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Articles

Synthesis of Pentafluorophenyl-Substituted Cyclopentadienes and Their Use as Transition-Metal Ligands

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The reaction of NaC_5H_5 (NaCp) and hexafluorobenzene (1:1 ratio) in THF at 25 °C for 15 h afforded, after hydrolysis, a mixture of regioisomeric (pentafluorophenyl)cyclopentadienes. This mixture was isolated as a monoisomeric dimer of 1-(pentafluorophenyl)cyclopentadiene. The structure of the dimer was determined crystallographically. Flash vacuum thermolytic cracking of the dimer at 200 °C regenerated (pentafluorophenyl)cyclopentadiene as a mixture of regioisomers. In contrast, the reaction of NaCp, NaH, and C_6F_6 (1:2:5 ratio) in THF at reflux for 3 d affords, after hydrolysis, 1,4-bis(pentafluorophenyl)cyclopentadiene, which does not dimerize. Either the mono- or the disubsubstituted diene reacts with NaH in THF to afford the corresponding stable substituted sodium cyclopentadienides in high yields. Sodium (pentafluorophenyl)cyclopentadienide, $(C_6F_5)C_5H_4Na$, reacted with $FeBr_2$, $Re(CO)_5Br$, and $ZrCl_4(THF)_2$, to afford the transition metal complexes $(\eta^5\text{-}C_5H_4C_6F_5)_2Fe$, $(\eta^5\text{-}C_5H_4C_6F_5)Re(CO)_3$, and $(\eta^5\text{-}C_5H_4C_6F_5)_2ZrCl_2$. Sodium 1,3-bis(pentafluorophenyl)cyclopentadienide reacted with $FeBr_2$ and $Re(CO)_5Br$ to give the corresponding complexes $[\eta^5\text{-}1,3\text{-}C_5H_3(C_6F_5)_2]_2Fe$ and $[\eta^5\text{-}1,3\text{-}C_5H_3(C_6F_5)_2]Re(CO)_3$. Infrared spectroscopic analysis of the tricarbonylrhenium(I) complexes and cyclic voltammetric analysis of the substituted ferrocenes quantified the strong electron-withdrawing effects of the pentafluorophenyl substituents.

Introduction

The physical and chemical properties of $\eta^5\text{-}C_5H_5$ (Cp) metal complexes may be widely varied or finely tuned by changing the Cp ring substituents.[1] However, published accounts of *electron-withdrawing* ring substituent effects on the physical properties or chemical reactivity of Cp complexes are relatively sparse.[2] Challenges to the design of Cp ligands with electron-withdrawing substituents include (1) the isolation of the ligands as stable cyclopentadienyl anions and (2) the stability of the Cp ring substituents toward electrophilic/oxophilic transition metal fragments, including the reactive intermediates of important catalytic processes. Circumventing the synthetic challenges by attaching substituents to Cp ligands *after* formation of the metal complex is reliable for only a few highly stable late transition metal species.[3]

We now report the straightforward synthesis of pentafluorophenyl-substituted cyclopentadienes from routinely available, relatively inexpensive starting mate-

