# Direct Syntheses of Pentakis(trifluoromethyl)cyclopentadienide Salts and Related Dienes

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Direct routes for the synthesis of pentakis(trifluoromethyl)cyclopentadienide salts, hexakis(trifluoromethyl)cyclopentadiene and 5H-pentakis(trifluoromethyl)cyclopentadiene are described.

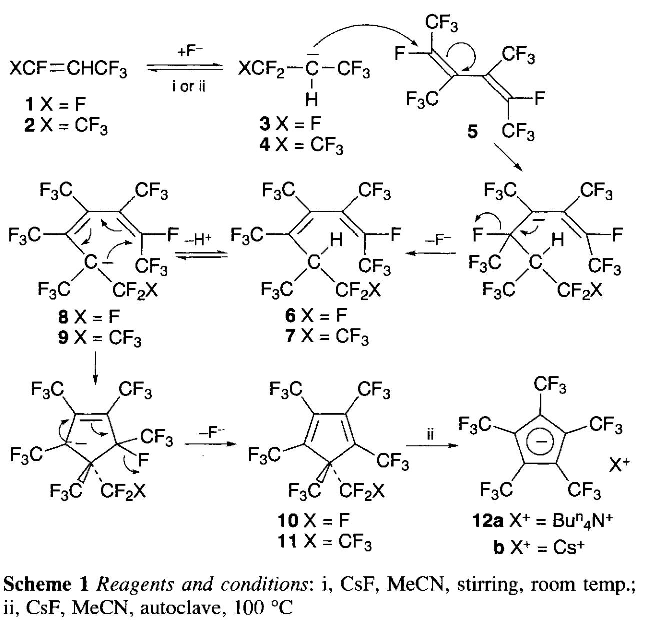
There is a general interest in the synthesis of cyclopentadienyl derivatives containing trifluoromethyl groups, bearing in mind the possibility of attachment to transition metals and subsequent potential enhanced catalytic activity. Systems containing up to four trifluoromethyl groups have been described[1] and an elegant but largely academic route to the pentakis(trifluoromethyl)cyclopentadienide anion **12** has also been reported.[2]

We have recently reported an efficient synthesis of the fluorinated diene **5** and some derived tetrakis(trifluoromethyl)cyclopentadienide derivatives[3,4] and here we describe some novel applications of this methodology, including a new approach to the synthesis of **12** that is outlined in Scheme 1. Reaction of pentafluoropropene **1** with fluoride ion generates the anion **3**, which then reacts with fluorinated diene **5**. The presumed intermediate **6** reacts further with fluoride ion (now as a base, rather than nucleophile), generating a new anion **8**, which then cyclises, with loss of fluoride ion, giving the new diene, hexakis(trifluoromethyl)cyclopentadiene **10**, in 74% isolated yield.

