Reactions involving fluoride ion. Part 41.[1,2] Synthesis of hexakis(trifluoromethyl)cyclopentadiene and derived cyclopentadienide salts

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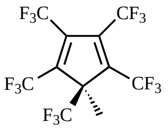
An efficient synthesis of hexakis(trifluoromethyl)cyclopentadiene 4, which shows a remarkably low reduction potential, is described. Various donors promote one-electron transfer to 4, leading to corresponding salts of pentakis(trifluoromethyl)cyclopentadienide 5. A novel approach to the synthesis of metal derivatives involves heating, or photolysis, of 4 directly with metals (including Cu, Ni, Fe and Co), leading to the corresponding ionic salts. X-Ray structural analysis was difficult because of rotation of trifluoromethyl groups in these salts, but structural data on 20, 24 and 30 has been obtained that reveals interesting conformations and stacking of the ions.

There is a general interest in the synthesis of cyclopentadiene derivatives that contain fluorocarbon groups, which stems partly from the possibility of attachment of highly fluorinated cyclopentadienide ligands to transition metals. Indeed, cyclopentadienide derivatives, with various counter species, have been obtained with the cyclopentadienide group containing one,[3,4] two[3,5] and four[6–12] trifluoromethyl substituents. Pentakis(trifluoromethyl)cyclopentadiene **1** has been obtained previously, but using a complex route. Nevertheless, it was shown that **1** is an extremely strong carbon acid (pK_a = −2; *cf.* nitric acid, pK_a = −1.2).[6]



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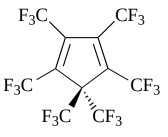
In earlier work,[11] we have approached the synthesis of tetrakis(trifluoromethyl)cyclopentadienides **3** *via* the novel diene **2** (Scheme 1), and we now demonstrate that a similar approach can be used for the synthesis of hexakis(trifluoromethyl)cyclopentadiene **4** and the corresponding cyclopentadienide salts **5**, using remarkably direct procedures. Our approach to fluorinated cyclopentadiene derivatives, described here, required difunctional carbon nucleophile equivalents with attached fluorocarbon groups. Consequently, we have developed a procedure that employs hydrogen-containing fluorinated alkenes from which anions were then generated by addition of fluoride ion, using methodology that has been described in earlier parts of this series.[2,13] As the fluorinated alkenes, we have used both 1,1,3,3,3-pentafluoropropene **6** and 1,1,1,3,4,4,4-heptafluorobut-2-ene **7** for reaction with the acyclic diene **2**, and the overall process is outlined in Scheme 2.



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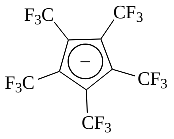

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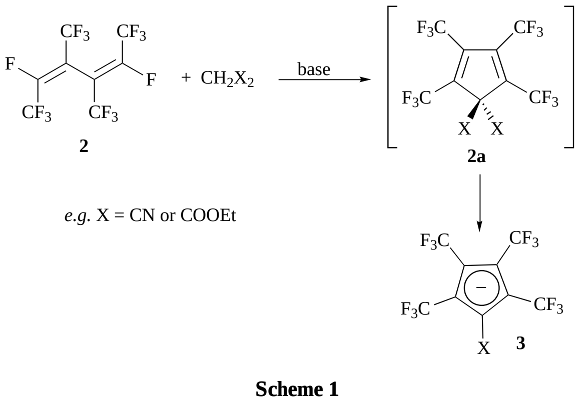
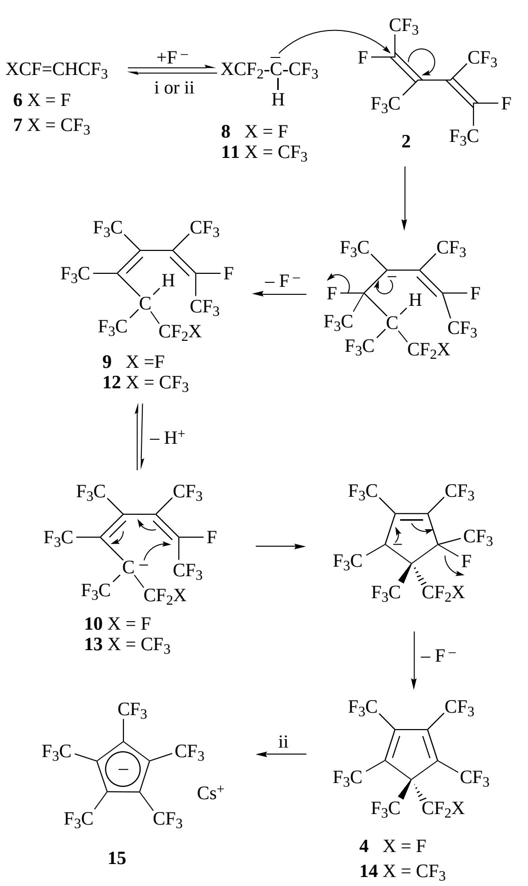


Scheme 1

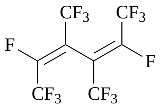
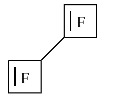
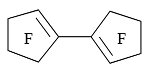
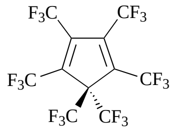
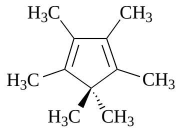
Reaction of pentafluoropropene generates anion **8**, which then reacts with the diene **2** leading to vinylic displacement of fluoride ion. We have established earlier that diene **2** is extremely reactive to nucleophilic attack.[14] The presumed intermediate **9** reacts further with fluoride ion (which is a strong base,[15] as well as being an effective nucleophile), generating a new ion **10**, which then cyclises with loss of fluoride ion, giving hexakis(trifluoromethyl)cyclopentadiene **4**, in 74% isolated yield. The cyclisation step is interesting because, as a 5-*endo-trig* process, it is formally disallowed by the Baldwin rules.[16] It is more likely, therefore, that the process involves the initial electrocyclic ring closure, shown in Scheme 2, and this is a rare example of an open-chain pentadienyl anion undergoing ring closure to give a carbocyclic system.[11,17,18] The diene **4** was easily identified by NMR data, giving: δ_F −55.6, −59.4 and −59.7 (all relative intensity 1). Elemental analysis and mass-spectral data also confirmed structure **4**.

In similar examples of this process we have been unable to isolate the dienes **2a** (Scheme 1) but, instead, further elimin-



Scheme 2 *Reagents and conditions:* i, CsF, MeCN, stirring, room temp.; ii, CsF, MeCN, autoclave, 100 °C

Table 1 Ultraviolet data for some conjugated dienes[19]

	$\pi \longrightarrow \pi^*$ Transition	
Diene	$\lambda_{\max}$/nm	ε/dm^3 mol^{-1} cm^{-1}
 **2**	234	272
 **16**	277	18 800
 **17**	278	10 900
 **4**	253	1 674
	252	4 140[22]

ation occurred to give cyclopentadienide salts **3**.[11] Indeed, when we used the more accessible 1,1,1,3,4,4,4-heptafluorobut-2-ene **7** the process proceeded *via* **11**, **12** and **13** but, remarkably, the corresponding diene **14** could not be isolated and this reaction led directly to the caesium salt **15** (43% yield).[1] The anion **11** is less reactive than **8** and so the reaction of **11** did not occur at room temperature; it is almost certainly the higher reaction temperature of 100 °C that is required for the alkene derivative **7** that allows the reaction to proceed directly to **15**. The step **14** to **15** is clearly of considerable interest because, formally, this represents nucleophilic displacement of a perfluoroalkyl group from the diene **14**, and nucleophilic attack at a tertiary site in a perfluorocarbon seems a highly unlikely process. Similarly, when diene **4** was heated in the presence of caesium fluoride, loss of a trifluoromethyl group occurred to give salt **15**. However, in the light of the further chemistry of diene **4** described below, it now seems clear that this displacement, converting **14** to **15**, must proceed *via* a single-electron transfer rather than an S_N2 process.

Data from the ultraviolet spectrum of diene **4** are contained in Table 1, together with those of other fluorinated dienes for comparison.[19] It is important to emphasise that all of the other dienes have at least one fluorine atom directly attached to a double bond. It is well established that homoannular conjugated dienes have lower extinction coefficients than analogous acyclic and heteroannular systems[20,21] and, consistent with these findings for various hydrocarbon systems, the extinction coefficient for the cyclic system **4** is, indeed, smaller than *e.g.* for **16** or **17**. Remarkably, however, if we assume that the trifluoromethyl group has an incremental effect on $\lambda_{\max}$ values that is approximately equivalent to that of chlorine or bromine,[20] *i.e.* inducing a bathochromic shift of *ca.* 5 nm, then the $\lambda_{\max}$ values that are recorded in Table 1 are very close to calculated values. Crowding probably causes the low extinction coefficient of **4** (trifluoromethyl is claimed to be isosteric with isopropyl),[23] as well as **2**. Indeed, we have been unable to effect any cycloaddition reactions, with either **2** or **4**, when using a variety of either electron rich or deficient mono- or di-enes, and this can be entirely attributed to steric effects.

