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THE SYNTHESIS AND CHEMISTRY OF 1,2,3,4,5-PENTAFLUOROCHROMARENE; ELECTRONIC EFFECT OF A π-Cr(C_6H_6) MOIETY

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Summary

(C_6F_5H)Cr(C_6H_6), which is synthesisable by the metal atom cocondensation procedure, can be metallated at —78°C using BuLi and is thus readily functionalisable. Infrared spectroscopic evidence suggests that a π-Cr(C_6H_6) moiety is an electron-donating substituent. Attempts to produce the benzyne π-complex (C_6F_4)Cr(C_6H_6) were unsuccessful and led to bichromarene formation. 1,2,3,5- and 1,2,4,5-tetrafluorochromarenes have also been synthesised and their potential for incorporation into polymers is discussed.

Introduction

While the effect of the π-Cr(CO)$_3$ moiety on the chemistry of arenes has been widely investigated [1,2], the influence of the π-Cr(C_6H_6) grouping on an aromatic ring is less well understood [3]. A logical approach would be to compare the chemical behaviour of the ArX in the uncomplexed state with that of the corresponding chromarene *, viz., (η-ArX)Cr(η-C_6H_6). Such a study requires ready

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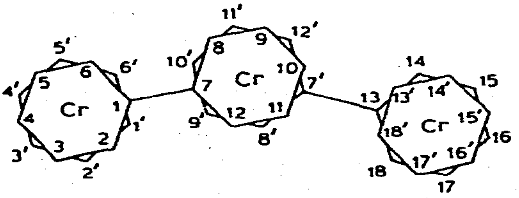
* We here define $(C_6H_6)_2Cr$ as chromarene and name its derivatives analogously to ferrocene. Polychromarenes are numbered as shown below e.g.,



[1.7;7'.13]-Trichromarene

access to functionalised chromarenes and this has been a source of difficulty for a number of years [4].

The pioneering work of Fischer and his colleagues [5] demonstrated that the direct synthesis of usefully functionalised chromarenes is negated by the presence of the Lewis acid catalyst ($AlCl_3$) which interacts with any substituents possessing non-bonding electron pairs in the valence shell [6]. Furthermore, electrophilic or free-radical attack on the complexed ring is disfavored due to the presence of the relatively electron-rich chromium atom which provides a more attractive target for the incoming electrophile. Nucleophilic substitution on the complexed arene ring has recently been achieved [7] using complexes in which the required leaving group was incorporated beforehand via the metal atom cocondensation technique [8—11]. Although nucleophilic substitution may yet provide routes to specifically functionalised chromarenes, low yields and polysubstitution are still the rule rather than the exception [7].

Early attempts [12,13] to metallate chromarenes required impeccable experimental technique in order to handle the very air-sensitive products; furthermore, the scope of this reaction was limited to "relatively acidic" hydrocarbons [14]. The use of a diamine such as *N,N,N',N'*-tetramethylethylenediamine (TMEDA) to activate the alkyllithium has somewhat alleviated the situation [15], and a few substituted chromarenes have since been reported [16,17].

The known versatility of pentafluorophenyllithium as a synthetic reagent [18] coupled with the thermal and oxidative stability of fluoro-substituted chromarenes [7,19—22] prompted us to attempt the synthesis of 1-lithio-2,3,4,5,6-pentafluorochromarene. It was hoped that such a study would allow a comparison of molecules of the type C_6F_5X and $(C_6F_5X)Cr(C_6H_6)$ and a consequent evaluation of the role of the π-$Cr(C_6H_6)$ moiety.

Discussion

Synthesis and lithiation of 1,2,3,4,5-pentafluorochromarene

By analogy to C_6F_5Li, two routes to 1-lithio-2,3,4,5,6-pentafluorochromarene appeared viable [23,24]; first, treatment of 1-bromo(or chloro-) 2,3,4,5,6-pentafluorochromarene with lithium amalgam, or second, by the action of butyllithium on 1,2,3,4,5-pentafluorochromarene (I). The former process was attempted via the direct synthesis of $(C_6F_5Cl)Cr(C_6H_6)$ by the cocondensation of chromium vapor with a mixture of the two arenes; however, $CrCl_3$ was the major product and the desired sandwich compound was not isolated. In contrast, cocondensation of chromium vapor with a mixture of pentafluorobenzene and benzene produced $(C_6F_5H)Cr(C_6H_6)$ (I), entirely analogous to the synthesis of $(C_6F_6)Cr(C_6H_6)$ [7,25].

I exists as air-stable orange crystals and was identified by its mass spectrum which showed the parent ion and ions derived by successive loss of fluorines. Cleavage of the pentafluorobenzene—chromium bond with loss of $(C_6H_6)Cr$ (*m/e* 130) was also observed in this spectrum as is common with molecules of this type [20]. The ^{19}F NMR spectrum showed peaks at 185.0, 194,9 and 196.8 ppm upfield of $CFCl_3$ which were assigned to *ortho-*, *meta-* and *para-*fluorines. respectively. The ^1H NMR spectrum (Fig. 1) showed a triplet (9 Hz) of triplets (6 Hz) of doublets (2 Hz) at δ 4.97 ppm (1H), due to coupling with the *ortho-*, *meta-* and *para-*fluorine nuclei, respectively, and a multiplet at δ 4.43 ppm (6H); this multiplet fine structure is due to the coupling via the chromium atom to the C_6F_5H ring. As with $(C_6F_6)Cr(C_6H_6)$ [7], the inter-ring H—F coupling constants are of the order of 1—2 Hz. Although it has not been possible to resolve completely these couplings, the ^{19}F NMR peaks showed small splittings of this magnitude.

