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Reactions of C_6F_5Li with Tetracyclone and 3-Ferrocenyl-2,4,5-triphenylcyclopentadienone: An ^{19}F NMR and X-ray Crystallographic Study of Hindered Pentafluorophenyl Rotations

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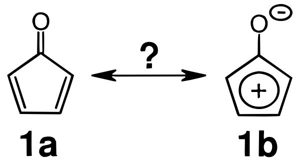
Tetracyclone, **2a**, reacts with C_6F_5Li to yield 2-pentafluorophenyl-2,3,4,5-tetraphenylcyclopent-3-en-1-one, **7**, and 5-hydroxy-5-pentafluorophenyl-1,2,3,4-tetraphenylcyclopentadiene, **8**, as the result of 1,6 and 1,2 additions, respectively. In contrast, treatment of 3-ferrocenyl-2,4,5-triphenylcyclopentadienone, **2b**, with lithiopentafluorobenzene leads to 4-ferrocenyl-4-pentafluorophenyl-2,3,5-triphenylcyclopent-2-en-1-one, **9**, and 5-hydroxy-5-pentafluorophenyl-2-ferrocenyl-1,3,4-triphenylcyclopentadiene, **10**, the products of 1,4 and 1,2 addition, respectively. The structures of **7**−**9** have been established by X-ray crystallography, and the barriers to rotation (19−21 kcal mol^{-1}) of the pentafluorophenyl groups in **8**−**10** have been studied by variable-temperature ^{19}F NMR. Nucleophilic attack at the ferrocenyl-bearing carbon in **2b** is rationalized in terms of a zwitterionic structure in which the positive charge of the "cyclopentadienyl cation" is delocalized onto the iron atom in the organometallic substituent.

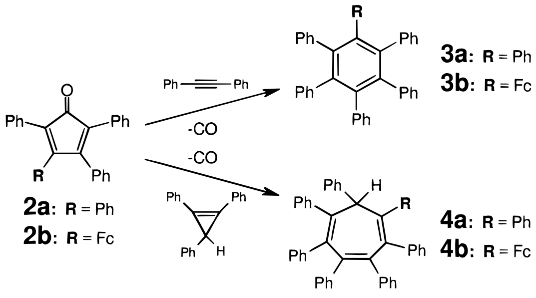
Introduction

The chemistry of cyclopentadienones, **1**, continues to fascinate both theoreticians and experimentalists. For the former, there is the question of the antiaromatic character inherent in a resonance structure such as **1b**, whereby the π manifold of the ring possesses only four electrons. Thus, molecular orbital calculations yield a rather small HOMO−LUMO gap,[1] and the compounds are normally intensely colored. For the experimentalist, the challenge lies in synthesis and in controlling their reactivity (Chart 1).

Chart 1



Scheme 1. Diels−Alder Reactions of 3-Ferrocenyl-2,4,5-triphenylcyclopentadienone



These molecules resist Diels−Alder dimerization only when bulky substituents are present;[2] the most commonly investigated systems are tetraarylcyclopentadienones that have recently been exploited as templates from which to build dendrimers[3] and polyphenyl polycyclic aromatic hydrocarbons.[4] Our own studies have focused on tetracyclone, **2a**, and 3-ferrocenyl-2,4,5-triphenylcyclopentadienone, **2b**, which readily undergo [4 + 2] cycloadditions with alkynes or cyclopropenes to give polyphenylated arenes **3a**,**b** or cycloheptatrienes **4a**,**b** as in Scheme 1.[5,6] Such sterically hindered systems not only pose interesting structural problems but also raise the possibility of exhibiting *correlated* rotations[7] with their attendant relevance to molecular machines.[8] We note in particular the recent characterization of the heptaphenyltropylium ion, $C_7Ph_7^+$, as a seven-bladed propeller.[9]

Surprisingly, the reactions of cyclopentadienones with nucleophiles are less well understood, even though the reaction of tetracyclone with a phenyl Grignard reagent to give 1,2,3,4,5-pentaphenylcyclopentadienol has been known since 1925.[10] This reaction has been extended to many other pentaaryl systems[11] and has also led to a plethora of (η^5-C_5Ph_5)ML_n complexes.[12] However, there are reports of nucleophilic attack at sites other than the

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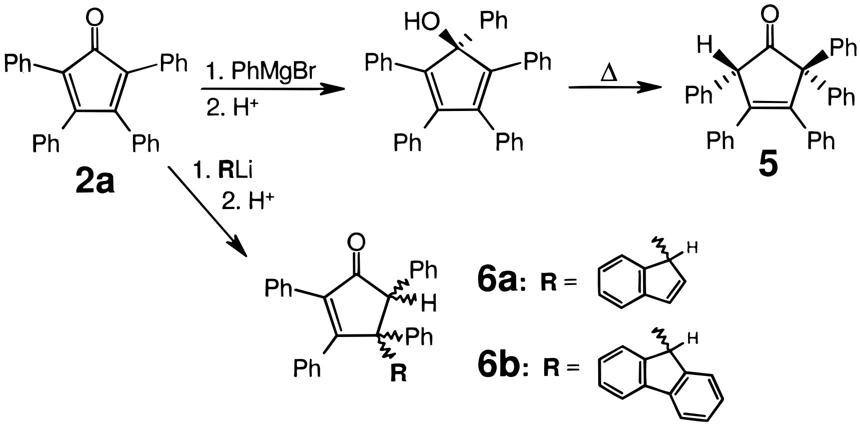
Scheme 2. Reactions of Tetracyclone with Aryllithium Reagents



carbonyl carbon. For example, it has been claimed[13] that treatment of $C_4Ph_4C{=}O$, **2a**, with PhMgBr in refluxing isoamyl ether yields the 1,6-addition product **5**; this observation was rationalized by Ogliaruso,[14] who showed that the initially formed 1,2,3,4,5-pentaphenylcyclopentadienol undergoes [1,5]-sigmatropic shifts at elevated temperatures, as in Scheme 2.