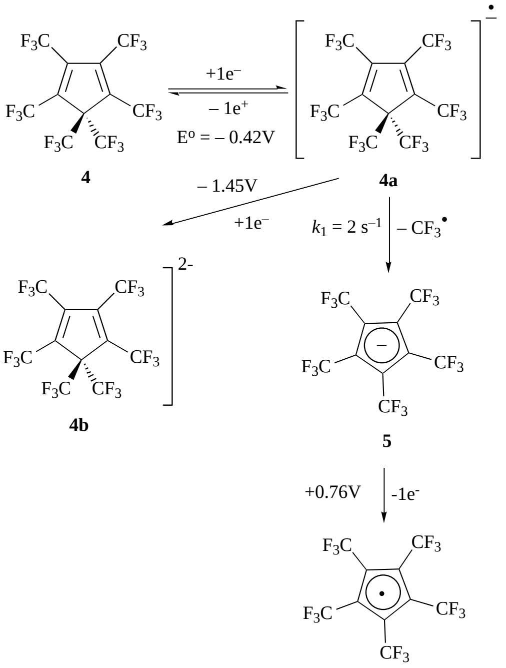
The ease of electron transfer to **4** is dramatically illustrated by a low reduction potential, $E\mathrm{pc}_1 = -0.46$ V, at a carbon electrode (*vs.* SCE at 0.2 V s^{-1}, in $\mathrm{CH_3CN}$ + 0.1 M $\mathrm{Bu_4NBF_4}$, where $E\mathrm{pc}_1$ represents the first cathodic peak potential in cyclic voltammetry). Conditions for the quasi-reversible reduction of **4** were obtained at 5 V s^{-1} ($E\mathrm{pc}_1 = -0.57$ V *vs.* SCE, $E\mathrm{pa}_1 = -0.27$ V *vs.* SCE, $\Delta E\mathrm{p} = 301$ mV) and the normal potential standard was calculated as $E^\circ = (E\mathrm{pc}_1 + E\mathrm{pa}_1)/2 = -0.42$ V (*vs.* SCE). The rate constant of the decay of the radical anion **4a** (Scheme 3) has been calculated as $k_1 = 2$ s^{-1} on the basis of an electrochemical (EC) mechanism. The diene **4** also presents an irreversible reduction wave at more negative potential ($E\mathrm{cp}_2 = -1.45$ V *vs.* SCE at 0.2 V s^{-1}, where $E\mathrm{pc}_2$ represents the second cathodic peak potential in cyclic voltammetry), which remains irreversible up to 100 V s^{-1} and has been assigned as the reduction of the radical anion **4a** into the corresponding unstable dianion **4b**. For comparison with systems explored earlier,[19] see Table 2, it has been established that the diene **4** has a peak potential of −0.67 V (*vs.* SCE at 0.2 V s^{-1}), using a platinum electrode. Thus, there is a remarkable difference in reduction potential arising from replacement of fluorine by trifluoromethyl and, of course, the fact that **4** is a cyclic diene. Irreversible oxidation of the cyclolpentadienide **5** was observed at +0.76 V (*vs.* SCE in $\mathrm{CH_3CN}$ + 0.1 M $\mathrm{Bu_4NBF_4}$) with a second irreversible oxidation step at a potential close to +0.90 V (*vs.* SCE). These two steps remain irreversible at 100 V s^{-1}. The rather high first oxidation step of **5** is consistent with the fact that **5** is a very poor nucleophile, *e.g.* we have been unable to effect reaction between **5** and either iodomethane, iron(II) chloride or acetyl bromide.

Iodide ion is easily oxidised (E° for the couple $\mathrm{I^{\bullet}/I^-}$ is +0.89 V *vs.* SCE in $\mathrm{CH_3CN}$)[24,25] and, consistent with the electrochemical data, we have found that reaction of the diene **4** by heating with various tetraalkylammonium iodides, in acetonitrile, provides a

Table 2 Reduction potentials of some perfluorinated dienes[19]

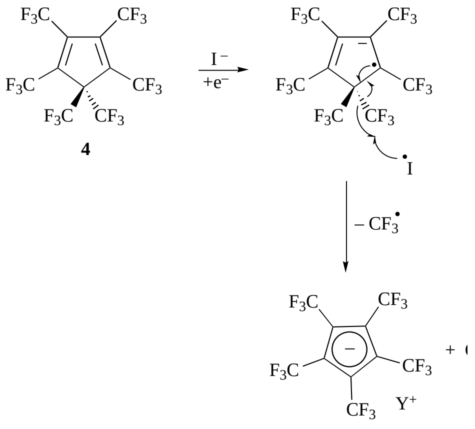
Diene	*E*pc (V *vs.* SCE)[a]
2	−2.35
16	−2.25
17	−2.03
4	−0.67

[a] Peak potential at 0.2 V s^{-1} on a platinum electrode, in acetonitrile, using tetrabutylammonium tetrafluoroborate as the electrolyte.



Scheme 3

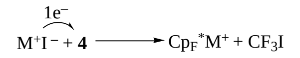
simple method for obtaining the corresponding tetraalkylammonium salts of the pentakis(trifluoromethyl)cyclopentadienide ion **5**. This procedure is also very revealing about mechanism because not only are the salts **18–20** obtained, but they are accompanied by quantitative formation of trifluoroiodomethane, as established by ^{19}F NMR, when the procedure was carried out using a sealed system. The mechanism involves one-electron transfer, as outlined in Scheme 4, and support for this stems from the observation of considerable inhibition of the reaction by the addition of α-pinene or *m*-dinitrobenzene. Furthermore, ultraviolet irradiation effected complete conversion to the same products over a short period of time. These observations also strongly suggest a single-electron transfer process for the step **14** to **15** in Scheme 2, although in that case it is not clear which nucleophile is the donor.



Where $Y^+ = {}^+NEt_4$ **18**, $^+NPr_4$ **19**, or $^+NBu_4$ **20**

Scheme 4

The problem of synthesis of metal derivatives of the cyclopentadienide **5** has been addressed in various ways. As indicated above, nucleophilic displacement of groups from metal salts was unsuccessful because the anion is such a poor nucleophile, and it is noteworthy that the corresponding cyclopentadienide system containing four trifluoromethyl groups was also ineffective in most cases, although some success was achieved in one case *via* ruthenium derivatives.[10,26] However, we have usefully applied the fact that the diene **4** is readily reduced by iodide ion and, consequently, we have found that reaction with various metal iodides proceeds very efficiently, *via* a mechanism corresponding to that outlined in Scheme 4.



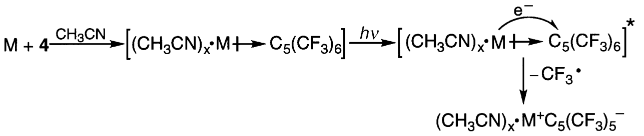
$$M^+I^- + \overset{\frown}{\mathbf{4}}^{\;1e^-} \longrightarrow Cp_F{}^*M^+ + CF_3I$$

Where $Cp_F{}^* = C_5(CF_3)_5{}^- =$ **5**; $M^+ =$ Li **21**, Na **22**, K **23**, Cs **15**

These reactions proceeded in acetonitrile at reflux temperature, but other salts, *e.g.* copper(I) and silver(I) iodides, did not react under these conditions, although both of these iodides gave cyclopentadienide salts in reactions promoted by photolysis.

A more remarkable finding, however, is that the diene **4** reacts with a range of powdered *metals*, in acetonitrile specifically, induced by irradiation under a medium pressure mercury lamp. It is particularly puzzling that other media like tetrahydrofuran, diethyl ether, nitrobenzene and cyclohexane are ineffective for the process, especially considering the fact that the diene **4** forms a separate layer even with acetonitrile. A possible explanation of these results is that the diene **4** forms a complex on the surface of the metal, which is sufficiently stabilised by acetonitrile (well known to form strong complexes with transition metal ions)[27] to allow excitation and subsequent reaction.

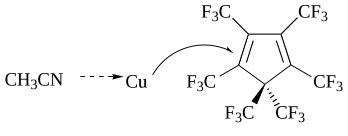
We are not aware of any analogous systems described in the literature for which this approach to the synthesis of transition metal derivatives has been successfully adopted, and the approach is made possible, in this case, by the extremely low reduction potential of the diene **4**. The uncertainty remaining in the reaction outlined in Scheme 5 is the fate of the trifluoromethyl radical; analysis of the crude reaction product by ^{19}F NMR spectroscopy showed the anion **5**, together with a number of resonances in the trifluoromethyl region (*ca.* −56 to −78 ppm), and these integrate approximately 5 : 1 for **5** and the various by-products, one of which was identified as trifluoromethane. This is further confirmation that a trifluoromethyl radical is formed and that the integrity of the trifluoromethyl group is retained in the by-products whereas, if an intermediate trifluoromethyl anion had been formed we may have anticipated at least some loss of fluoride ion. Only in the case of copper is the analogous process observed in a thermally induced reaction. This is surprising on consideration of the oxidation potentials for the metals (standard reduction potentials: $Cu^+ = +0.522$ V, $Ni^{2+} = -0.23$ V, $Co^{2+} = -0.28$ V and $Fe^{2+} = -0.4402$ V).[24] What



Metal (M)	Salt
Cu	$(CH_3CN)_4\cdot Cu^+C_5(CF_3)_5{}^-$ **24**
Ni	$(CH_3CN)_6\cdot Ni^{2+}[C_5(CF_3)_5]_2{}^-$ **25**
Fe	$(CH_3CN)_6\cdot Fe^{2+}[C_5(CF_3)_5]_2{}^-$ **26**
Co	$(CH_3CN)_6\cdot Co^{2+}[C_5(CF_3)_5]_2{}^-$ **27**

Scheme 5

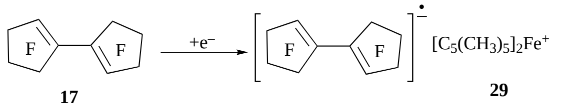
is remarkable and very significant, however, is the fact that the presence of acetonitrile is also critical in the *thermal* process. Therefore, we can only conclude that there is a *concerted* mechanism involved, where complex formation with the acetonitrile occurs in tandem with transfer of an electron from the metal (see Scheme 6). Indeed, the propensity of acetonitrile to complex with copper metal has been noted previously.[27] The large value for the extinction coefficient of salt **24** (λ_{max} 208, ε/dm^3 mol^{-1} cm^{-1} 70 000) confirms the high degree of conjugation expected within the aromatic pentakis(trifluoromethyl)cyclopentadienide anion.

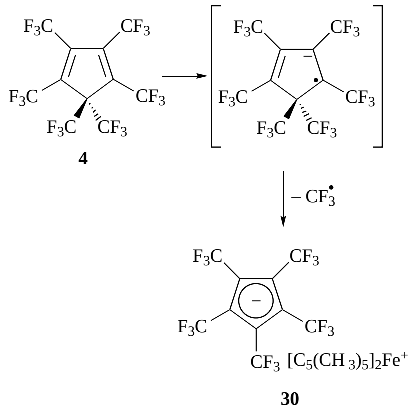


Scheme 6

Clearly, it would be of interest to eliminte solvent ligands from these transition metal derivatives in order to obtain π-bonded systems. To date, however, our attempts to achieve this by heating under high vacuum have led to decomposition, probably by formation of metal fluorides, and the diene **1** was formed most likely by abstraction of hydrogen from the ligand. Interestingly, an ill-characterised product believed to be an ionic derivative of pentamethoxycarbonylcyclopentadiene, rather than the corresponding ferrocene derivative, has been claimed.[28]

Decamethylferrocene is also a one-electron donor to fluorinated dienes and charge-transfer salts have been obtained and fully characterised *e.g.* formation of **29** from **17**, below.[29] The diene **4** is also an acceptor with decamethylferrocene, but the radical ion intermediate (see Scheme 7) readily loses trifluoromethyl radical and in this case the product is the salt **30**.