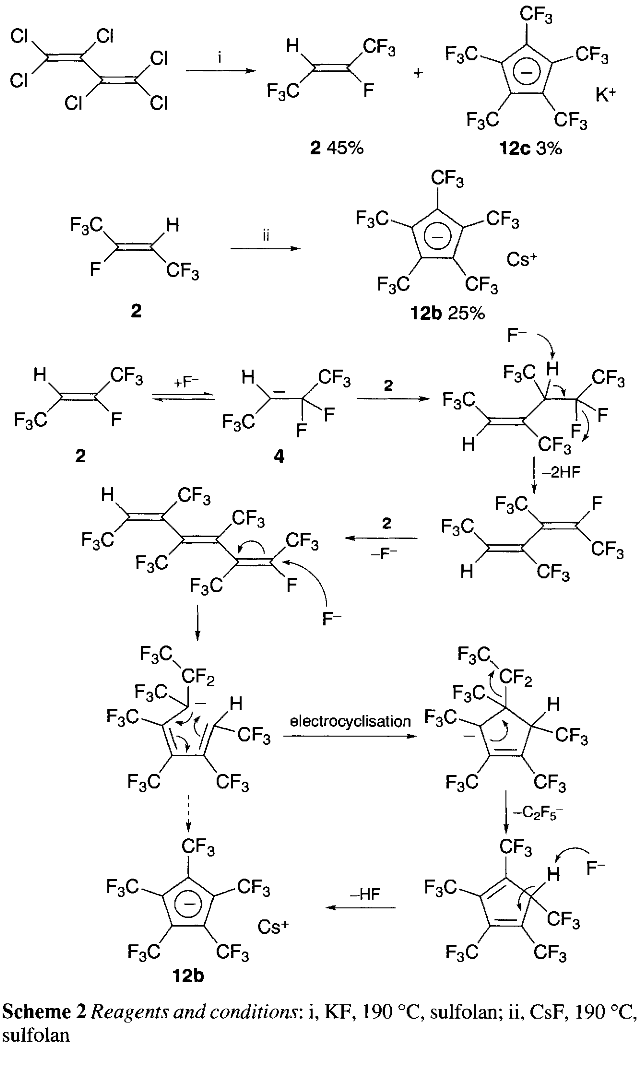
The diene **10** was easily identified by NMR data, giving: $\delta_F$ −55.6, −59.4, and −59.7 (all relative intensity 1). Elemental analysis and MS data also confirmed the structure **10**. We have been unable, previously, to isolate the diene stage that corresponds with **10** in related systems.[4] Subsequently, we obtained the pentakis(trifluoromethyl)cyclopentadienide anion **12a** (70% yield) by reaction of **10** with tetrabutylammonium iodide. The salt **12a** gave very simple NMR data: $\delta_F$ −50.5 and $\delta_C$ 109.6 and 123.6 (excluding data for the counter-ion). In an alternative approach to **12**, we used the more accessible 2H-heptafluorobut-2-ene **2** and this process, Scheme 1, proceeded *via* **4**, **7**, **9** and **11** but, remarkably, the diene **11** could not be isolated and this reaction led directly to the caesium salt **12b** (43% yield). The anion **4** is less reactive than **3** and reaction with **5** did not occur at room temperature, as with **3**, and at the higher reaction temperature of 100 °C the process clearly proceeds to **12b**. However, the step **11** to **12b** is itself unusual, as is the conversion of **10** to **12a** with iodide ion. Formally, each of these steps represents a nucleophilic attack on a perfluoroalkyl group ($CF_3$ in **10**, and $CF_3CF_2$ in **11**) with displacement of the pentakis(trifluoromethyl)cyclopentadienide anion. The mechanism of these steps could involve $S_N2$, $S_N2'$ or single electron transfer processes and this problem will be addressed in a full publication.

The synthesis of 2H-heptafluorobut-2-ene was described many years ago,[5] Scheme 2, and subsequently repeated many times by various workers, including ourselves. However, since we have synthesised the pentakis(trifluoromethyl)cyclopentadienide anion, we have been able to establish the remarkable fact that the potassium salt **12c** is produced directly from hexachlorobutadiene and potassium fluoride!

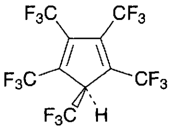
We treated the sulfolan residue, obtained in the synthesis of **2**, with concentrated sulfuric acid and were able to remove the diene **13** by vacuum transfer.



Scheme 1 *Reagents and conditions*: i, CsF, MeCN, stirring, room temp.; ii, CsF, MeCN, autoclave, 100 °C



Scheme 2 *Reagents and conditions*: i, KF, 190 °C, sulfolan; ii, CsF, 190 °C, sulfolan



**13**

Also, the caesium salt **12b** can be obtained very simply by reaction of heptafluorobut-2-ene **2** with caesium fluoride, a possible mechanism is shown in Scheme 2.

These new direct procedures allow the realistic pursuit of the chemistry of these interesting systems.

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