I provides an ideal system in which to study the metallation of sandwich compounds for a number of reasons. First, it is much more air-stable than the $(C_6H_6)Cr(C_6H_6)$ complex. Second, it contains a relatively highly acidic proton. Thus the metallation can be performed easily without using an extremely powerful base such as amylsodium, nor does one need to activate an alkyllithium with TMEDA. Third, compared to chromarene itself or ferrocene, the pentafluorochromarene (I) can be easily lithiated in only one ring, thus avoiding the separation problems associated with mono- and di-lithiated products. Finally, in the $(C_6F_5H)Cr(C_6H_6)$ case there was an easily observable colour change when lithiation occurred. Hence, the acidic proton of the π-complexes C_6F_5H ring was lithiated using t-butyllithium at —78°C, without adding any TMEDA, and gave the lithio derivative II in excellent yield.

The electronic effect of the π-Cr(C₆H₆) substituent

II reacts readily with organic molecules containing the carbonyl function and, as expected, converts aldehydes and ketones to 2° and 3° alcohols, respectively,

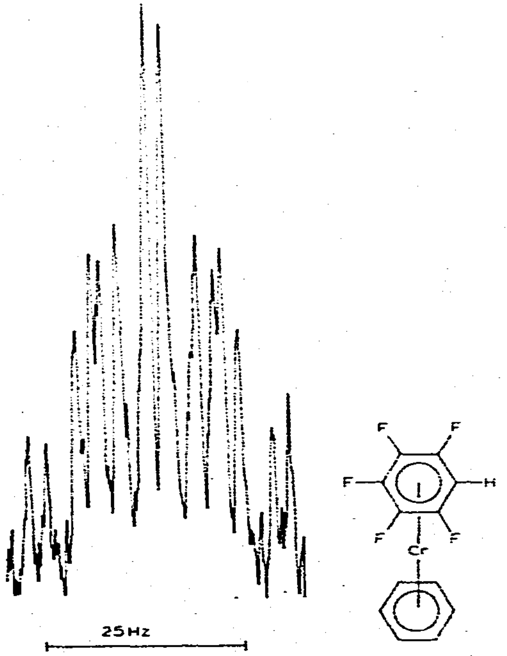
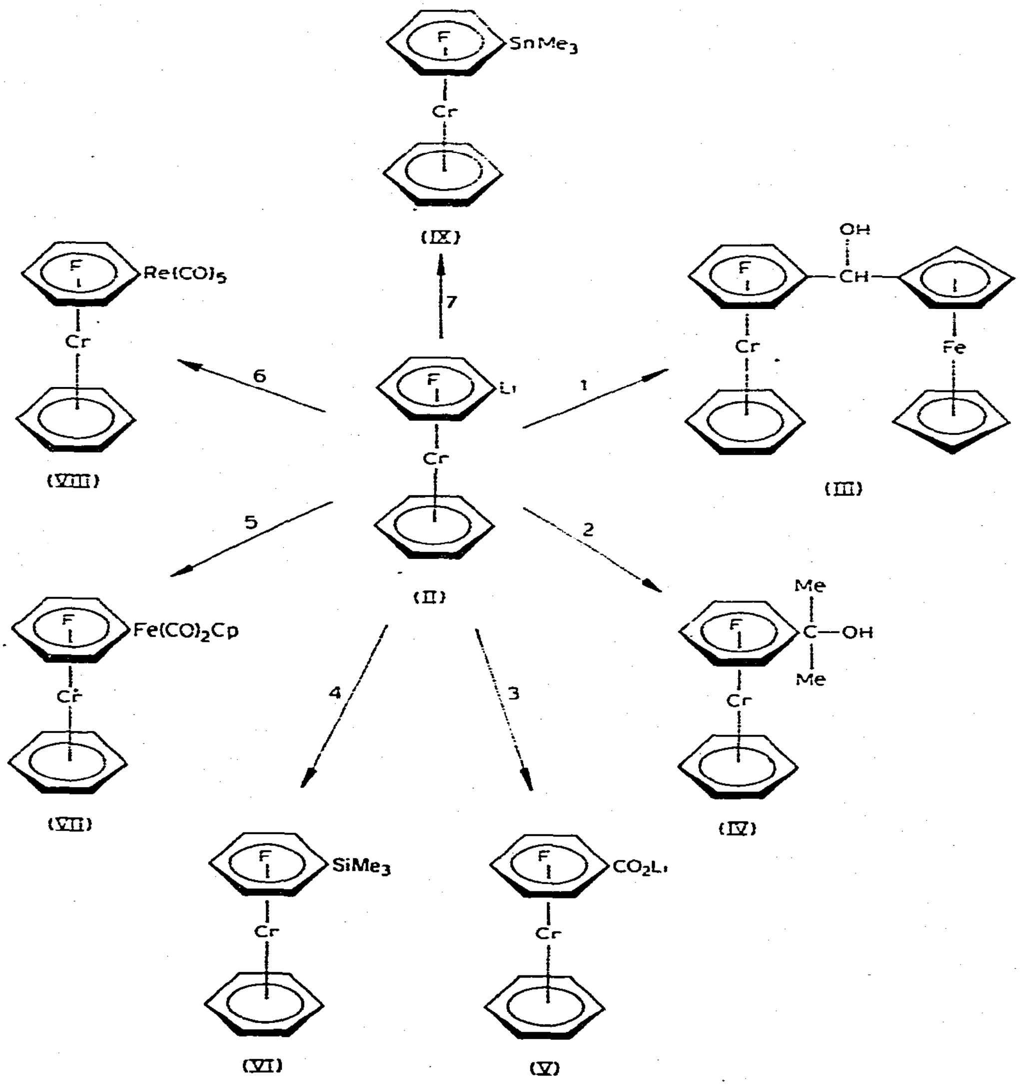


Fig. 1. The ^1H NMR spectrum of $(C_6F_5\underline{H})Cr(C_6H_6)$.

(see Scheme 1). An amusing corollary shows that reaction of II with formylferrocene allows the incorporation of the ferrocenyl and chromarenyl moieties within the same molecule, viz., III.



SCHEME 1. Reactions of $(C_6F_5Li)Cr(C_6H_6)$ (II).