Scheme 7 *Reagents and conditions:* decamethylferrocene (+1e$^-$), CH_3CN, reflux, 17.5 h (64%)

X-Ray diffraction studies

We have now undertaken an extensive structural study of these systems by means of single-crystal X-ray diffraction, particularly because of recent interest in relation to π-bonding in alkali metal salts.[30–32] Though crystals of apparently good quality were obtained for most compounds, structure determinations encountered substantial difficulties due to the peculiar stereochemistry of the cyclopentadienide anion, making it exceedingly prone for disorder, both static and dynamic, in the crystal (*vide infra*). Further evidence for molecular motion within the crystal was obtained from a room temperature solid state ^{19}F NMR spectroscopy study on copper salt **24** which showed a single relatively sharp peak (width at half height 8 kHz). However, we have been able to obtain good-quality X-ray crystal structures of the copper salt **24** and decamethylferrocenium salt **30**, and a less accurate one of the tetrabutylammonium salt **20**.

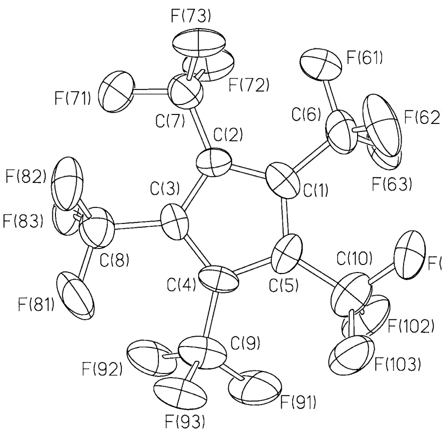


Fig. 1 Structure of $[C_5(CF_3)_5]^-$ anion in the crystal of **24** showing 50% probability ellipsoids. Selected bond distances (Å, esd 0.01): C(1)–C(2) 1.388, C(2)–C(3) 1.390, C(3)–C(4) 1.403, C(4)–C(5) 1.419, C(5)–C(1) 1.415; average C(ring)–CF_3 1.49(1), C–F 1.36(2).

Compound **24** crystallises in an orthorhombic lattice (space group *Pmmn*) with remarkably anisotropic parameters, $a = 21.100(2)$, $b = 43.273(4)$, $c = 5.216(1)$ Å. The structure is built of isolated cyclopentadienide anions (in a general position; see Fig. 1) and of three symmetrically non-equivalent types of $(CH_3CN)_4Cu^+$ cations in special positions, one with a crystallographic symmetry C_s and two with C_{2v}. The copper atoms Cu(1), Cu(2) and Cu(3) occupy Wyckoff sites m(*e*), mm2(*b*) and mm2(*a*), respectively. They have similar, slightly distorted tetrahedral environments with Cu–N distances of 1.977(10) to 2.004(6) Å, average 1.99(1) Å, which is consistent with the only structure reported that contains ordered $(CH_3CN)_4Cu^+$ cations (the perchlorate salt).[33] Methyl groups, except one at C(32), are rotationally disordered over two mirror-related positions.

Anions in the crystal are arranged in a stair-like stack, in which the adjacent anions are related *via* lattice translation *c* (inclined by 58° to the ring mean plane), with the interplane separation of 4.4 Å, parallel slip of 2.8 Å and ring-over-CF_3 overlap. Stacks are separated from each other by 'honeycombs' of cations (Fig. 2). Cations and anions contact by their CF_3 and methyl groups, with six shortest F · · · H contacts (2.40–2.53 Å) about the sum of van der Waals radii (2.47 Å).[34]

Compound **30** forms monoclinic crystals. At $T = 150$ K, the cell is primitive; space group $P2_1/n$ was found from systematic absences and intensity statistics and confirmed by successful structure solution. Both the cyclopentadienide anion and decamethylferrocenium cation are located at inversion centres and exhibit a complicated disorder. For the anion, this disorder was rationalised as two essentially coplanar, but slightly eccentric, inversion-related positions [Fig. 3(*a*),(*b*)], the ring centroid of each being shifted from the inversion centre by 0.22 Å. The direction of the shift is almost parallel to the monoclinic axis *y*. Nevertheless, the space occupied by both orientations is essentially identical [Fig. 3(*c*),(*d*)]; that is probably why the disorder occurs.

The iron atom of the cation rests strictly at the inversion centre and there is one C_5Me_5 ligand per asymmetric unit. However, we observed this ligand disordered over two positions, differing by a *ca.* 24° rotation around the five-fold axis and by a 6° inclination between their mean ring planes (Fig. 4).

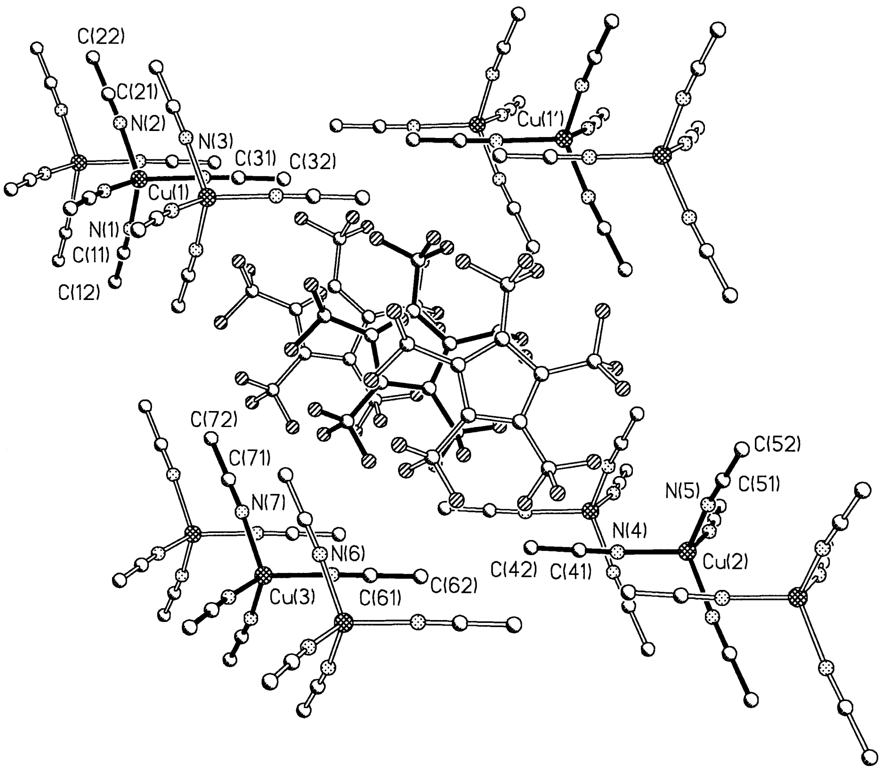


Fig. 2 Stack of anions surrounded with cations in **24**, showing atom numbering in the cations; projection on the (0 0 1) plane

There are thus two possibilities to be considered: (i) each individual cation possesses a centre of inversion and therefore adopts a staggered and parallel conformation of the rings, different cations are rotated as a whole relative to each other; (ii) in each individual cation the rings are twisted by 12° and are slightly non-parallel, the inversion symmetry is spurious (*i.e.* reflects only statistical distribution of the cations). The neutral molecule of decamethylferrocene in the crystal adopts a staggered (centrosymmetric) conformation,[35] while for its cation, eclipsed,[36] staggered[37,38] and intermediate[39] conformations have been observed. A slightly (<10°) twisted conformation, masked by disorder to give a spuriously centrosymmetric structure, is believed to be the case in the monoclinic phase of ferrocene.[40] On the other hand, non-parallel rings are unlikely to occur in the symmetrically substituted ferrocene derivatives. In any case, distances between the iron atom and the C_5H_5 rings (average 1.713 Å) are typical for pentamethylferrocenium cations,[36–39] and much longer than in neutral decamethylferrocene (1.657 Å),[35] leaving no doubt of the full charge transfer between the moieties.

Crystal packing of **30** is shown in Fig. 5. All the C_5H_5 rings in the crystal are approximately parallel to each other and to the crystal plane (0 0 1). Each ion has a distorted 'hexagonal bipyramidal' environment. 'Equatorial' positions are occupied by four counter ions and two ions of the same kind, and the 'apical' sites by two more counter ions, part of an infinite stack of alternating cations and anions, running parallel to the crystal axis *c* at *ca.* 70° angle with the C_5H_5 planes. Interplanar separations between adjacent cation and anion rings in this stack are 4.0–4.1 Å. Similar mixed donor–acceptor stacks (but with the ring plane and stack direction perpendicular), of a $D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}$ composition, exist in the structures of decamethylferrocenium salts with planar cyano-substituted carbanions,[37–39] which exhibit interesting magnetic behaviour (metamagnetism, *i.e.* transition from anti-ferromagnetic to ferromagnetic state).

There are a few F ··· H contacts shorter than the sum of van der Waals radii (2.47 Å);[34] the shortest of them being F(73) ··· H(171) 2.23, F(71) ··· H(182) 2.22 and F(63) ··· H(301) 2.20 Å. As *both* fluorine and hydrogen atoms are disordered, it remains unclear whether these contacts are really present in the structure (and can be interpreted as hydrogen bonds) or are merely a spurious 'product' of the disorder.

Approximately, such packing corresponds to a body-centred cell (in the same setting, space group *I*2/*n* or one of its subgroups). The additional two-fold rotation axis should pass through the Fe atom of the cation and through C(2), C(7) atoms and the midpoint of the C(4)–C(5) bond of the anion. In the latter, this two-fold symmetry can describe roughly the positions of carbon atoms, but not the ring folding (*vide infra*) or fluorine positions. In the cation only one position of the ligand, comprising the C(11) to C(20) atoms, fits the additional two-fold, as well as the mirror symmetry. At 150 K, reflections with $h + k + l$ odd (absent in *I* lattice) are indeed about three times weaker than the average, but definitely observed. At room temperature, however, the diffraction pattern (from a crystal obtained in a different crystallisation) really corresponded to an *I*-centred lattice. Though a full diffraction experiment was collected, the disorder of the structure so far proved intractable (low-temperature model with half-occupancy gave $R = 0.12$, but led to no stable refinement).