In contrast, indenyl- and fluorenyllithium are thought to yield the cyclopentenones **6a**,**b**.[15] As evidence for these latter structures, the authors reported carbonyl IR stretches at 1710 and 1701 cm^{-1}, respectively, and also the slow formation of the corresponding 2,4-dinitrophenylhydrazones.[16] These observations were rationalized on the basis of a relatively weak polarization of the carbonyl group on account of the antiaromatic cyclopentadienyl cation resonance structure discussed above. Nevertheless, in the absence of more definitive data, such structures must remain speculative.

The first conclusive evidence, of which we are aware, for 1,4-addition to tetracyclone involved the crystallographic characterization of *cis*-4-cyano-2,3,4,5-tetraphenylcyclopent-2-en-1-one and of its *trans*-4-cyano-5-methyl analogue;[17] the factors controlling the kinetic versus thermodynamic product distribution were also discussed.

It has been reported that the rotation of the peripheral phenyl rings in $(C_5Ph_5)Ru(CO)Br(PPh_3)$ or $(C_5Ph_4Ar)Mo({=}O)_2Br$, where Ar = 2,5-dimethoxyphenyl, can be slowed on the NMR time scale;[18,19] on the other hand, in $(C_5Ph_5)Fe(CO)(CHO)(PMe_3)$, where there is unequivocal evidence for restricted tripodal rotation, the case for slowed peripheral ring rotation is less definitive.[20] For these reasons, we chose to study the reaction of pentafluorophenyllithium with the cyclopentadienones **2a**,**b** with the ultimate goal of taking advantage of the large chemical shift dispersion of ^{19}F NMR spectroscopy to probe the molecular dynamics of $[C_5Ar_4(C_6F_5)]ML_n$ complexes.

Results and Discussion

Synthetic and Structural Aspects. When tetracyclone, **2a**, was treated with C_6F_5Li at −78 °C and slowly allowed to warm to ambient temperature, two isomeric products **7** and **8** were obtained in 23% and 18% yields, respectively, after hydrolysis and chromatographic separation. Their mass spectra exhibited parent peaks at m/z 552, corresponding to overall addition of a pentafluorobenzene moiety to **2a**; however, their mass spectral fragmentation patterns were strikingly different, implying that they were not merely epimers.

The complexity of the ^{13}C NMR spectrum of **7** (four nonequivalent phenyl rings), together with the $\nu_{C=O}$ IR absorption at 1762 cm^{-1}, suggested that it was a nonconjugated cyclopentenone, $(C_6F_5)Ph_4C_4(H)C{=}O$, rather than the alcohol $Ph_4C_5(C_6F_5)OH$. Gratifyingly, **7** yielded colorless crystals of X-ray quality; the resulting structure appears as Figure 1 and confirms it to be 2-pentafluorophenyl-2,3,4,5-tetraphenylcyclopent-3-en-1-one, the product of a formal 1,6-addition (Scheme 3). The structure of **7** also reveals that the hydrogen at C(5) is cis with respect to the C_6F_5 moiety.

The infrared spectrum of the second product, **8**, revealed no $\nu_{C=O}$ resonance but did exhibit a broad absorption at ~3400 cm^{-1}, indicative of the desired alcohol. The relative simplicity of the ^{13}C NMR spectrum (only two phenyl environments) contrasted with the ^{19}F NMR data, which yielded five clearly resolved multiplets for the pentafluorophenyl ring. Once again, the structure was secured by X-ray crystallography (Figure 2a), which confirmed the product **8** as 5-hydroxy-5-pentafluorophenyl-1,2,3,4-tetraphenylcyclopentadiene. Furthermore, as shown by the space-filling model depicted in Figure 2b, the pentafluorophenyl ring is in an unusually crowded environment. This feature is reflected in the ^{19}F NMR spectra of **8**−**10**, which are discussed below.

Likewise, treatment of 3-ferrocenyl-2,4,5-triphenylcyclopentadienone, **2b**, with lithiopentafluorobenzene at