(1) $(C_5H_5)Fe(C_5H_4CHO)$ (2) $(CH_3)_2CO$

(3) CO_2 (4) $(CH_3)_3SiCl$ (5) $(C_5H_5)Fe(CO_2)I$

(6) $IRe(CO)_5$ (7) $(CH_3)_3SnCl$

Having demonstrated that II mimicked the behaviour of C_6F_5Li in many respects, it was clearly feasible to prepare a series of molecules $(C_6F_5X)Cr(C_6H_6)$ for comparison with the corresponding C_6F_5X systems. An immediate target was $(C_6F_5CO_2H)Cr(C_6H_6)$ so that measurement of the pK_a would indicate whether the π-$Cr(C_6H_6)$ functionality was an electron donor or an acceptor. (Such an experiment with $(C_6H_5CO_2H)Cr(CO)_3$ indicated that the π-$Cr(CO)_3$ group was in some ways comparable to the *p*-nitro substituent) [26]. However, although II reacted readily with solid CO_2 to give what was presumably the carboxylate V, all attempts to protonate and thus produce the pentafluorobenzoic acid complex led to rapid decomposition. Apparently, the acid preferred to attack the zero-valent chromium atom rather than the carboxylate function.

An indirect spectroscopic approach was therefore required to probe the effect of complexation. Hence, II was treated with chlorotrimethylsilane to give the trimethylsilyl derivative VI in good yield. The ^{19}F NMR spectrum of VI showed peaks at 175.2, 193.7 and 200.7 ppm and followed the usual pattern of *ortho*-, *meta*- and *para*-fluorines previously established. The ^1H NMR data (in C_6D_6) showed a multiplet (6H) at δ 4.6 ppm and a triplet (9H) at δ 0.35 ppm corresponding to complexed benzene ring and side-chain methyl groups respectively. It had previously been noted [27] that the methyl triplet in $C_6F_5SiMe_3$ occurred at δ 0.41 ppm in $CDCl_3$. The increased shielding upon complexation might be taken as evidence for an overall electron-donation by the π-$Cr(C_6H_6)$ moiety. However, resynthesis of $C_6F_5SiMe_3$ and measurement of its proton spectrum in C_6D_6 showed the methyl triplet at δ 0.37 ppm, and such a difference is too small to be attributed, with any great confidence, to a simple inductive effect of the π-$Cr(C_6H_6)$ system. It is interesting, however, to note that ^5J(H—F) ($C\underline{H}_3$—*ortho*-$\underline{F}$) is identical in the free and complexed systems which may support Graham's postulate [27] that the H—F coupling occurs through space rather than through the bonds.

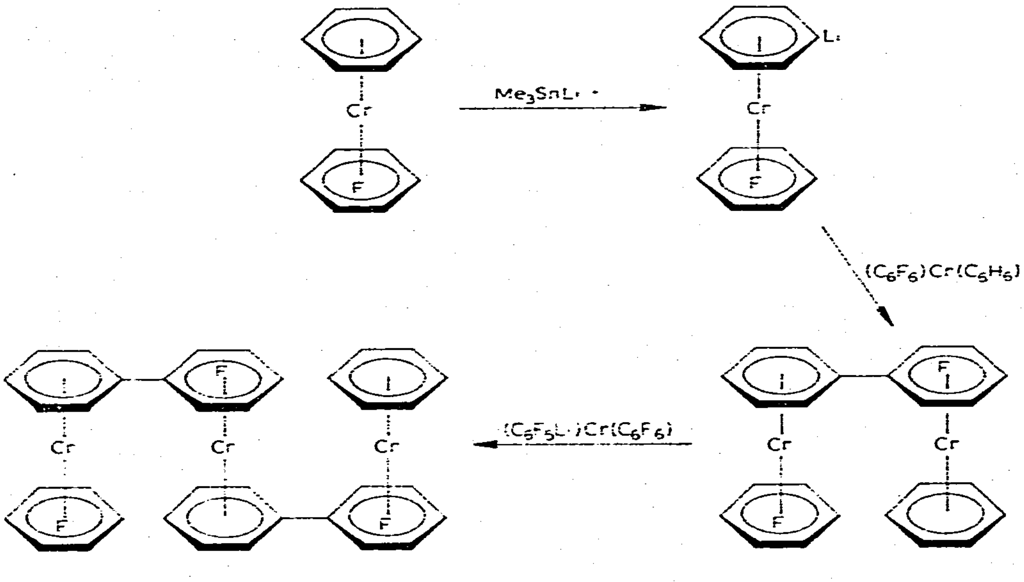
More definitive conclusions could be drawn from an infrared spectroscopic approach. It is well established that ν(CO) in metal carbonyls is a measure of the ability of the metal to back-donate electron density into the carbon monoxide π^* orbitals [28]. This is in turn a reflection of the ability of the ligands to supply electron density to the metal in question. Now a comparison of corresponding ν(CO) values in the molecule $C_6F_5M(CO)_x$ and its chromarene analogue reveals a pronounced decrease in frequency upon incorporation into a sandwich compound (Table 1). These data clearly demonstrate that the π-$Cr(C_6H_6)$ group is donating electron density to the pentafluorophenyl ring which in turn enhances the back-donating ability of the metal σ-bonded to the ring. One would therefore predict than when $(C_6F_5CO_2H)Cr(C_6H_6)$ is eventually synthesized its pK_a will be higher than the pK_a of perfluorobenzoic acid.