In both structures, bond lengths in the cyclopentadienide ring are equivalent within experimental error, averaging 1.403(13) Å in **24** and 1.408(10) Å in **30**. These values are typical of an aromatic bond and similar to those found in a planar tetrakis(trifluoromethyl)cyclopentadienide moiety, in its complexes [Ru{η^5-$C_5H(CF_3)_4$}(C_5Me_5)] [average 1.428(13) Å],[10] [WCp(N)(Bu^t){η^1-$C_5(CF_3)_4$}] [1.42(2) Å][9] and organic zwitterionic derivatives Admt–C≡N$^+$[$C_5(CF_3)_4$]$^{-8}$ where Admt = adamantyl and $PhMe_2POC_5(CF_3)_4$ [1.40(1) Å].[26]

The tetrabutylammonium salt **20** crystallises in a trigonal lattice, with the diffraction pattern ambiguous between the space groups $P3_2$ and $P3_221$. In the former, the asymmetric unit comprises one anion and one cation. In fact, the position and geometry of the cation are consistent with the higher symmetry (*i.e.* the axis 2 through the nitrogen atom), but the anion, which in the $P3_221$ space group must also lie on a twofold axis [passing through the atoms C(5) and C(10) and the midpoint of the C(2)–C(3) bond], fits this symmetry only as a crude (and unrefinable) approximation. The structure solution and refinement

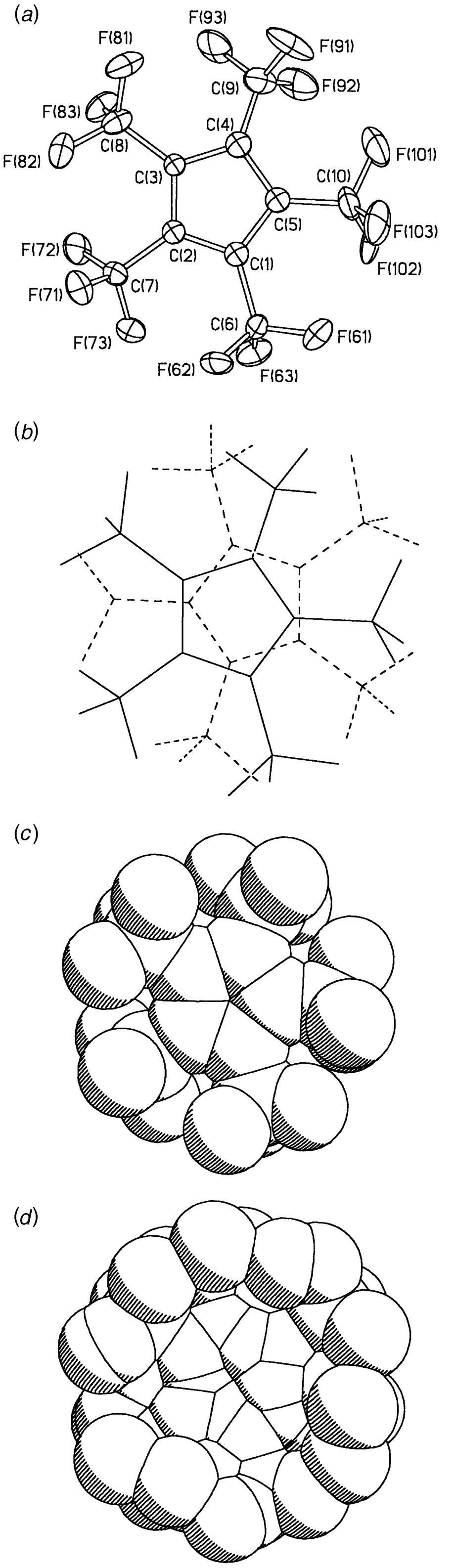


Fig. 3 $[C_5(CF_3)_5]^-$ anion in the crystal of **30**; (*a*) individual anion, showing 50% probability ellipsoids; (*b*) overlap of two positions, disordered over the inversion centre; (*c*) and (*d*) space-filling (van der Waals radii) representations, corresponding to (*a*) and (*b*), respectively. Both positions of the anion occupy essentially the same space. Bond distances (Å): C(1)–C(2) 1.393(13), C(2)–C(3) 1.398(13), C(3)–C(4) 1.413(18), C(4)–C(5) 1.419(11), C(5)–C(1) 1.414(18); average C(ring)–CF_3 1.51(1), C–F 1.34(1).

in the $P3_2$ space group was more successful. It revealed a striking difference between the behaviour of the cation and the anion (see Fig. 6). The former exhibits normal atomic displacement parameters and a usual molecular geometry, with an

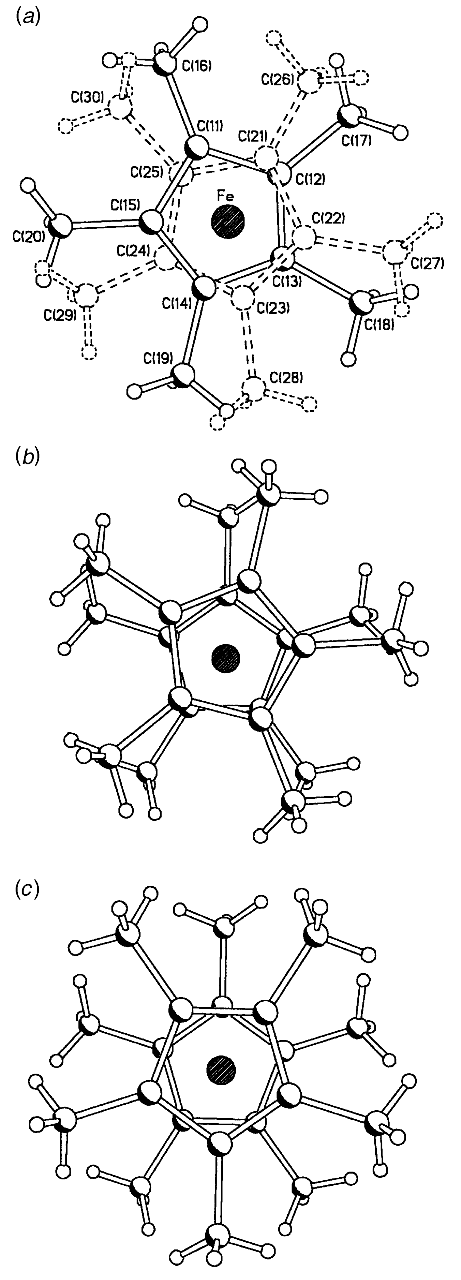


Fig. 4 $(C_5Me_5)_2Fe^+$ cation of **30**: (*a*) disorder of the C_5Me_5 ligand and atomic numbering (another ring is omitted); (*b*) and (*c*) two possible conformations of the cation. Bond distances (Å): Fe–C 2.091(6)–2.118(7), av. 2.100(8), C–C(ring) 1.43(2), C(ring)–Me 1.50(2).

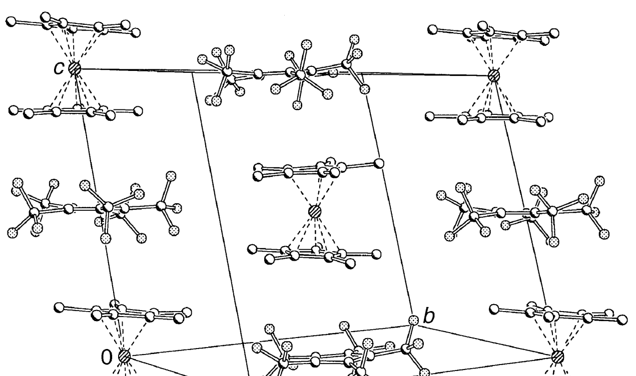


Fig. 5 Crystal packing in **30**, projection on the $(\bar{1}10)$ plane. Disorder is not shown.

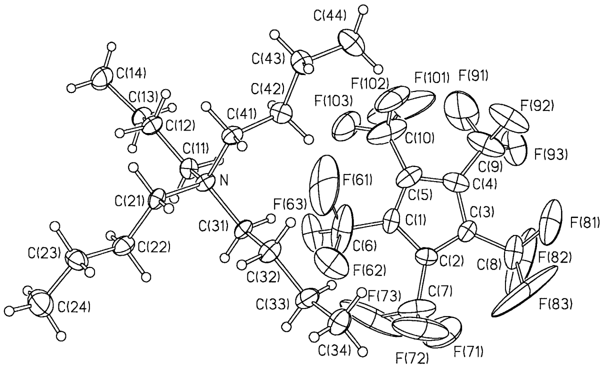


Fig. 6 Cation and anion in **20** (showing 30% probability ellipsoids); projection on the (0 1 0) plane. Average bond distances (Å): N–C 1.52(1), C–C(cation) 1.51(2), C–C(anion, ring) 1.39(2), C–C(anion, exocyclic) 1.45(3), C–F 1.35(8).

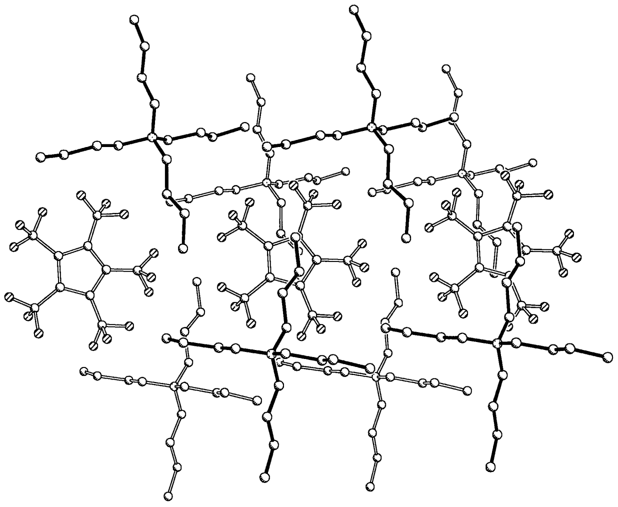


Fig. 7 A chain of anion surrounded with cations in the structure of **20**, projection on the (0 1 0) plane

almost ideal *trans* conformation of all the butyl groups. In the anion, the excessively elongated thermal ellipsoids and a substantial (up to 1.0 e Å^{-3}) residual electron density between the CF_3 groups indicate a strong disorder, probably in the form of simultaneous rotations of all CF_3 groups around the C–C bond, and of the anion as a whole around its five-fold axis. All our attempts to rationalise the disorder and distinguish individual positions of the anion were frustrated; the actual refinement of it as a single position naturally gave rather inaccurate molecular geometry.