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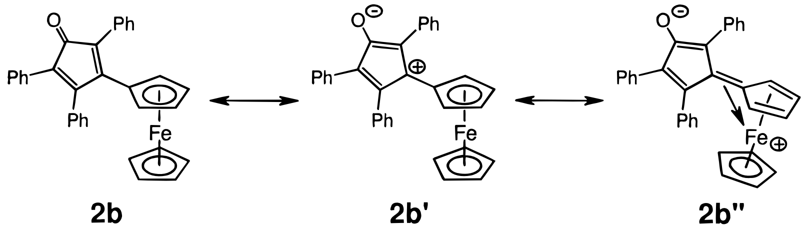
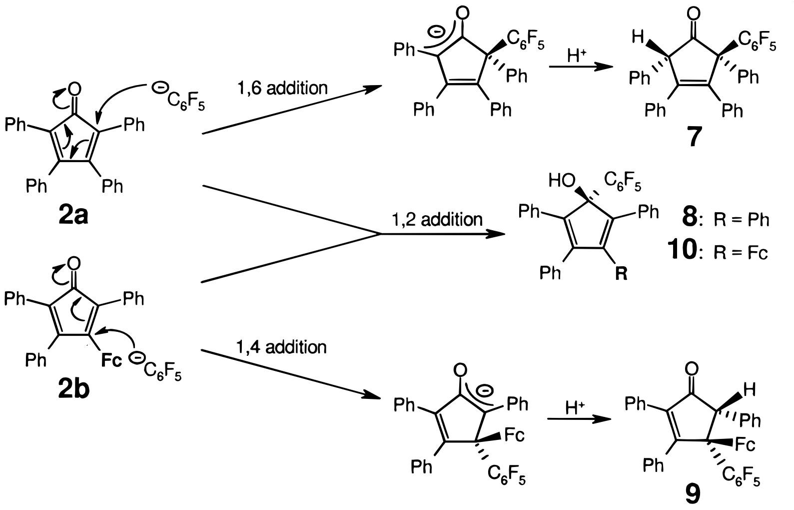
Chart 2



Scheme 3. Products from Reactions of C_6F_5Li with 2a and 2b



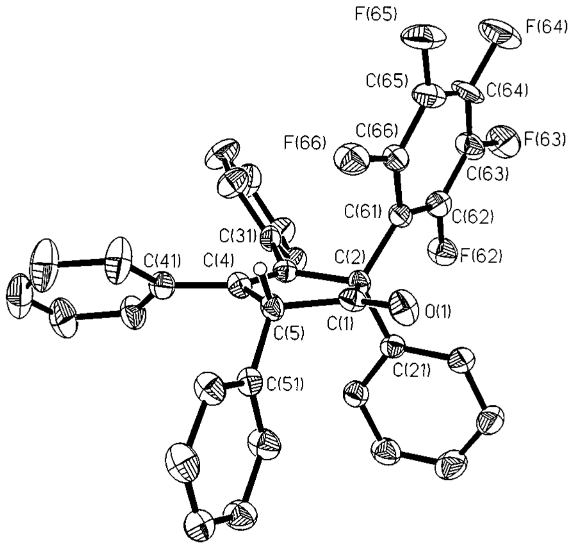


Figure 1. Crystal structure of 2-pentafluorophenyl-2,3,4,5-tetraphenylcyclopent-3-en-1-one, **7** (25% thermal ellipsoids), with phenyl hydrogen atoms omitted for clarity.

−78 °C gave two isomeric products **9** and **10**. The former crystallized as yellow needles suitable for X-ray diffraction and was identified as 4-ferrocenyl-4-pentafluorophenyl-2,3,5-triphenylcyclopent-2-en-1-one, **9**. Once again, the hydrogen at C(5) is cis to the bulkier substituent, i.e., the ferrocenyl group whose presence places the pentafluorophenyl moiety in a highly crowded locale, as illustrated in Figure 3.

One may rationalize the site of attack at the ferrocenyl-bearing ring carbon in **2b** on the basis of partial positive charge at this site, as in the extreme canonical form, **2b′** (Chart 2). Although the zwitterionic structure is normally disfavored on account of the antiaromatic 4π electron count, in this case the formal charge can be readily delocalized onto the iron atom, as in **2b″**. Ferrocenyl-stabilized cations have been crystallographically characterized[21] and their formulation as fulvenes η^6-complexed to a $(C_5H_5)Fe^+$ moiety gains support from molecular orbital calculations.[22]

If the presence of a ferrocenyl substituent does indeed alleviate the antiaromatic character of a zwitterionic resonance structure, such as **2b′**, this phenomenon should be reflected in a decreased $\nu_{C=O}$ value for the ferrocenyl ketones. As shown below for the cyclopentadienones **2a** and **2b**, and also for the corresponding conjugated enones **11a** and **11b**,[23] there is a marked decrease in $\nu_{C=O}$ (by ~16 cm^{-1}) when a phenyl substituent is replaced by a ferrocenyl moiety (Chart 3). Interestingly, we note that in 1963 Brown reported a similar, but less pronounced, effect whereby incorporation of a π-bonded $Cr(CO)_3$ unit onto a phenyl ring of tetracyclone also led to a weakening of the ketonic linkage.[24] However, since the aryl-$Cr(CO)_3$ unit is less capable of stabilizing a benzylic cation than is a ferrocenyl group, and moreover since the isomeric mixture of $(C_4Ph_4C{=}O)Cr(CO)_3$ complexes could not be separated, those workers were unable to draw firm conclusions.