TABLE 1

ν(CO) (cm^{-1}) FOR C_5F_5X MOLECULES AND THEIR CHROMARENE ANALOGUES

X	C_6F_5X	$(C_6F_5X)Cr(C_6H_6)$
$CpFe(CO)_2$	2045, 1997 [29]	2006, 1963
$Re(CO)_5$	2145, 2046, 2006 [30]	2066, 2007, 1898

In order to compare the Sn Mössbauer parameters of $C_6F_5SnMe_3$ and its chromarene analogue II was treated with chlorotrimethylstannane but gave only a very low yield of the desired product IX, which was identified solely by mass spectrometry. A viable alternative route appeared to be nucleophilic substitution upon $(C_6F_6)Cr(C_6H_6)$ using $(CH_3)_3SnLi$ analogously to the alkyl substitution previously reported [7]. The products isolated, however, contained no tin and were identified as the previously known [7] bichromarene X and the novel trichromarene XI. Apparently, the high basicity of the trimethyltin anion predominates over its nucleophilicity leading to telomerisation, as shown in Scheme 2.

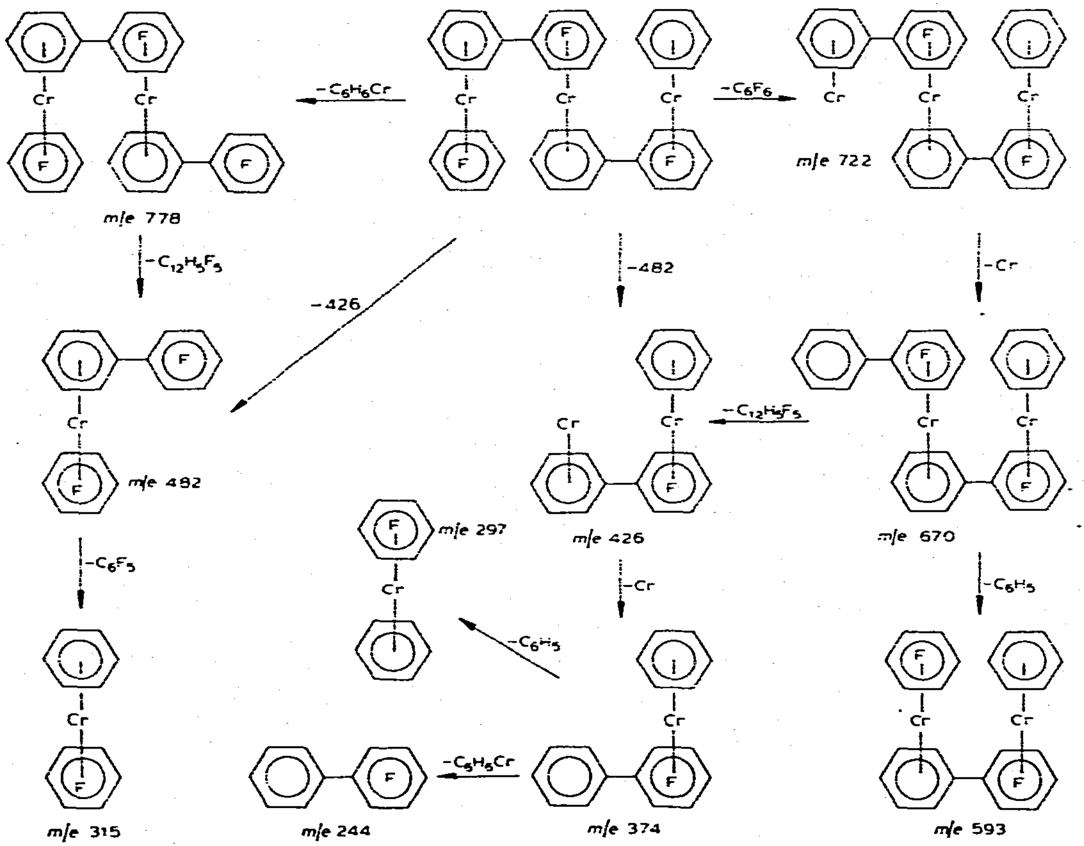


(XI) (X)

SCHEME 2. The proposed mechanism of telomerisation of $(C_6F_6)Cr(C_6H_6)$.

The mass spectral fragmentation pattern for XI is readily rationalisable by the indicated cleavages as can be seen in Scheme 3.

In a continuation of the comparison of free and complexed pentafluorophenyllithium it was of interest to determine whether the complex eliminated lithium fluoride to produce a π-complexed tetrafluorobenzyne. The ready accessibility of tetrafluorobenzyne from pentafluorophenyllithium itself is well documented [31] and the dienophilic aryne undergoes the Diels—Alder reaction with suitable traps such as benzene or thiophene [32,33]. One of the more reactive benzyne traps is furan, and so an ethereal solution of II was allowed to warm to room temperature in the presence of furan. The Diels—Alder adduct was not observed but instead the bichromarene XII was obtained; XII is apparently produced by nucleophilic displacement of fluoride (see Scheme 4) and the accompanying tarry residue suggests that we have merely isolated the lowest homologue of a polymeric series. The bichromarene XII is also produced in other reactions of II which failed to yield the intended product. Thus from the reaction of II with

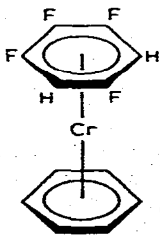


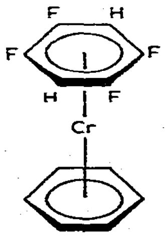
SCHEME 3. The mass spectral breakdown pattern of the trichromarene (XI).