Like in **24**, in **20** the cations divide the crystal space into separate infinite channels, filled with anions (Fig. 7), but the latter form chains rather than stacks. The axes of the channels are situated where the two-fold axis in a $P3_221$ space group would be, and the adjacent anions are related *via* the crystal lattice translation *a*.

Even in the more accurately determined structures, **24** and **30**, fine details of the cyclopentadienide anion geometry must be discussed with some circumspection, given its disorder and substantial flexibility (*vide infra*). Nevertheless, in both structures the anion shows rather similar conformations (see Table 3). The rings adopt a slight envelope conformation, folding along the C(2) · · · C(4) line by 2.9(7)° (**24**) or 3.9(3)° (**30**), with small tilting of exocyclic C–C bonds out of the ring plane. Conformations of the CF_3 groups relative to the ring are also similar. Such conformations can be described by two ultimate cases: (i) one of the C–F bonds lying in the ring plane, (ii) one of the C–F bonds lying in a plane perpendicular to the ring. The smallest of the CCCF torsion angles (τ) will be 0 for the former

Table 3 Conformation of the $[C_5(CF_3)_5]^-$ anion in structures **24** and **30**

	24		**30**		Calculation	
Position	φ°	τ_1°	φ°	τ_2°	φ°	τ_1°
1	1.4	−8.9	1.4	19.8	−0.3	−10.4
2	−3.4	−2.3	−3.4	−21.8	−4.3	−10.4
3	8.6	9.9	8.2	17.6	11.9	22.6
4	−7.5	−15.7	−6.5	−10.6	−7.0	−28.9
5	1.1	19.6	2.6	−6.2	0.1	28.7

φ = angle between a C–CF_3 bond and the C(1)C(2)C(4)C(5) plane; τ_1 = the smallest of C(n + 1)C(n)C(n + 5)F torsion angles, τ_2^- that of C(n − 1)C(n)C(n + 5)F.

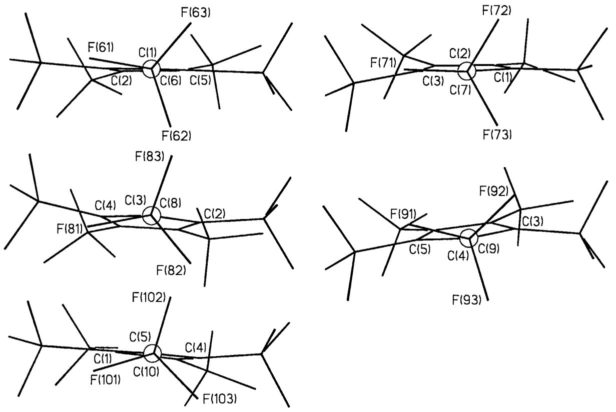


Fig. 8 Newman projections down all C–CF_3 bonds in the anion of **24**

conformation and 30° for the latter one. As far as F · · · F repulsions are concerned, conformation (i) of *all* CF_3 groups (giving the anion an overall D_{5h} symmetry) is intuitively the most favourable, as each in-plane fluorine atom fits into the gap between two of the next trifluoromethyl group, which are out-of-plane, while also coming closer to its positively charged carbon atom. Conformation (ii) can be relatively free from steric interactions only when orientations of adjacent CF_3 groups differ by a 180° rotation, which is only possible if the ring has an even number of atoms. In fact, in the present structures the conformations (Fig. 8) are intermediate between (i) and (ii), with τ varying from nil to 22°, but the C–F vectors closest to the plane all point in the same direction. Thus the main steric feature of conformation (i) is retained.

To clarify this problem, we performed a molecular-mechanics modelling of the dynamic behaviour of an isolated cyclopentadienide anion at $T = 150$ and 300 K. It proved that the lowest-energy conformation (presented in Table 3 for 150 K data) really corresponds to an envelope-like distortion of the ring, albeit with a somewhat larger folding (*ca.* 10° at 150 K, 13° at 300 K) than the observed one. The calculated out-of-plane bending of the exocyclic C–C bonds is in a semi-quantative agreement with the observed one. However, half-chair ring deformations of similar magnitude are only marginally higher in energy. Therefore, even at low temperature the ring is quickly migrating between various envelope conformations, accompanied by concerted out-of-plane bendings and rotations of the CF_3 groups. Such a puckering (revealed by both the experiment and the calculations) of the C_{10} skeleton illustrates clearly the severe crowding between trifluoromethyl groups in the anion and the even greater crowding that must exist in the corresponding cyclopentadiene **4** is clearly appreciated.

Experimental

^{1}H NMR Spectra were recorded on a Bruker AC250 spectrometer operating at 250.13 MHz or a Varian VXR400S spectrometer operating at 399.95 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 NMR Spectra were recorded on a Bruker AC250 spectrometer operating at 62.9 MHz or a Varian VXR400S spectrometer operating at 100.58 MHz. All spectra were recorded with tetramethylsilane and fluorotrichloromethane as internal references. *J* Values 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. All mass spectra were generated by electron impact or fast atom bombardment (FAB).

CAUTION: The unsaturated fluorocarbons described in this paper should be assumed to be toxic.

Synthesis of hexakis(trifluoromethyl)cyclopentadiene 4

Samples of 1,1,3,3,3-pentafluoropropene (2.20 g, 16.67 mmol), perfluoro-3,4-dimethylhexa-2,4-diene **2** (3.00 g, 8.29 mmol) and anhydrous acetonitrile (5 cm^3) were transferred under vacuum into a Carius tube (60 cm^3) containing dried caesium fluoride (5.00 g, 32.90 mmol), which was then sealed *in vacuo* and rotated, using a mechanical arm, at ambient temperature for 48 h. The tube was opened, volatile material was then removed by vacuum transfer, and the lower layer contained one component (by GLC) which was identified as *hexakis*(*trifluoromethyl*)*cyclopentadiene* **4** (2.9 g, 6.12 mmol, 74%), bp 109 °C (Found: C, 27.6; F, 72.3. $C_{11}F_{18}$ requires C, 27.8; F, 72.2%); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F); $\lambda_{max}(CH_2Cl_2)$/nm 253 (ε/dm^3 mol^{-1} cm^{-1} 1674); δ_F(376 MHz; $CDCl_3$) −55.58 [6 F, m, $(CF_3)_2C{-}CC\mathit{F}_3$], −59.35 [6 F, pseudo-septet, J_{CF_3,CF_3+CF_3} 10.9, $C{=}C(C\mathit{F}_3){-}C(C\mathit{F}_3){=}C$], −59.68 [6 F, m, $(C\mathit{F}_3)_2C{-}CCF_3$]; δ_C(100 MHz; $CDCl_3$) 66.51 [s, $(CF_3)_2\mathit{C}$], 117.83 (q, $J_{C,F}$ 276.5, CF_3), 118.83 (q, $J_{C,F}$ 274.7, CF_3), 120.23 (q, $J_{C,F}$ 288.5, CF_3), 137.69 (q, $J_{C,F}$ 40.7, C=C); *m/z* 474 (M^+, 10%) and 455 (40).

Distilled water (10 cm^3) was then added to the involatile material and a lower layer formed (1.76 g) which contained two resolved components by GLC (*ca.* 1:2), both with *m/z* = 586 as the highest value. The ^{19}F NMR spectrum showed *ca.* 11 CF_3 resonances (δ 54–80), and several which could be attributed to a CF_2 group (δ 98–108). Preparative scale gas chromatography was attempted to separate these components, with only limited success, and no further investigation was made.

Reaction of perfluoro-3,4-dimethylhexa-2,4-diene 2 with (*E*)-1,1,1,3,4,4,4-heptafluorobut-2-ene

A stainless steel autoclave was charged with a mixture of diene **2** (3.0 g, 8.29 mmol), (*E*)-2*H*-heptafluorobut-2-ene (1.5 g, 8.24 mmol) and dry caesieum fluoride (5.1 g, 33.55 mmol) in anhydrous acetonitrile (25 cm^3). The autoclave was then heated with rocking at 100 °C for 48 h. Analysis by ^{19}F NMR spectroscopy demonstrated the presence of a complex mixture (50:13:26) of *caesium pentakis*(*trifluoromethyl*)*cyclopentadienide* **15**, perfluoro-1,2,3,4-tetramethylcyclobutene, tetrakis(trifluoromethyl)furan and some diene **2**, after comparison with the data from authentic samples. This mixture was filtered and volatile components were removed under reduced pressure. The remaining oil partially crystallised over 168 h, and this was then washed with chloroform (20 cm^3) to give a white powder which was identified as *caesium pentakis*(*trifluoromethnyl*)*cyclopentadienide* **15** (1.9 g, 43%, 3.53 mmol), mp >300 °C (Found: C, 22.5. $C_{10}CsF_{15}$ requires C, 22.3%); ν_{max}/cm^{-1} 1110s–1250s (C–F), 1505m (C=C); δ_F(376 MHz; CD_3CN) −49.74 (s, CF_3); δ_C(100 MHz; $CDCl_3$) 124.67 (q, $J_{C,F}$ 270.6, CF_3), 110.63 (q, $J_{C,F}$ 19.2, $\mathit{C}{-}CF_3$); *m/z* FAB$^-$ 405 (M^+, 100%) and FAB$^+$ 133 (M^+, 100%), 225 (Cs + glycerol, 6).