The second product from the reaction of **2b** with pentafluorophenyllithium yielded red crystals that, despite our best efforts, did not yield an acceptable X-ray data set; nevertheless, the absence of a $\nu_{C=O}$ resonance

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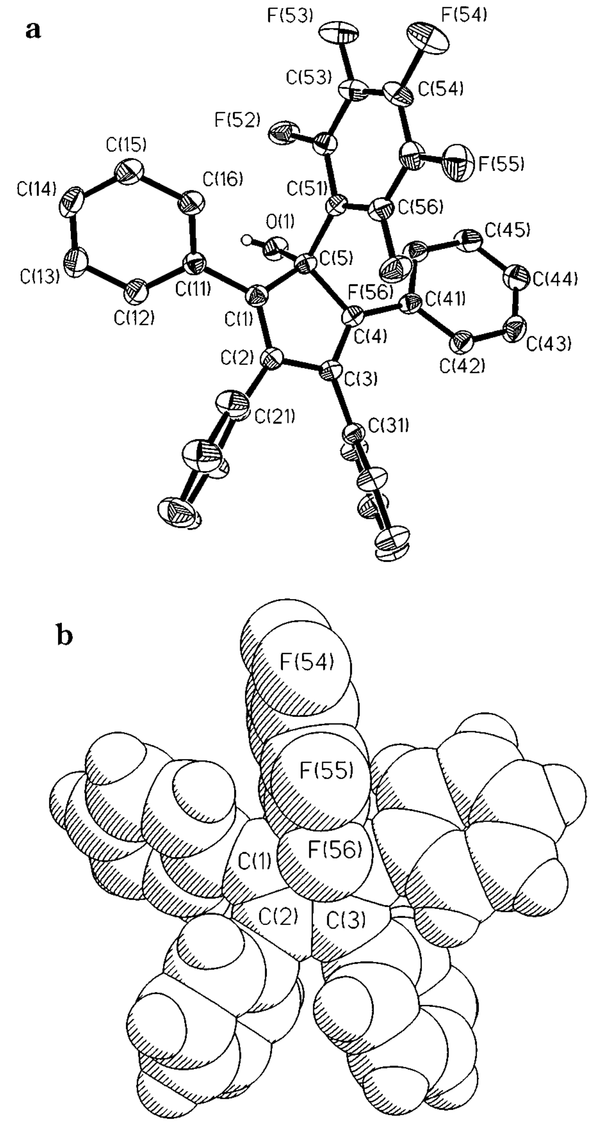

Figure 2. (a) Crystal structure of 5-hydroxy-5-pentafluorophenyl-1,2,3,4-tetraphenylcyclopentadiene, **8** (25% thermal ellipsoids), with phenyl hydrogen atoms omitted for clarity. (b) Bird's eye view of a space-filling model of **8** showing the sterically crowded environment of the C_6F_5 ring.

and presence of a broad absorption at ~3390 cm^{-1} favor its assignment as the alcohol **10**. We note the marked differences between the mass spectral fragmentation patterns of **7** and **8** and of their ferrocenyl analogues **9** and **10**. For example, **8** exhibits the loss of PhCHO, to yield $[C_4Ph_3(C_6F_5)]^{\bullet+}$ and subsequently $[C_4Ph_3]^+$, $[C_3Ph_3]^+$, and $[C_2Ph_2]^+$ ions, entirely typical of the behavior of C_5Ar_5OH systems.[25] In contrast, the fragmentation of **9** and **10** is dominated by the presence of the metal center, giving rise to such species as $[(C_5H_5)_2FeF]^+$, $[(C_5H_5)_2Fe]^+$, and $[(C_5H_5)FeO]^+$.

^{19}F NMR Spectra. Apart from the regiochemistry of the adducts **7**−**10**, there are other points of interest arising from the structures of these molecules. In particular, the ^{19}F NMR spectra of **8**, and also of both ferrocenyl complexes **9** and **10**, exhibit five different fluorine resonances, suggesting that restricted rotation of the pentafluorophenyl rings is evident even at room temperature.

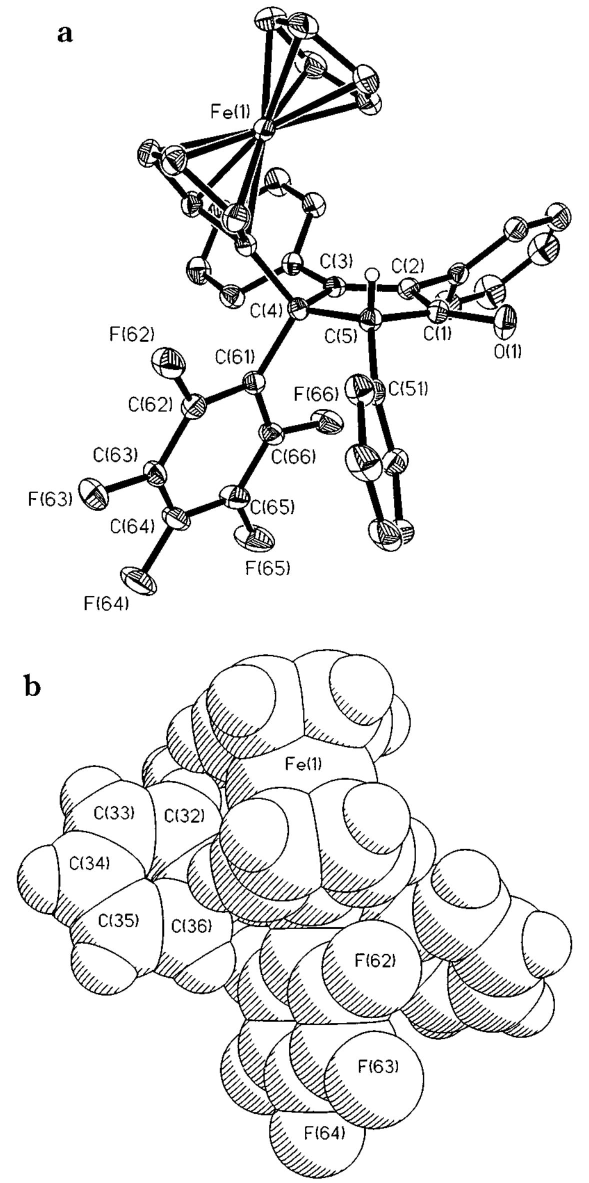

Figure 3. (a) Crystal structure of 4-ferrocenyl-4-pentafluorophenyl-2,3,5-triphenylcyclopent-2-en-1-one, **9** (25% thermal ellipsoids), with hydrogen atoms omitted for clarity. (b) Space-filling model of **9** showing the sterically crowded environment of the C_6F_5 ring.