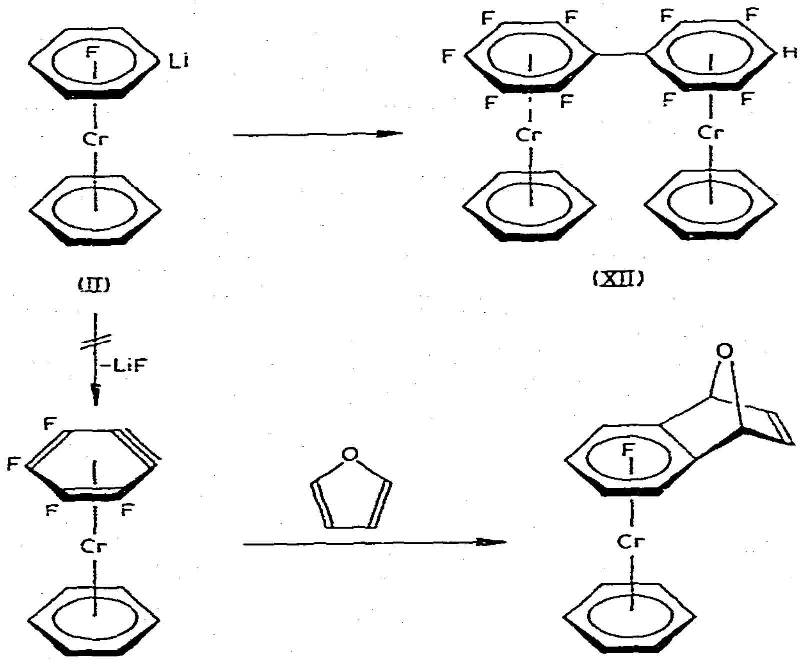
Cp_2TiCl_2, the desired bis(chromarenyl)titanocene was not observed but instead XII was isolated.

Potential chromarene polymers

The propensity of the fluorochromarenes to homopolymerise led to the hope that controlled copolymerisation processes might be viable. To this end, a route to difunctionalised fluorochromarenes was required, and indeed the 1,2,3,5- and 1,2,4,5-tetrafluorochromarenes, XIII and XIV, respectively, are readily synthesisable from chromium vapor and the appropriate arene mixtures.


(XIII)


(XIV)



SCHEME 4. The attempt to trap a tetrafluorobenzyne π-complex.

The NMR spectra of XIV follow the pattern of such systems in that, upon complexation, the ^{19}F resonances are shifted upfield by ~50 ppm [7,20], the ^1H resonances in the fluoroarene ring are shielded by ~1.3 ppm and H—F coupling constants decrease by ~25%. Once again, the inter-ring H—F coupling (0.93 Hz) is clearly distinguishable and presumably is transmitted via the chromium atom. These difunctionalisable molecules are readily dilithiated as shown by quenching experiments with D_2O. A future publication will describe the reactions of these chromarenes with potential copolymerising agents such as adipoyl chloride or dichlorodimethylsilane.

An interesting problem is the delicate balance between thermodynamic and kinetic factors which accounts for the thermal and oxidative stability of these variously substituted chromarenes. While electron-withdrawing substituents on the ring undoubtedly retard the one-electron oxidation of the complex [21] it is also true that sufficient π-electron density must be available to form the arene—metal bond [22]. Minor changes in substituents can substantially reduce the stability of the complex. Thus, while the complexes $(C_6F_nH_{6-n})Cr(C_6H_6)$ are readily synthesisable when n is 4, 5 or 6, symmetrical complexes of the type $(C_6F_nH_{6-n})_2Cr$ have not been reported when n exceeds 2. The introduction of methyl groups, which enhance the π-donating ability of an arene ring but do not retard the oxidation of the central metal, has an overall destabilising effect. Typically, we have isolated 1,1'-dimethyl-2,3,4,5,6-pentafluorochromarene (XV), only with difficulty and identified it only mass spectrometrically.

Somewhat surprisingly, the symmetry of the chromarenes also seems to be important. Thus, 1,2,4,5-tetrafluorochromarene (XIV) is quite stable while the *meta* isomer XIII is much less so; the explanation may lie in the relative contributions of hydrogen bonding in the crystalline state.

Experimental

Nuclear magnetic resonance spectra (^1H and ^{19}F) were recorded on a Varian HA-100 spectrometer using tetramethylsilane and trichlorofluoromethane as internal references. Mass spectra were recorded on a C.E.C. 21-110-B spectrometer. Infrared spectra were recorded on a Perkin—Elmer 337 grating spectrometer. Melting points are uncorrected. Elementary analyses were performed by Gygli Microanalysis Laboratory, Toronto.

1,2,3,4,5-Pentafluorochromarene (I)

Chromium vapor (90 mg, 1.73 mmol) and 50 ml of 60/40 v/v mixture of pentafluorobenzene and benzene were cocondensed as previously described [7] over a period of 90 min. After removal of excess substrate, the residue was heated using a hot water bath, and the crude mixture of chromarene and 1,2,3,4,5-pentafluorochromarene (I) collected on the water-cooled surface of the flask as previously described [7]. The mixture was left in air for only a few hours to allow decomposition of the $(C_6H_6)_2Cr$ without destroying I which is somewhat more air-sensitive than is $(C_6F_6)Cr(C_6H_6)$. Sublimation of the residue at 35°C/0.2 mmHg gave I (89 mg, 0.3 mmol; 22%); subsequent recrystallization from aqueous ethanol gave air-stable, orange needles, m.p. 117°C, whose ^{19}F NMR spectrum in C_6D_6 showed multiplets at 185.0 (*ortho*), 194.9 (*meta*) and 196.8 (*para*) ppm upfield of $CFCl_3$. The ^1H NMR spectrum exhibited a triplet (9 Hz) of triplets (6 Hz) of doublets (2 Hz) at δ 4.97 ppm (1H), and a multiplet (6H) at δ 4.43 ppm. Mass spectral data: *m/e* 298, $C_{12}H_7F_5Cr^+$ (53); 168, $C_6F_5H^+$ (52); 149, $C_6F_4H^+$(49); 130, $C_6H_6Cr^+$ (67); 78, $C_6H_6^+$ (100); 52, Cr^+ (24). Anal. Found: C, 48.5; H, 2.3. $C_{12}H_7CrF_5$ calcd.: C, 48.3; H, 2.4%.