Reactions using diene 4

With tetraethylammonium iodide. Tetraethylammonium iodide (0.49 g, 1.91 mmol) was added to anhydrous acetonitrile (10 cm^3) and heated under reflux at 80 °C. Diene **4** (1.00 g, 2.11 mmol) was then added slowly, with the formation of a red colour, and the mixture was refluxed for 48 h, after which time the solution was cooled and filtered. Solvent was then removed under reduced pressure and the residue redissolved in dichloromethane (10 cm^3), which was then washed with saturated aqueous sodium metabisulfite (10 cm^3), in order to remove any iodine which was present. The lower layer was then isolated, hexane (10 cm^3) was added and the mixture was cooled (−15 °C) for 2 days. Colourless crystals formed, which were identified as *tetraethylammonium pentakis*(*trifluoromethyl*)-*cyclopentadienide* **18** (0.85 g, 1.59 mmol, 75%), mp 241 °C (decomp.) (Found: C, 40.2; H, 3.8; N, 2.5. $C_{18}H_{20}F_{15}N$ requires C, 40.4; H, 3.7; N, 2.6%); ν_{max}/cm^{-1} 2780w and 2990w (C–H), 1495m (aromatic C=C), 1180s–1240s (C–F); δ_H(400 MHz; CD_3CN) 1.20 (3 H, tt, J_{CH_3,CH_2} 7.2, $J_{CH_3,N}$ 1.6, CH_3), 3.15 (2 H, q, J_{CH_2,CH_3} 7.2, CH_2); δ_F(376 MHz; CD_3CN) −50.99 (s, CF_3); δ_C(100 MHz; CD_3CN) 15.67 (s, CH_3), 53.04 (t, $J_{CH_2,N}$ 2.6, CH_2), 110.21 (q, $J_{C,F}$ 19.2, $\mathit{C}{-}CF_3$), 124.63 (q, $J_{C,F}$ 270.9, CF_3); *m/z* FAB$^-$ 405 (M +, 100%) and FAB$^+$ 130 (M^+, 25%).

With tetrapropylammonium iodide. Tetrapropylammonium iodide (0.59 g, 1.89 mmol) was added to anhydrous acetonitrile (10 cm^3), the mixture was refluxed at 80 °C and then diene **4** (1.00 g, 2.11 mmol) was added. Using the procedure described earlier, colourless crystals were isolated and identified as *tetrapropylammonium pentakis*(*trifluoromethyl*)*cyclopentadienide* **19** (0.90 g, 1.47 mmol, 73%), mp 141–142 °C (Found: C, 44.7; H, 4.8; N, 2.5. $C_{22}H_{28}F_{15}N$ requires C, 44.9; H, 4.8; N, 2.4%); ν_{max}/cm^{-1} 2900w–3000w (C–H), 1400s (aromatic C=C), 1170s–1250s (C–F); δ_H(400 MHz; CD_3CN) 0.94 (3 H, t, J_{CH_3,CH_2} 7.2, CH_3), 1.65 (2 H, sextet, J_{CH_2,CH_3+CH_2} 7.6, $CH_2C\mathit{H}_2CH_3$), 3.04 (2 H, m, $C\mathit{H}_2CH_2CH_3$); δ_F(376 MHz; CD_3CN) −50.99 (s, CF_3); δ_C(100 MHz; CD_3CN) 15.28 (s, CH_3), 30.95 (s, $CH_2\mathit{C}H_2CH_3$), 55.20 (s, $\mathit{C}H_2CH_2CH_3$), 110.11 (q, $J_{C,F}$ 19.0, $\mathit{C}{-}CF_3$), 123.31 (q, $J_{C,F}$ 269.7, CF_3); *m/z* FAB$^-$ 405 (M^+, 100%) and FAB$^+$ 186 (M^+, 100%).

With tetrabutylammonium iodide. Tetrabutylammonium iodide (0.70 g, 1.90 mmol) was added to anhydrous acetonitrile (10 cm^3), the mixture was refluxed at 80 °C and then diene **4** (1.00 g, 2.11 mmol) was added. Using the procedure described earlier, colourless cuboidal crystals were isolated and identified as *tetrabutylammonium pentakis*(*trifluoromethyl*)*cyclopentadienide* **20** (0.95 g, 1.47 mmol, 70%), mp 118–119 °C (Found: C, 48.2; H, 5.4; N, 2.2. $C_{26}H_{36}F_{15}N$ requires C, 48.2; H, 5.6; N, 2.2%); ν_{max}/cm^{-1} 2880w–3000m (C–H), 1495m (aromatic C=C), 1180s–1300s (C–F); δ_H(400 MHz; CD_3CN) 0.96 [3 H, t, J_{CH_3,CH_2} 7.2, $(CH_2)_3C\mathit{H}_3$], 1.35 [2 H, sextet, J_{CH_2,CH_3+CH_2} 7.6, $(CH_2)_2C\mathit{H}_2CH_3$], 1.60 (2 H, quintet, J_{CH_2,CH_2+CH_2} 8.4, $CH_2C\mathit{H}_2CH_2CH_3$), 3.08 [2 H, m, $C\mathit{H}_2(CH_2)_2CH_3$]; δ_F(376 MHz; CD_3CN) −50.51 (s, CF_3); δ_C(100 MHz; CD_3CN) 13.13 (s, CH_3), 19.22 [s, $(CH_2)_2\mathit{C}H_2CH_3$], 23.43 (s, $CH_2\mathit{C}H_2CH_2CH_3$), 58.46 [s, $\mathit{C}H_2(CH_2)_2CH_3$], 109.62 (q, $J_{C,F}$ 18.5, $\mathit{C}{-}CF_3$), 123.57 (q, $J_{C,F}$ 269.0, CF_3); *m/z* FAB$^-$ 405 (M^+, 100%) and FAB$^+$ 242 (M^+, 23%).

With tetrabutylammonium iodide under ultraviolet irradiation. A quartz Carius tube (30 cm^3) containing a small magnetic stirrer bar was charged with tetrabutylammonium iodide (0.70 g, 1.90 mmol), diene **4** (1.00 g, 2.11 mmol) and anhydrous acetonitrile (10 cm^3). The tube was sealed *in vacuo* and irradiated with a medium pressure mercury lamp (1 kW) for 24 h with continuous stirring. After this time a sample of the neat mixture was analysed by ^{19}F NMR and shown to contain iodotrifluoromethane and *tetrabutylammonium pentakis*(*trifluoromethyl*)-*cyclopentdienide* **20**, after comparison with the data from authentic samples; see above.

With tetraburylammonium iodide in the presence of *m*-dinitrobenzene. Tetrabutylammonium iodide (0.70 g, 1.90 mmol), *m*-dinitrobenzene (0.20 g, 1.21 mmol) and diene **4** (1.00 g, 2.11 mmol) were added to anhydrous acetonitrile (10 cm^3) and the mixture was refluxed, for 48 h, with the development of a red colour. After this time a sample was analysed by ^{19}F NMR and shown to contain diene **4** and *tetrabutylammonium pentakis*(*trifluoromethyl*)*cyclopentadienide* **20** (50% yield by integration), after comparison with the data from authentic samples; see above.

With tetrabutylammonium iodide in the presence of α-pinene. Tetrabutylammonium iodide (0.70 g, 1.90 mmol), α-pinene (0.20 g, 0.46 mmol) and diene **4** (1.00 g, 2.11 mmol) were added to anhydrous acetonitrile (10 cm^3) and the mixture was refluxed, for 48 h, with the development of a red colour. After this time a sample was analysed by ^{19}F NMR and shown to contain diene **4** and *tetrabutylammonium pentakis*(*trifluoromethyl*)*cyclopentadienide* **20** (40% yield by integration), after comparison with the data from authentic samples; see above.

With caesium iodide. Caesium iodide (0.70 g, 2.69 mmol), diene **4** (1.00 g, 2.11 mmol) and anhydrous acetonitrile (10 cm^3) were refluxed at 80 °C for 7 days. Using the procedure described for **18**, *caesium pentakis*(*trifluoromethyl*)*cyclopentadienide* **15** was isolated (65% yield by ^{19}F NMR integration of the crude mixture against trifluorotoluene as a marker, 0.30 g, 0.56 mmol, 26%) and identified by comparison with the data from an authentic sample; see above.

With potassium iodide. Potassium iodide (0.44 g, 2.70 mmol), diene **4** (1.00 g, 2.11 mmol) and anhydrous acetonitrile (10 cm^3) were refluxed at 80 °C for 4 days. Using the procedure described for **18**, *potassium pentakis*(*trifluoromethyl*)*cyclopentadienide* **23** was isolated (75% yield by ^{19}F NMR integration of the crude mixture against trifluorotoluene as a marker, 0.40 g, 0.90 mmol, 42%), mp >300 °C (Found: C, 27.3. $C_{10}F_{15}K$ requires C, 27.0%); ν_{max}/cm^{-1} 1150s–1260s (C–F), 1510m (aromatic C=C); δ_F(376 MHz; CD$_3$CN) −49.8 (s, CF$_3$); δ_C(100 MHz; CDCl$_3$) 123.7 (q, $J_{C,F}$ 269.9, CF$_3$); *m/z* FAB$^-$ 405 (M$^+$, 100%) and FAB$^+$ 39 (M$^+$, 42%), 131 (K$^+$ + glycerol, 2).

With sodium iodide. Sodium iodide (0.40 g, 2.70 mmol), diene **4** (1.00 g, 2.11 mmol) and anhydrous acetonitrile (10 cm^3) were refluxed at 80 °C for 48 h. Using the procedure described for **18**, *sodium pentakis*(*trifluoromethyl*)*cyclopentadienide* **22** was isolated (95% yield by ^{19}F NMR integration of the crude mixture against trifluorotoluene as a marker, 0.20 g, 0.47 mmol, 22%), mp > 300 °C (Found: C, 28.1. $C_{10}F_{15}Na$ requires C, 28.0%); ν_{max}/cm^{-1}1100s–1230s (C–F); δ_F(376 MHz; CD$_3$CN) −49.6 (s, CF$_3$); *m/z* FAB$^-$ 405 (M$^+$, 100%) and FAB$^+$ 23 (M$^+$, 42%), 115 (Na$^+$ + glycerol, 100%).