A search of the literature reveals an early report of the observation of sterically hindered pentafluorophenyls in $(C_6F_5)_2E(C_6H_5)_2$, where E = Ge or Sn.[26a] This claim, based on a slight broadening of the *m*-fluorine ^{19}F NMR resonances, was later withdrawn[26b] and attributed instead to inter-ring coupling; similar behavior has been noted for $(C_6F_5)_3COH$.[27] Thus, although the fluxional character of a variety of Ar_4E systems has been fully analyzed in a series of now classic papers by Mislow,[28] it

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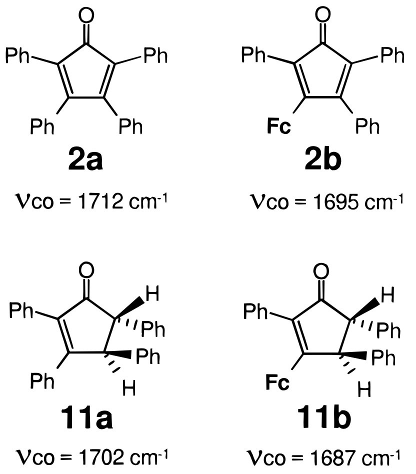
Chart 3



2a ν_{CO} = 1712 cm^{-1}

2b ν_{CO} = 1695 cm^{-1}

11a ν_{CO} = 1702 cm^{-1}

11b ν_{CO} = 1687 cm^{-1}

appears that definitive proof of restricted rotation of pentafluorophenyl rings in organic systems remains an open question. Another relevant observation is Cowan's incorporation of a *m*-fluorotyrosine residue into a high-potential iron protein to probe the rotational freedom of a phenyl ring proximate to the [Fe_4S_4] prosthetic site.[29] Establishment of the factors controlling the barriers to aryl ring rotation is of particular interest at present because of the recent elegant syntheses of vancomycin whereby the natural material possesses a favored atropisomer in the 12-membered ring.[30] We note, however, that several groups[31] have reported the slowed rotation of pentafluorophenyl rings in sterically crowded molecules possessing a *cis*-$(C_6F_5)_2M$ moiety, where M = Pd or Pt. Similarly, hindered rotation has been observed in the rhodium complexes $[(C_5Me_5)Rh(C_6F_5)(PMe_3)(CO)]^+$ and in $(C_5H_5)Rh(C_6F_5)(PMe_3)Cl$.[32] Such behavior has also been observed in $(C_5Me_5)TiMe(C_6F_5)(\mu\text{-Me})B(C_6F_5)_3$.[33] The reported pentafluorophenyl rotation barriers range from approximately 9 kcal mol^{-1} to more than 15 kcal mol^{-1}. In contrast, when pentafluorophenylcyclopentadienyl or -indenyl ligands are coordinated to iron, cobalt, rhenium, or zirconium, no evidence for restricted rotation of the C_6F_5 fragment was reported.[34]

In light of these reports, we chose to investigate more thoroughly the ^{19}F NMR behavior of **8**–**10**. We are unaware of any previous examples of hindered pentafluorophenyl rotation in purely organic systems. It was initially necessary to establish that all five equal intensity fluorine resonances (two doublets, three triplets, as in Figure 4) were indeed in the same phenyl ring. Typically, the 470 MHz ^{19}F–^{19}F COSY experiment on **10** established the connectivity whereby the ortho doublets at −121.3 ppm and −129.5 ppm each couple to a meta triplet at −163.3 ppm and −162.7 ppm, respectively; both meta peaks correlate with the para triplet at −155.4 ppm. Moreover, the fluxional character of the ^{19}F spin system was readily detectable from the 2D-EXSY spectrum, which reveals off-diagonal cross-peaks between both ortho and between both meta environments.

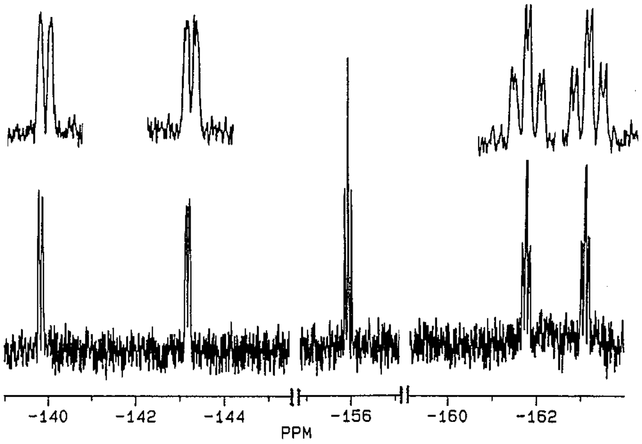


Figure 4. 282 MHz ^{19}F NMR spectrum of **8** in xylene at 30 °C showing five fluorine environments.