Lithiation of $(C_6F_5H)Cr(C_6H_6)$ (I)

Into a three-necked round-bottom flask, fitted with a septum cap, a water cooled condenser and a nitrogen inlet tube, was added freshly sublimed I (0.262 mmol) and dissolved in 120 ml sodium-dried diethyl ether. The solution was flushed with dry nitrogen for 20 min and then cooled to —78°C. t-Butyllithium (0.27 mmol) in ether solution (10 ml) was syringed into the system and the initially pale yellow solution became red-brown, indicative of the formation of the lithio derivative II.

Reactions of II with various reagents

(a) Acetone. To a solution of II (0.086 mmol) in diethyl ether at —78°C under a nitrogen atmosphere was added acetone (10 mg, 0.17 mmol) and the red-brown solution rapidly turned yellow. The solution was stirred at —78°C for 30 min and then allowed to warm to room temperature. The solvent and the excess acetone were removed in vacuo and the product was purified by sublimation at 35°C/0.2 mmHg to give yellow 2-[2,3,4,5,6-pentafluorochromarenyl)-propan-2-ol (IV) (24.6 mg, 0.069 mmol; 80%), m.p. 99°C, whose ^1H NMR spectrum in C_6D_6 showed a multiplet peak at δ 4.67 ppm (6H) and a singlet at δ

1.8 ppm (6H). The ^{19}F NMR spectrum in C_6D_6 showed absorptions at 182.3, 194.5 and 198.8 ppm upfield of $CFCl_3$ corresponding to *ortho-*, *meta-* and *para-*fluorines, respectively. Mass spectral data: *m/e* 356, $C_{15}H_{13}F_5CrO^+$ (5); 335, $C_{15}H_{13}F_4CrO^+$ (0.3); 298, $C_{12}H_7F_5Cr^+$ (30); 226, $C_9H_7F_5O^+$ (0.3); 168, $C_6HF_5^+$ (10); 149, $C_6HF_4^+$ (18); 130, $C_6H_6Cr^+$ (100); 78, $C_6H_6^+$ (75); 52, Cr^+ (80). Anal. Found: C, 50.4; H, 3.8. $C_{15}H_{13}F_5CrO$ calcd.: C, 50.6; H, 3.7%.

(b) Formylferrocene. An ethereal solution of formylferrocene (17 mg, 0.08 mmol) was added to the three-necked flask containing an ethereal solution of lithio derivative II (0.08 mmol) at —78°C under a nitrogen atmosphere. After stirring at —78°C for 30 min, the solution was then allowed to warm to room temperature. After removing the solvent, the residue was sublimed at 35°C/0.2 mmHg to give 2,3,4,5,6-pentafluorochromarenylferrocenylmethanol (III) as an orange-red waxy solid (28.7 mg, 0.056 mmol; 70%) m.p. 127°C. The ^{1}H NMR spectrum showed singlets at δ 3.98 (5H), 3.90 (4H) and 1.33 (1H) and a multiplet at 4.73 ppm (6H). The ^{19}F NMR spectrum showed peaks at δ 187.3 (*ortho*), 197.3 (*meta*) and 200.6 ppm (*para*). Mass spectral data: *m/e* 512, $C_{23}H_{17}F_5CrFeO^+$ (20); 434, $C_{17}H_{11}F_5CrFeO^+$ (9); 326, $C_{13}H_7F_5CrO^+$ (4); 310; $C_{13}H_7F_5Cr^+$ (3); 298; $C_{12}H_7F_5Cr^+$ (47); 214, $C_{11}H_{10}FeO^+$ (58); 186, $C_{10}H_{10}Fe^+$ (62); 168, $C_6HF_5^+$ (22); 130, $C_6H_6Cr^+$ (72); 78, $C_6H_6^+$ (100); 65, $C_5H_5^+$ (22); 56, Fe^+ (54); 52, Cr^+ (57). Anal. Found: C, 53.8; H, 3.3. $C_{23}H_{17}F_5CrFeO$ calcd.: C, 53.9; H, 3.3%.

(c) Carbon dioxide. To a cold (—78°C) ethereal solution of II (68 mmol) was added excess solid CO_2. A yellow precipitate was formed at room temperature presumably attributable to V. The whitish-yellow precipitate remaining after removal of the solvent was acidified using acetic or trifluoroacetic acid. In both cases a green coloration due to decomposition of the sandwhich compound occurred rapidly.

(d) Chlorotrimethylsilane. A slight excess of Me_3SiCl (35 mg, 0.32 mmol) was added to the dark red-brown solution of lithio derivative II which was obtained when 2 ml of a 0.135 *M* ethereal solution of t-butyllithium were added to I (78 mg, 0.262 mmol) in 120 ml diethyl ether at —78°C under a nitrogen atmosphere. The mixture was stirred at room temperature for 60 min. Filtration at room temperature, removal of solvent and excess Me_3SiCl in vacuo and sublimation at 32°C/0.2 mmHg gave orange 1-trimethylsilyl-2,3,4,5,6-pentafluorochromarene (VI) (75.5 mg, 0.204 mmol; 78%), m.p. 93.5°C. The ^{19}F NMR spectrum showed peaks at 175.2 (*ortho*), 193.7 (*meta*) and 200.7 (*para*) ppm upfield of $CFCl_3$. The ^{1}H NMR spectrum (in C_6D_6) exhibited a multiplet (6H) at δ 4.6 and a triplet (9H) at 0.35 ppm (^5J(H—F) 1.5 Hz). Mass spectral data: *m/e* 370, $C_{15}H_{15}F_5CrSi^+$ (5); 355, $C_{14}H_{12}F_5CrSi^+$ (1); 298, $C_{12}H_7F_5Cr^+$ (15); 240, $C_9H_9F_5Si^+$ (2); 225, $C_8H_6F_5Si^+$ (2); 168, $C_6HF_5^+$ (11); 149, $C_6HF_4^+$ (12); 130, $C_6H_6Cr^+$ (100); 78, $C_6H_6^+$ (94); 73, $C_3H_9Si^+$ (7); 52, Cr^+ (94); 43, CH_3Si^+ (2); 28, Si^+ (17). Anal. Found: C, 48.9; H, 4.2. $C_{15}H_{15}F_5CrSi$ calcd.: C, 48.7; H, 4.1%.