With lithium iodide. Lithium iodide (0.37 g, 2.76 mmol), diene **4** (1.00 g, 2.11 mmol) and anhydrous acetonitrile (10 cm^3) were refluxed at 80 °C for 36 h. Using the procedure described for **18**, *lithium pentakis*(*trifluoromethyl*)*cyclopentadienide* **21** was isolated (95% yield by ^{19}F NMR integration of the crude mixture against trifluorotoluene as a marker, 0.15 g, 17%), mp >300 °C (Found: C, 28.8. $C_{10}F_{15}Li$ requires C, 29.1%);ν_{max}/cm^{-1} 1100s–1230s (C–F); δ_F(376 MHz; CD$_3$CN) −49.9 (s, CF$_3$); *m/z* FAB$^-$ 405 (M$^+$, 100%) and FAB$^+$ 99 (Li$^+$ + glycerol, 100%), 191 (Li$^+$ + 2 glycerol).

With copper iodide under ultraviolet irradiation. A quartz Carius tube (20 cm^3) charged with diene **4** (1.00 g, 2.11 mmol), copper iodide (0.45 g, 2.37 mmol) and anhydrous acetonitrile (5 cm^3) was sealed *in vacuo* and agitated for 48 h on a rotating arm, whilst irradiating with a medium pressure mercury lamp (1 kW). After this time the tube was opened and the insoluble material filtered off to leave a brown solution. Solvent was removed under reduced pressure and the residue (1.05 g) was then dissolved in dichloromethane and stored at −15 °C for 3 days. Small needle-shaped crystals were formed and two subsequent recrystallisations (dichloromethane–hexane; 1:1) yielded *tetrakis*(*acetonitrile*)*copper*(I) *pentakis*(*trifluoromethyl*)*cyclopentadienide* **24** (0.55 g, 0.87 mmol, 41%), mp 100 °C (decomp.) (Found: C, 33.9; N, 8.7; H, 1.8. $C_{18}H_{12}CuF_{15}N_4$ requires C, 34.2; N, 8.9; H, 1.9%); ν_{max}/cm^{-1} 2750w and 2950w (C–H), 2325 (C≡N), 1530m (aromatic C=C), 1215s and 1120s (C–F); λ_{max}(CH$_3$CN)/nm 208 (ε/dm^3 mol^{-1} 70 000); δ_H(400 MHz; CDCl$_3$) 2.00 (s, CH$_3$); δ_F(376 MHz; CD$_3$CN) −49.72 (s, CF$_3$); δ_C(100 MHz; CDCl$_3$) 1.00 (4 C, s, CH$_3$), 118.03 (4 C, s, CN), 123.44 (5 C, q, $J_{C,F}$ 269.3, CF$_3$); *m/z* FAB$^-$ 405 (M$^+$, 100%) and FAB$^+$ 227 (Cu$^+$ + 4CH$_3$CN, 13%), 186 (Cu$^+$ + 3CH$_3$CN, 8), 145 (Cu$^+$ + 2CH$_3$CN, 100), 104 (Cu$^+$ + CH$_3$CN, 77), 63 (Cu$^+$, 36).

With silver iodide under ultraviolet irradiation. A quartz Carius tube (20 cm^3) was charged with diene **4** (1.00 g, 2.11 mmol), silver iodide (0.60 g, 2.55 mmol) and anhydrous acetonitrile (5 cm^3). Using the procedure described for **24**, *tetrakis*(*acetonitrile*)*silver*(I) *pentakis*(*trifluoromethyl*)*cyclopentadienide* **28** was isolated (85% yield by ^{19}F NMR integration against trifluorotoluene as a marker, 0.40 g, 28%), mp >300 °C (decomp.) (Found: C, 31.9; N, 8.0; H, 1.8. $C_{18}H_{12}AgF_{15}N_4$ requires C, 31.9; N, 8.2; H, 1.8%); ν_{max}/cm^{-1} 2750w and 2950w (C–H), 2325 (C≡H), 1496m (aromatic C=C), 1215s and 1120s (C–F); δ_H(400 MHz; CDCl$_3$) 2.00 (s, CH$_3$); δ_F(376 MHz; CD$_3$CN) −49.70 (s, CF$_3$); *m/z* FAB$^-$ 405 (M$^+$, 100%) and FAB$^+$ 108 (Ag$^+$, 100%).

Thermal reaction with copper powder. Copper powder (0.25 g, 3.94 mmol) was added to anhydrous acetonitrile (10 cm^3) which was refluxed at 80 °C. Diene **4** (1.00 g, 2.11 mmol) was then slowly added and the solution was refluxed for 48 h, with the formation of a dark green colour. After this time the solution was cooled and filtered to leave a brown solution. The crude solution was studied by ^{19}F NMR which revealed a large peak at δ_F −49.8 (rel. int. 5) and a range of smaller peaks between δ_F −56 and −78 (rel. int. 1). Solvent and volatile products were removed under reduced pressure and the residue (1.24 g) was then dissolved in dichloromethane and refrigerated (−15 °C) for 3 days. Small needle-shaped crystals were formed and two subsequent recrystallisations (dichloromethane–hexane; 1:1) yielded *tetrakis*(*acetonitrile*)*copper*(I) *pentakis*(*trifluoromethyl*)-*cyclopentadienide* **24** (0.80 g, 1.27 mmol, 60%), which was identified by comparison with data from an authentic sample; see above.

Copper powder with ultraviolet irradiation. A quartz Carius tube (20 cm^3) was charged with diene **4** (1.00 g, 2.11 mmol), copper powder (0.20 g, 3.17 mmol) and anhydrous acetonitrile (5 cm^3). Using the procedure described above, small needle-shaped crystals were isolated and identified as *tetrakis*(*acetonitrile*)*copper*(I) *pentakis*(*trifluoromethyl*)*cyclopentadienide* **24** (0.85 g, 1.35 mmol, 64%) by comparison with data from an authentic sample; see above.

Nickel powder with ultraviolet irradiation. A quartz Carius tube (20 cm^3) charged with diene **4** (1.00 g, 2.11 mmol), nickel powder (0.20 g, 3.38 mmol) and anhydrous acetonitrile (5 cm^3), was sealed *in vacuo* and agitated for 48 h on a rotating arm, whilst irradiating with a medium pressure mercury lamp (1 kW). After this time the tube was opened in a glove box under an atmosphere of dry nitrogen and insoluble material was filtered off to leave a pale blue upper layer and a lower clear colourless layer of unreacted diene (0.55 g, 1.16 mmol, 45% conversion). The upper layer was isolated and solvent removed under reduced pressure, and the residue (0.50 g) was then washed with dichloromethane to give a fine white powder which was shown to be *hexakis*(*acetonitrile*)*nickel*(II) *bis*[*pentakis*(*trifluoromethyl*)*cyclopentadienide*] **25** (0.40 g, 0.36 mmol, 76% based on reacted diene), mp >300 °C (decomp.) (Found: C, 34.1; N, 7.2; H, 1.5. $C_{32}H_{18}F_{30}N_6Ni$ requires C, 34.4; N, 7.5; H, 1.6%); ν_{max}/cm^{-1} 2753w and 2950w (C–H), 2320 (C≡N), 1505m (aromatic C=C), 1210s and 1125s (C–F); δ_H(400 MHz; CDCl$_3$) 2.00 (br s, CH$_3$); δ_F(376 MHz; CD$_3$CN) −49.84 (s, CF$_3$); δ_C(100 MHz; CDCl$_3$) 1.00 (s, CH$_3$), 118.05 (s, CN), 121.00 (br, CF$_3$); *m/z* FAB$^-$ 405 (M$^+$, 100%) and FAB$^+$ 58 (Ni^{2+}, 16%).

Cobalt powder with ultraviolet irradiation. A quartz Carius tube (20 cm^3) was charged with diene **4** (1.00 g, 2.11 mmol), cobalt powder (0.20 g, 3.38 mmol) and anhydrous acetonitrile (5 cm^3). Using the procedure described for **25** (recovered diene; 0.45 g, 0.95 mmol, 55% conversion), a fine white powder was identified as *hexakis*(*acetonitrile*)*cobalt*(II) *bis*[*pentakis*(*trifluoromethyl*)*cyclopentadienide*] **27** (0.40 g, 0.36 mmol, 62%

based on reacted diene), mp >300 °C (decomp.) (Found: C, 34.1; N, 7.0; H, 1.5. $C_{32}H_{18}CoF_{30}N_6$ requires C, 34.4; N, 7.5; H, 1.6%); ν_{max}/cm^{-1} 2753w and 2947w (C–H), 2330 (C≡N), 1497m (aromatic C=C), 1215s and 1127s (C–F); δ_H(400 MHz; $CDCl_3$) 2.00 (br s, CH_3); δ_F(376 MHz; CD_3CN) −49.82 (s, CF_3); δ_C(100 MHz; $CDCl_3$) 121.00 (br, CF_3); *m/z* FAB$^-$ 405 (M$^+$, 100%) and FAB$^+$ 59 (Co^{2+}, 21%).

Iron powder with ultraviolet irradiation. A quartz Carius tube (20 cm^3) was charged with diene **4** (1.00 g, 2.11 mmol), iron powder (0.20 g, 3.63 mmol) and anhydrous acetonitrile (5 cm^3). Using the procedure described for **25** (recovered diene; 0.48 g, 1.01 mmol, 52% conversion), a fine white powder was identified as *hexakis*(*actonitrile*)*iron*(II) *bis*[*pentakis*(*trifluoromethyl*)*cyclopentadienide*] **26** (0.45 g, 0.40 mmol, 74% based on reacted diene), mp > 300 °C (decomp.) (Found: C, 34.5; N, 7.2; H, 1.6. $C_{32}H_{18}F_{30}FeN_6$ requires C, 34.5; N, 7.5; H, 1.6%); ν_{max}/cm^{-1} 2750w and 2954w (C–H), 2325 (C≡N), 1500m (aromatic C=C), 1210s and 1117s (C–F); δ_H(400 MHz; $CDCl_3$) 2.00 (br s, CH_3); δ_F(376 MHz; CD_3CN) −49.93 (s, CF_3); δ_C(100 MHz; $CDCl_3$) 121.00 (br, CF_3); *m/z* FAB$^-$ 405 (M$^+$, 100%) and FAB$^+$ 56 (Fe^{2+}, 21%).