The barriers toward pentafluorophenyl ring rotation in **8**–**10** could not be evaluated directly from line-broadening measurements. The chemical shift differences between the *o*-fluorines in these molecules are so large as to preclude the observation of coalescence between these peaks at an instrumentally accessible temperature; for example, in **10** the *o*-fluorines are separated by 8.13 ppm, which is 2296 Hz even on a 300 MHz instrument. Furthermore, the more closely spaced *m*-fluorine resonances had not fully coalesced even at ~130 °C. However, approximate barriers for **8**, **9**, and **10** (20 ± 1, 19 ± 1, and 21 ± 1 kcal mol^{-1}, respectively) were obtained by simulation of their variable-temperature 282 MHz ^{19}F NMR spectra. In contrast, there is no evidence for slowed pentafluorophenyl ring rotation in **7**, and this is in accord with its X-ray crystal structure which indicates no major steric problems.

The availability of 5-hydroxy-5-pentafluorophenyl-1,2,3,4-tetraphenylcyclopentadiene should permit entry to complexes of the type $[C_5Ph_4(C_6F_5)]ML_n$ with their potential to function as molecular bevel gears whereby the rotation of the peripheral rings and the ML_n unit may be correlated. Such molecules will be the focus of future reports.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. All solvents were dried according to standard procedures before use.[35] Silica gel (particle size: 20–45 microns) was employed for flash column chromatography.

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^{1}H, ^{13}C, and ^{19}F solution NMR spectra were acquired on Bruker DRX 500 or AC 300 spectrometers and were referenced to the residual proton or ^{13}C solvent signal, or to $CFCl_3$, respectively. Mass spectra were obtained using a Finnigan 4500 spectrometer by direct electron impact (DEI) or direct chemical ionization (DCI) with NH_3. Infrared spectra were recorded on a Bio-Rad FTS-40 spectrometer. Melting points (uncorrected) were determined on a Thomas-Hoover melting point apparatus. Elemental analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario.

Reaction of Tetracyclone, 2a, with Lithiopentafluorobenzene. Butyllithium (3.1 mL of a 1.6 M hexane solution, 5 mmol) was added dropwise to a solution of pentafluorobenzene (0.6 mL, 5 mmol) in THF (20 mL) at −78 °C via microsyringe over a period of 30 min and the mixture stirred for 1 h at this temperature. The C_6F_5Li thus prepared was added dropwise to a solution of tetracyclone (1.92 g, 5 mmol) in THF (50 mL) at −78 °C under a nitrogen atmosphere. The reaction mixture stirred for 2 h. at −78 °C, allowed to warm slowly to room temperature, and hydrolyzed with acidifed water (40 mL). The products were extracted with ether (100 mL) and dried over $MgSO_4$, the volume was reduced in vacuo, and the residue was chromatographed over silica gel and eluted with CH_2Cl_2/hexane. The products isolated were as follows: tetracyclone, **2a** (1.50 g, 3.9 mmol; 78% recovered), as a purple-red powder; 2-pentafluorophenyl-2,3,4,5-tetraphenylcyclopent-3-en-1-one, **7**, as colorless crystals, mp 197−198 °C (140 mg, 0.25 mmol, 23%); 5-hydroxy-5-pentafluorophenyl-1,2,3,4-tetraphenylcyclopentadiene, **8**, as yellow crystals, mp 165 °C (110 mg, 0.20 mmol; 18%).

Data for **7**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.5−7.1 (m, 20H, phenyl rings), 5.20 (s, 1H, H-5); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 207.4 (C═O), 142.3, 139.1, 137.9, 136.1, 135.3, 130.2, 129.6, 129.0, 128.8, 128.7, 128.6, 128.4, 127.5, 61.5; ^{19}F NMR (282.4 MHz, CD_2Cl_2) −133.77 (d, 2F, ^3J(F−F) = 19 Hz, *o*-F), −155.52 (t, 1F, ^3J(F−F) = 21 Hz, *p*-F), −163.12 (t, 2F, ^3J(F−F) = 21 Hz, *m*-F); IR (CH_2Cl_2) ν_{CO} at 1762 cm^{-1}; MS (DEI) *m/z* 552 $[M]^+$ (17), 524 $[M - CO]^+$ (23), 446 $[M - CO - C_6H_6; C_4Ph_3(C_6F_5)]^+$ (10), 267 $[C_3Ph_3]^+$ (90), 167 $[C_6F_5]^+$ (100); (DCI) *m/z* 570 $[M + NH_4]^+$ (100), 552 $[M]^+$ (14), 524 $[M - CO]^+$ (25), 267 $[C_3Ph_3]^+$ (43), 167 $[C_6F_5]^+$ (50). Anal. Calcd for $C_{35}H_{21}F_5O$: C, 76.08; H, 3.83. Found: C, 76.06; H, 3.84.