(e) (η-Cyclopentadienyl)iododicarbonyliron(II). An ethereal solution of $CpFe(CO)_2I$ (24 mg, 0.08 mmol) was syringed into the freshly prepared lithio derivative solution (0.08 mmol) at —78°C under a nitrogen atmosphere. The mixture was stirred at —78°C for 30 min, then allowed to warm to room temperature, filtered and the solvent removed in vacuo. The crude product was

sublimed at 60°C/0.2 mmHg to obtain (2,3,4,5,6-pentafluorochromarenyl)-(η-cyclopentadienyl)dicarbonyliron(II) (VII) a red waxy solid (5 mg, 0.011 mmol; 13%) showing infrared peaks (nujol mull) at 2006 and 1963 cm^{-1}. Mass spectral data: *m/e* 474, $C_{19}H_{11}F_5CrFeO_2^+$ (2); 409, $C_{14}H_6F_5CrFeO_2^+$ (8); 381, $C_{13}H_6F_5CrFeO^+$ (4); 353, $C_{12}H_6F_5CrFe^+$ (10); 344, $C_{13}H_5F_5FeO_2^+$ (6); 298, $C_{12}H_7F_5Cr^+$ (60); 279, $C_8F_5FeO_2^+$ (18); 251, $C_7F_5FeO^+$ (4); 177, $C_7H_5FeO_2^+$ (6); 168, $C_6F_5H^+$ (62); 149, $C_6H_5FeO^+$, $C_6HF_4^+$ (20); 130, $C_6H_6Cr^+$ (44); 121, $C_5H_5Fe^+$ (24); 78, $C_6H_6^+$ (100); 56, Fe^+ (40); 52, Cr^+ (43).

(f) Iodopentacarbonylrhenium(I). An ethereal solution of $Re(CO)_5I$ (36 mg, 0.08 mmol) was syringed into a solution of II (0.08 mmol) at −78°C under nitrogen. The mixture was stirred at room temperature for 30 min, the solvent removed and the residue heated to 40°C in vacuo to remove I. Extraction of the residue with ether/benzene and subsequent recrystallisation gave (2,3,4,5,6-pentafluorochromarenyl)pentacarbonylrhenium(I) (VIII) (9 mg, 0.014 mmol; 18%) showing infrared absorption at 2066, 2007 and 1898 cm^{-1}. Mass spectral data: *m/e* 622/624, $C_{17}H_6CrF_5O_5Re^+$ (4); 594/596, $C_{16}H_6CrF_5O_4Re^+$ (3); 566/568, $C_{15}H_6CrF_5O_3Re^+$ (3); 538/540, $C_{14}H_6CrF_5O_2Re^+$ (2); 492/494, $C_{11}F_5O_5Re^+$ (11); 464/466, $C_{10}F_5O_4Re^+$ (8); 436/438, $C_9F_5O_3Re^+$ (8); 408/410, $C_8F_5O_2Re^+$ (10); 352/354, $C_6F_5Re^+$ (17); 325/327, $C_5O_5Re^+$ (6); 297/299, $C_4O_4Re^+$ (9); 297, $C_{12}H_6CrF_5^+$ (40); 185/187, Re^+ (53); 167, $C_6F_5^+$ (23); 130, $C_6H_6Cr^+$ (82); 78, $C_6H_6^+$ (100); 52, Cr^+ (81).

(g) Chlorotrimethylstannane. A solution of Me_3SnCl (13.9 mg, 0.07 mmol) in dry ether was added to an ethereal solution of II (0.07 mmol) at −78°C under a nitrogen atmosphere. The mixture was stirred at room temperature for 60 min. Filtration at room temperature, removal of solvent in vacuo and sublimation at 30°C/0.2 mmHg gave 1-trimethylstannyl-2,3,4,5,6-pentafluorochromarene (IX) an orange-red powder in very low yield (2 mg, 0.004 mmol; 6%). Mass spectral data: *m/e* 443/451, $C_{15}H_{15}F_5CrSn^+$ (7); 428/436, $C_{14}H_{12}F_5CrSn^+$ (2); 313/321, $C_9H_9F_5Sn^+$ (5); 298/306, $C_8H_6F_5Sn^+$ (3); 298, $C_{12}H_7F_5Cr^+$ (22); 168, $C_6HF_5^+$ (8); 161/169, $C_3H_9Sn^+$ (10); 149, $C_6HF_4^+$ (7); 131/139, CH_3Sn^+ (2); 130, $C_6H_6Cr^+$ (100); 116/124, Sn^+ (23); 78, $C_6H_6^+$ (88); 52, Cr^+ (91).

(h) Furan. 2 ml of a 0.135 *M* ethereal solution of t-butyllithium were added to I (78 mg, 0.26 mmol) in 150 ml dry ether at −78°C under a nitrogen atmosphere to obtain the ethereal solution of II. To this solution of II was added dry furan (0.3 mmol), the mixture allowed to warm to room temperature and stirred for 60 min. The solvent was removed in vacuo and the residue sublimed at 55—60°C/0.2 mmHg to yield 2,3,4,5,6,8,9,11,12-nonafluorobichromarene (XII) a waxy air unstable orange material with ^1H NMR peaks at δ 4.60 (multiplet, 12H) and 4.95 ppm (broadened triplet, 1H). The ^{19}F NMR spectrum shows complex multiplets at 185 (2 F) and 195—205 (7 F) ppm upfield of $CFCl_3$. Mass spectral data: *m/e* 576, $C_{24}H_{13}F_9Cr_2^+$ (6); 446, $C_{18}H_7F_9Cr^+$ (10); 316, $C_{12}HF_9^+$, $C_{12}H_6F_6Cr^+$ (10); 298, $C_{12}H_7F_5Cr^+$ (20); 168, $C_6HF_5^+$ (41); 149, $C_5HF_4^+$ (32); 130, $C_6H_6Cr^+$ (62); 78, $C_6H_6^+$ (100); 52, Cr^+ (91).