With decamethylferrocene. A mixture containing decamethylferrocene (0.60 g, 1.84 mmol) and dry acetonitrile (70 cm^3) was heated under reflux at 85 °C. Diene **4** (1.00 g, 2.1 mmol) was then slowly added, and a dark green colour immediately formed. The mixture was refluxed for 17.5 h, after which the solvent was evaporated to half its volume and the solution cooled to −30 °C for 6 h using a cryostat. No crystalline material was observed, so the solvent was removed and the resultant residue recrystallised from a minimum of dry acetonitrile to give small, dark green crystals, identified as *decamethylferrocenium pentakis*(*trifluoromethyl*)*cyclopentadienide* **30** (0.86 g, 1.18 mmol, 64%), mp >330 °C (Found: C, 49.2; H, 4.2; Fe, 8.2. $C_{30}H_{30}F_{15}Fe$ requires C, 49.3; H, 4.10; Fe, 7.7); ν_{max}/cm^{-1} 2905w and 2985w (C–H), 1505s (aromatic C=C), 1200s and 1120s (C–F); δ_H(400 MHz; CD_3CN) 5.45 (s, CH_3); δ_F(376 MHz; CD_3CN) −49.73 (s, CF_3); δ_C(100 MHz; CD_3CN) 55.38 (s, *C*–CH_3), 124.70 (q, $J_{C,F}$ 269.0, CF_3); *m/z* FAB$^-$ 405 (M$^+$, 100%) and FAB$^+$ 326 [$(C_{10}H_{15})_2Fe$, 31%].

Electrochemistry

General apparatus. Cyclic voltammetry was performed using a 'home-made' potentiostat[41] with a positive feedback ohmic drop compensation and a Tacussel GSTP4 signal generator. The working electrode was a glassy carbon (Tokai Corp.) disc (3 mm diameter) and the reference electrode a saturated calomel electrode (SCE). Calculations were made using a Digisim 2.0, Cyclic Voltammetric Simulator (Bioanalytical Systems, Inc.) on a Pentium 90 computer. The supporting electrolyte was tetraethylammonium tetrafluoroborate (Et_4NBF_4; Fluka *puriss.*) and acetonitrile was used as a solvent, without purification.

Electrolysis of diene **4**. A solution of hexakis(trifluoromethyl)cyclopentadiene **4** (0.24 g, 0.51 mmol) and Et_4NBF_4 (2.17 g, 10 mmol) in acetonitrile (80 cm^3) was reduced at −0.45 V (*vs.* SCE), in a three-compartment cell, until all the starting material was consumed (0.7 F mol^{-1} as checked by cyclic voltammetry). A circular carbon felt (5 cm × 5 cm) was used as the cathode, and was separated from the anolyte (carbon felt) with a glass frit of porosity 4. The solution was then evaporated to dryness, using a water aspirator (bath temperature below 40 °C), to give a white residue as crude material. The presence of pentakis(trifluoromethyl)cyclopentadienide ion **5** was confirmed by ^{19}F NMR spectroscopy; δ_F(376 MHz; CD_3CN) −51.2 (s). Two other resonances were observed (δ_F 75.9 and −83.7; rel. int. 1), which integrated to approximately 9 (anion **5**) : 1 (two other components).

X-ray crystallography

Low-temperature X-ray diffraction experiments were carried out using Cryostream open-flow N_2 cryostats. SHELXTL-Plus VMS software[42] was used for structure solutions and refinement, the latter was performed against F^2 of all data with a two term weighting scheme. Of the discrepancy factors given below, *wR* and goodness-of-fit *S* refer to F^2 of all data, *R* to *F* of observed data, with $I \geq 2\sigma(I)$. Atomic coordinates and thermal parameters, bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/56.

Compound **24**: $C_8H_{12}N_4{\cdot}Cu^+C_{10}F_{15}^-$, $M = 632.9$, orthorhombic, $T = 150$ K, $a = 21.100(2)$, $b = 43.273(4)$, $c = 5.216(1)$ Å, $V = 4763(1)$ Å^3 from 399 reflections with $12 < \theta < 23°$, space group *Pmmn* (No. 59), $Z = 8$, $D_C = 1.765$ g, cm^{-3}, $F(000) = 2496$, $\mu = 10.5$ cm^{-1}, colourless crystal of dimensions 0.3 × 0.2 × 0.1 mm. Data collection on a Siemens 3-circle diffractometer with a CCD area detector, graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å, ω scan mode, $2\theta \leq 51.5°$, 19 425 total, 4390 unique and 2907 observed data. Substantial overlap of reflections along the b^* axis resulted in a rather high R_{int} of 0.136 and an irreducible final *R*. The structure was solved by a combination of Patterson and direct methods. All non-H atoms were refined by full-matrix least-squares with anisotopic displacement parameters and all methyl groups as rigid bodies with refined U_{iso} [all of them, except C(32)H$_3$, were treated as disordered over two symmetrically-related orientations]. The refinement of 390 variables against 3827 non-negative data converged at $wR = 0.229$, $R = 0.082$, $S = 1.08$, max. final shift/esd, ratio of 0.13 (Me group rotation). The largest residual peaks of electron density (0.7–1.1 e Å^{-3}) were located in the vicinity of Cu atoms and some smaller ones (0.4–0.6 e Å^3) between CF_3 groups of the anion. The latter peaks could be interpreted as a small (10–15%) contribution of another orientation of the anion, staggered with respect to the major one, but refinement of this model gave no meaningful improvement.

Compound **30**: $C_{20}H_{30}{\cdot}Fe^+C_{10}F_{15}^-$, $M = 731.4$, monoclinic, $T = 150$ K, $a = 9.089(2)$, $b = 14.956(2)$, $c = 11.976(2)$ Å, $\beta = 110.73(1)°$, $V = 1522.5(5)$ Å^3, from 25 reflections with $16 < \theta < 25°$, space group $P2_1/n$ (No. 14), $Z = 2$, $D_C = 1.595$ g cm^{-3}, $F(000) = 742$, $\mu = 6.1$ cm^{-1}, green crystal of dimensions 0.5 × 0.25 × 0.1 mm. Data collection on a Rigaku AFC6S 4-circle diffractometer, graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å), ω–2θ scan mode, $2\theta \leq 56°$, 3124 total, 2959 unique ($R_{int} = 0.060$) and 1663 observed data. Empirical absorption correction (TEXSAN software[43]) was insignificant ($T_{min} = 0.96$, $T_{max} = 1.00$). Structure solution by direct methods proved impossible, while the position of the Fe atom at the inversion centre (clear from the Patterson map) rendered it useless for phase determination. In the event, the first coordination sphere of the Fe atom was determined from Patterson vectors. Subsequent Fourier expansion revealed the entire cation, but a rather shapeless cloud of electron density at the anion position. The latter was rationalised essentially by a trial-and-error fitting of a rigid-body pentamethylcyclopentadienyl skeleton. All fluorine positions were then located from a Fourier map. With the anion disordered over two inversion-related positions and the C_5Me_5 ring over two symmetrically independent positions with essentially equal occupancies (proved by refinement of occupancy factors), every atom in the structure was refined with a 50% occupancy. Final refinement was performed by full-matrix least-squares with *no* geometrical restraints for non-H atoms. Ring carbon atoms were refined in isotropic approximation, other non-H atoms with anisotropic displacement parameters, and methyl groups were refined as rigid bodies with refined isotropic U for each three hydrogens. The refinement of 357 variables converged at $R = 0.042$, $wR = 0.108$, $S = 1.03$, residual $\Delta\rho_{max} = 0.28$, $\Delta\rho_{min} = 0.26$ e Å^{-3}, max. final shift/esd ratio of 0.002. Our attempts to refine the structure in space groups $P2_1$ and *Pn*, or as a twinned crystal, did not lead to any meaningful improvement. At room temperature, the lattice is monoclinic I, $a = 9.308(2)$, $b = 15.023(4)$, $c = 12.164(3)$ Å, $\beta = 110.34(2)°$, $V = 1594.9(7)$ Å^3 from 24 reflections with $12 < \theta < 13°$, measured on a 4-circle Siemens P4 diffractometer (Mo-Kα radiation). Zonal checks did not reveal any larger cell.

Compound **20**: $C_{16}H_{36}N^+C_{10}F_{15}^-$, $M = 647.6$, trigonal, $T = 150$ K, $a = 9.5179(6)$, $c = 28.926(2)$ Å, $V = 2269.3(3)$ Å^3, from 35 reflections with $7 < \theta < 13°$, space group $P3_2$ (No. 145), $Z = 3$, $D_C = 1.42$ g cm^{-3}, $F(000) = 1002$, $\mu = 1.5$ cm^{-1}, colourless crystal of dimensions 0.4 × 0.35 × 0.25 mm. Data collection on a 4-circle Siemens P4 diffractometer, graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å), ω–2θ scan mode, $2\theta \le 50°$, 5129 total, 4178 unique ($R_{int} = 0.027$) and 2592 observed data. The structure was solved by direct methods and refined by full-matrix least-squares (all non-H atoms with anisotropic displacement parameters, all H atoms 'riding'). Soft restraints were imposed on the anion geometry (five-fold symmetry on the C_{10} skeleton, three-fold symmetry on the CF_3 groups). The refinement of 379 variables (with 76 restraints) converged at $wR = 0.285$, $S = 1.57$, $R = 0.111$, max. shift/esd ratio 0.01, residual $\Delta\rho_{max} = 1.00$, $\Delta\rho_{min} = -0.52$ e Å^{-3}. Various models of disorder in the anion were tested (two staggered positions of the ring, 'ideal' disorder of all CF_3 groups, eccentric overlap similar to the pattern of **24**, *etc.*); none of them gave R below 0.20 with meaningful geometrical parameters. The refinement in the space group $P3_221$ (No. 154) with the (disordered) anion in a 2(a) special position gave $R = 0.14$ and much worse geometric parameters.

Molecular dynamics calculations

Molecular dynamics calculations for the pentakis(trifluoromethyl)cyclopentadienide anion were performed using CHEM-X software.[44] A molecular dynamics run was extended over 50 ps at 150 K with 0.5 fc steps. The observed energy range was 0.0 to 18.7 kcal mol^{-1}. Twenty-three conformations with lowest energies (≤2.0 kcal mol^{-1}) were sampled from this run and their structural parameters (torsion angles, distortions of the ring planarity, *etc.*) were determined. A run for $T = 300$ K was performed in the same manner, giving energy variations from 0 to 20.0 kcal mol^{-1}; 29 conformations with the energy below 2.5 kcal mol^{-1} were sampled for geometrical analysis.

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