Data for **8**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.25−6.9 (m, 20H, phenyl rings), 2.98 (s, 1H, OH); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 130.0, 129.5, 128.6, 128.3, 128.0, 127.8; ^{19}F NMR (282.4 MHz, CD_2Cl_2) −139.37 (d, 1F, ^3J(F−F) = 22 Hz, *o*-F), −144.75 (d, 1F, ^3J(F−F) = 21 Hz, *o*-F), −156.71 (t, 1F, ^3J(F−F) = 21 Hz, *p*-F), −162.25 (t, 1F, ^3J(F−F) = 21 Hz, *m*-F), −163.28 (t, 1F, ^3J(F−F) = 22 Hz, *m*-F); ^{19}F NMR 282.4 MHz, xylene) −139.84 (d, 1F, ^3J(F−F) = 24 Hz, *o*-F), −143.20 (d, 1F, ^3J(F−F) = 20 Hz, *o*-F), −155.97 (t, 1F, ^3J(F−F) = 21 Hz, *p*-F), −161.76 (t, 1F, ^3J(F−F) = 24 Hz, ^4J(F−F) = 7 Hz, *m*-F), −163.12 (t, 1F, ^3J(F−F) = 22 Hz, ^4J(F−F) = 7 Hz, *m*-F); IR (CH_2Cl_2) ν_{OH} at 3550 (br) cm^{-1}; MS (DEI) *m/z* 552 $[M]^+$ (57), 474 $[M - C_6H_6]^+$ (13), 446 $[M - CO - C_6H_6; C_4Ph_3(C_6F_5)]^+$ (13), 397 $[C_5Ph_2(C_6F_5)O]^+$ (5), 369 $[C_4Ph_2(C_6F_5)]^+$ (10), 279 $[C_4Ph_3]^+$ (10), 267 $[C_3Ph_3]^+$ (11), 195 $[C_6F_5CO]^+$ (12), 178 $[C_2Ph_2]^+$ (23), 167 $[C_6F_5]^+$ (30), 152 (9), 105 $[PhCO]^+$ (100), 78 $[C_6H_6]^+$ (50); (DCI) *m/z* 553 $[M + H]^+$ (100), 474 $[M - C_6H_6]^+$ (6), 178 $[C_2Ph_2]^+$ (15), 105 $[PhCO]^+$ (35). Anal. Calcd for $C_{35}H_{21}F_5O$: C, 76.08; H, 3.83. Found: C, 76.05; H, 3.85.

Reaction of 3-Ferrocenyl-2,4,5-triphenylcyclopentadienone, 2b, with Lithiopentafluorobenzene. As for **2a**, 3-ferrocenyl-2,4,5-triphenylcyclopentadienone (492 mg, 1 mmol), prepared according to the literature method,[6,36] was treated with lithiopentafluorobenzene (1 mmol) and stirred at −78 °C for 2 h. The mixture was allowed to warm slowly to room temperature, hydrolyzed, extracted with ether, dried over $MgSO_4$, and chromatographed on silica gel and eluted with CH_2Cl_2/hexane to give the following: **2b** (350 mg, 0.07 mmol; 70% recovered) as a blue powder; 4-ferrocenyl-4-pentafluorophenyl-2,3,5-triphenylcyclopent-2-en-1-one, **9**, as golden yellow crystals (52 mg, 0.078 mmol, 26%), mp 255 °C dec; 5-hydroxy-5-pentafluorophenyl-2-ferrocenyl-1,3,4-triphenylcyclopentadiene, **10**, as red crystals (35 mg, 0.053 mmol; 18%), mp 132 °C.

Data for **9**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.45−7.05 (m, 15H, phenyl rings), 5.19 (s, 1H, H-5), 4.62 (m, 1H, C_5H_4), 4.33 (m, 1H, C_5H_4), 4.19 (s, 5H, C_5H_5), 4.09 (m, 1H, C_5H_4), 3.22 (m, 1H, C_5H_4); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 130.5, 130.4, 130.1, 129.7, 128.8, 128.5, 127.7, 70.2 (C_5H_4), 69.7 (C_5H_5), 69.5 (C_5H_4), 67.7 (C_5H_4), 65.0 (C_5H_4); ^{19}F NMR (282.4 MHz, CD_2Cl_2) −126.59 (d, 1F, ^3J(F−F) = 23 Hz, *o*-F), −131.10 (d, 1F, ^3J(F−F) = 22 Hz, *o*-F), −153.83 (t, 1F, ^3J(F−F) = 21 Hz, *p*-F), −160.85 (t, 1F, ^3J(F−F) = 22 Hz, *m*-F), −162.08 (t, 1F, ^3J(F−F) = 20 Hz, *m*-F); IR (CH_2Cl_2) ν_{CO} at 1662 cm^{-1}; MS (DEI) *m/z* 660 $[M]^+$ (5), 595 $[M - C_5H_5]^+$ (4), 523 $[M - (C_5H_5)FeO]^+$ (6), 434 $[M - (C_5H_5)Fe - (PhCO)]^+$ (4), 398 $[M - (C_6H_5C_5H_4)Fe(C_5H_5)]^+$ (4), 186 $[C_{10}H_{10}Fe]^+$ (20), 121 $[C_5H_5Fe]^+$ (100); (DCI) *m/z* 661 $[M + H]^+$ (10), 435 $[(M + 1) - (C_5H_5)Fe - (PhCO)]^+$ (30), 205 $[C_{10}H_{10}FeF]^+$ (50), 76 $[C_6H_4]^+$ (100). Anal. Calcd for $C_{39}H_{25}F_5FeO$: C, 70.92; H, 3.82. Found: C, 71.03; H, 3.95.