Reaction of trimethyltinlithium with 1,2,3,4,5,6-hexafluorochromane

A THF solution of Me_3SnLi (0.5 mmol), prepared by Tamborski's method [34], was added to $(C_6F_6)Cr(C_6H_6)$ (100 mg, 0.32 mmol) in 15 ml dry THF at −78°C, under nitrogen. The solution was stirred at room temperature for 10 h, the solvent blown off using a nitrogen stream and the product sublimed at 25°C/0.2 mmHg. Gas chromatography (3 ft. Chromosorb W-HP column with 1.5% SE-30 at 150°C) revealed a small amount of the known bichromarene X with an identical mass spectrum to that previously reported [7]. The major product was identified as 1′,2′,3′,4′,5′,6′,8,9,10,11,12,14,15,16,17,18-hexadecafluoro[1,7 : 7′,13]trichromarene (XI) (61 mg, 0.07 mmol; 21%) m.p. 145°C. Mass spectral data: *m/e* 778, $C_{30}H_{10}F_{16}Cr_2^+$ (0.5); 759, $C_{30}H_{10}F_{15}Cr_2^+$ (1); 740, $C_{30}H_{10}F_{14}Cr_2^+$ (5); 722, $C_{30}H_{16}F_{10}Cr_3^+$ (3); 703, $C_{30}H_{16}F_9Cr_3^+$ (1); 670, $C_{30}H_{16}F_{10}Cr$ (1); 611, $C_{24}H_{10}F_{11}Cr_2^+$ (1); 593, $C_{24}H_{11}F_{10}Cr_2^+$ (7); 574, $C_{24}H_{11}F_9Cr_2^+$ (4); 522, $C_{24}H_{11}F_9Cr^+$ (2); 482, $C_{18}H_5F_{11}Cr^+$ (5); 463, $C_{18}H_5F_{10}Cr^+$ (7); 444, $C_{18}H_5F_9Cr^+$ (11); 426, $C_{18}H_{11}F_5Cr_2^+$ (5); 374, $C_{18}H_{11}F_5Cr^+$ (5); 315, $C_{12}H_5F_6Cr^+$ (4); 297, $C_{12}H_6F_5Cr^+$ (12); 278, $C_{12}H_6F_4Cr^+$ (6); 244, $C_{12}H_5F_5^+$ (6); 186, $C_6F_6^+$ (74); 167, $C_6F_5^+$ (44); 148, $C_6F_4^+$ (37); 130, $C_6H_6Cr^+$ (86); 78, $C_6H_6^+$ (91); 52, Cr^+ (100). Anal. Found: C, 47.3; H, 2.0. $C_{36}H_{16}F_{16}Cr_3$ calcd.: C, 47.6; H, 1.8%.

1,2,3,5-Tetrafluorochromarene (XIII)

In an analogous manner to the synthesis of I, chromium vapor (46 mg, 0.88 mmol) and a 60/40 v/v mixture of 1,2,3,5-tetrafluorobenzene and benzene gave 1,2,3,5-tetrafluorochromarene (XIII) (27 mg, 0.096 mmol; 14%), m.p. 147°C, a yellow waxy solid which sublimed at 45°C/0.2 mmHg. Mass spectral data: *m/e* 280, $C_{12}H_8F_4Cr^+$ (87); 261, $C_{12}H_8F_3Cr^+$ (2); 242, $C_{12}H_8F_2Cr^+$ (3); 150, $C_6H_2F_4^+$ (24); 131, $C_6H_2F_3^+$ (27); 130, $C_6H_6Cr^+$ (100); 78, $C_6H_6^+$ (46); 52, Cr^+ (99).

1,2,4,5-Tetrafluorochromarene (XIV)

As for XIII, chromium vapor and the appropriate arene mixture gave 1,2,4,5-tetrafluorochromarene (XIV) (149 mg, 0.53 mmol; 24%), m.p. 127°C. The ^1H NMR spectrum showed a quintet (J(HF) 6.35 Hz) at δ 5.26 ppm (2H) and a quintet J(HF) 0.93 Hz) at δ 4.35 ppm (6H). The ^{19}F spectrum showed a multiplet at 178.0 ppm upfield of $CFCl_3$. Mass spectral data: *m/e* 280, $C_{12}H_8F_4Cr^+$ (46); 261, $C_{12}H_8F_3Cr^+$ (3); 242, $C_{12}H_8F_2Cr^+$ (3); 150, $C_6H_2F_4^+$ (25); 131, $C_6H_2F_3^+$ (23); 130, $C_6H_6Cr^+$ (93); 78, $C_6H_6^+$ (95); 52, Cr^+ (100) Anal. Found: C, 51.3; H, 3.2. $C_{12}H_8F_4Cr^+$ calcd.: C, 51.4; H, 2.9%.

1,1′-Dimethyl-2-3,4,5,6-pentafluorochromarene (XV)

Condensation of chromium vapor with a 50/50 v/v mixture of toluene and pentafluorotoluene gave, after sublimation of the residue, a thermally and air-sensitive mixture containing, 1,1′-dimethyl-2,3,4,5,6-pentafluorochromarene (XV) and 1,1′-dimethylchromarene. Mass spectral data: *m/e* 326, $C_{14}H_{11}F_5Cr^+$ (1); 307, $C_{14}H_{11}F_4Cr^+$ (0.5); 297, $C_{12}H_6F_5Cr^+$ (5); 234, $C_7H_3F_5Cr^+$ (74); 182 $C_7H_3F_5^+$ (2); 150, $C_6HF_5^+$ (2); 144, $C_7H_8Cr^+$ (84); 91, $C_7H_7^+$ (100); 77, $C_6H_5^+$ (79); 52, Cr^+ (84).

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