_2$ requires C, 52.4; H, 2.9; F, 37.3; N, 6.9%); δ_H 3.8 (3H, s, CH$_3$), 6.1–6.3 (2H, overlapping multiplets, H$_d$ and H$_e$), 6.8 (1H, br s, H$_c$); δ_F −108.4 (1F, m, F$_a$ or F$_b$), −109.0 (1F, m, F$_a$ or F$_b$); *m/z* 408 (M$^+$, 21%).

Perfluoro-1,1′-bicyclopent-1-enyl 4 with aniline. A mixture of aniline (0.21 g, 2.26 mmol) and diene **4** (1.05 g, 2.72 mmol) in acetonitrile (7 ml) was stirred for 24 h at room temperature. Evaporation of the solvent and unreacted aniline gave a yellow solid. Recrystallisation (acetonitrile) yielded *2-(phenylamino)-tridecafluoro-1,1′-bicyclopent-1-enyl* **27** (0.38 g, 31% yield)

27
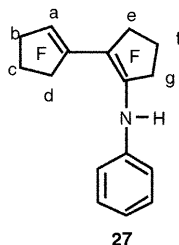
(Found: C, 41.5; H, 1.2; F, 54.7; N, 3.6. $C_{16}H_6F_{13}N$ requires C, 41.8; H, 1.3; F, 54.7; N, 3.1%); δ_H 7.2–7.4 (5H, unresolved aromatic H), ~9.5 (1H, br, NH); δ_F −100.3 (2F, br, F$_g$), −107.4 (1F, br, F$_a$), −115.1 (4F, br, F$_d$ and F$_e$), −118.3 (2F, br, F$_b$), −129.0 (2F, br, F$_c$ or F$_f$), −130.2 (2F, br, F$_f$ or F$_c$); *m/z* 459 (M$^+$, 16%).

Acknowledgements

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