Data for **10**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.9−6.8 (m, 15H, phenyl rings), 4.45 (m, 1H, C_5H_4), 4.27 (m, 2H, C_5H_4), 4.01 (m, 1H, C_5H_4), 3.61 (s, 5H, C_5H_5); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 133.5−123.8 (phenyl rings), 70.1 (C_5H_5); ^{19}F NMR (470.7 MHz, CD_2Cl_2) −121.26 (d, 1F, ^3J(F−F) = 19 Hz, *o*-F), −129.47 (d, 1F, ^3J(F−F) = 23 Hz, *o*-F), −155.42 (t, 1F, ^3J(F−F) = 21 Hz, *p*-F), −162.71 (t, 1F, ^3J(F−F) = 23 Hz, *m*-F), −163.33 (t, 1F, ^3J(F−F) = 21 Hz, *m*-F); ^{19}F NMR (282.4 MHz, xylene) −120.81 (d, 1F, ^3J = 23 Hz, *o*-F), −128.94 (d, 1F, ^3J(F−F) = 23 Hz, *o*-F), −155.87 (t, 1F, ^3J(F−F) = 21 Hz, *p*-F), −163.31 (t, 1F, ^3J(F−F) = 23 Hz, *m*-F), −163.76 (t, 1F, ^3J(F−F) = 21 Hz, *m*-F); IR (CH_2Cl_2) ν_{OH} (br) at 3390 cm^{-1}; MS (DCI) *m/z* 661 $[M + H]^+$ (10), 495 $[M - (PhC/CC_5H_4)]^+$ (7), 372 $[M - (C_6F_5)Fe(C_5H_5)]^+$ (32), 355 $[C_5Ph_3(C_5H_4)]^+$ (45), 285 $[M - (C_6F_5C/CC_5H_4)Fe(C_5H_5)$ (10), 231 $[C_6F_5C_5H_4]^+$ (26), 137 $[C_5H_5FeO]^+$ (12), 91 $[C_7H_7]^+$ (12), 69 $[CF_3]^+$ (100). Anal. Calcd for $C_{39}H_{25}F_5FeO$: C, 70.92; H, 3.82. Found: C, 70.87; H, 3.76.

Crystallographic Data for 7−9. X-ray crystallographic data for **7**,[37] **8**,[38] and **9**[39] were each collected from a suitable sample mounted with epoxy on the end of a thin glass fiber. Data were collected on a P4 Siemens diffractometer equipped with a Siemens SMART 1K CCD Area Detector (employing the program SMART[40]) and a rotating anode utilizing graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data processing was carried out by use of the program SAINT,[41] while the program SADABS[42] was utilized for the scaling of

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(37) Crystal data for **7**: colorless plate, 0.27 × 0.22 × 0.05 mm, monoclinic, $P2_1/n$; a = 12.130(1) Å, b = 10.832(1) Å, c = 21.343(3) Å, α = 90°, β = 101.217(4)°, γ = 90°, Z = 4. Data collection: Mo Kα, 13 176 reflections collected, 3598 independent reflections. Results of solution and refinement: data-to-parameter ratio = 9.5, residual electron density max/min 0.165/−0.188 e/Å^3, goodness-of-fit on F^2 = 0.966, final R indices ($I > 2\sigma(I)$) R1 = 0.0699, wR2 = 0.1195.

(38) Crystal data for **8**: yellow plate, 0.38 × 0.28 × 0.05 mm, triclinic, $P\bar{1}$; a = 10.774(4) Å, b = 12.070(5) Å, c = 12.474(5) Å, α = 112.105 (7)°, β = 98.768(7)°, γ = 107.213(9)°, Z = 2. Data collection: Mo Kα, 9092 reflections collected, 3309 independent reflections. Results of solution and refinement: data-to-parameter ratio = 8.8, residual electron density max/min 0.202/−0.184 e/Å^3, goodness-of-fit on F^2 = 0.936, final R indices ($I > 2\sigma(I)$) R1 = 0.0453, wR2 = 0.1083.

(39) Crystal data for **9**: golden yellow needle, 0.36 × 0.12 × 0.11 mm, triclinic, $P\bar{1}$; a = 9.6633(3) Å, b = 11.2009(4) Å, c = 15.5051(3) Å, α = 101.075(2)°, β = 106.608(2)°, γ = 107.127(1)°, Z = 2. Data collection: Mo Kα, 9435 reflections collected, 4322 independent reflections. Results of solution and refinement: data-to-parameter ratio = 10.4, residual electron density max/min 0.195/−0.320 e/Å^3, goodness-of-fit on F^2 = 1.019, final R indices ($I > 2\sigma(I)$) R1 = 0.0400, wR2 = 0.0864. The authors have deposited atomic coordinates for the structures of **7**−**9** with the Cambridge Crystallographic Data Centre. Further details of the crystal structure investigation, including the atomic coordinates, can be obtained on request from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

(40) Sheldrick, G. M. *SMART, Release 4.05*; Siemens Energy and Automation Inc., Madison, WI 53719, 1996.

(41) Sheldrick, G. M. *SAINT, Release 4.05*; Siemens Energy and Automation Inc., Madison, WI 53719, 1996.

diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. Structures were solved by using the direct methods procedure in the Siemens SHELXTL[43] program library and refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the carbon atom to which they are bonded, except for the hydroxyl hydrogen in **8**, which was located from the electron density difference map.

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Supporting Information Available: Tables of crystal data, atomic parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **7**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(42) Sheldrick, G. M. *SADABS* (*Siemens Area Detector Absorption Corrections*); Siemens Energy and Automation Inc., Madison, WI 53719, 1996.

(43) Sheldrick, G. M. *SHELXTL*, *Version 5.03*; Siemens Crystallographic Research Systems, Madison, WI, 1994.