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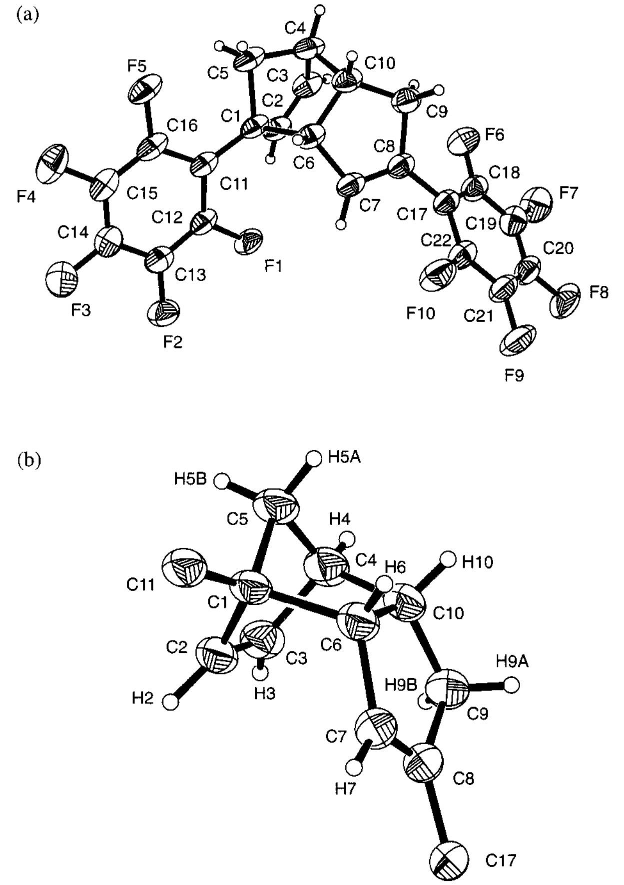
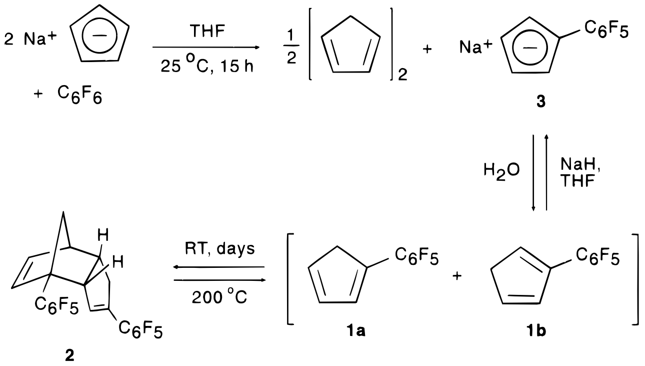


Figure 1. (a) Thermal ellipsoid plot of $C_{22}H_{10}F_{10}$ (**2**). (b) Thermal ellipsoid plot of the tricyclic core of $C_{22}H_{10}F_{10}$ (**2**) showing hydrogen atoms located and isotropically refined. Only the *ipso* carbon atoms the C_6F_5 groups are shown at C_{11} and C_{17}. Selected interatomic distances (Å): C(1)−C(2) = 1.523(3), C(2)−C(3) = 1.311(3), C(1)−C(11) = 1.495(3), C(1)−C(6) = 1.599(3), C(6)−C(7) = 1.498(3), C(6)−C(10) = 1.550(3), C(7)−C(8) = 1.320(3), C(8)−C(9) = 1.520(3), C(8)−C(17) = 1.478(3). Selected intramolecular conformational angles (deg): C(5)−C(1)−C(11)−C(16) = −14.8(3), C(7)−C(8)−C(17)−C(22) = −41.64.

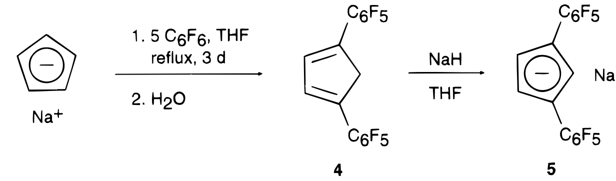
rials. We show that the C_6F_5-substituted cyclopentadienes are readily converted into corresponding cyclopentadienyl anions as *thermally stable* sodium salts in high yield; in particular, fluoride elimination is not observed. We then demonstrate the utility of the C_6F_5-substituted cyclopentadienylsodium compounds as transition metal ligands by presenting the syntheses of four late-transition-metal compounds and one early-transition-metal compound. Finally, we present spectroscopic and electrochcmical data data unequivocally demonstrating the additive electron-withdrawing influence of the pentafluorophenyl substitutent(s).[4]

Results and Discussion

Scheme 1. Synthesis of Sodium (Pentafluorophenyl)cyclopentadienide



Scheme 2. Synthesis of Sodium 1,3-Bis(pentafluorophenyl)cyclopentadienide



As shown in Scheme 1, the reaction of NaCp with C_6F_6 in THF at room temperature initially gave a mixture of isomeric (pentafluorophenyl)cyclopentadienes in 80% yield after hydrolysis (**1**).[5] Immediate formation of the Diels–Alder dimer (**2**) is minimized if the workup is carried out at 0 °C, and the diene mixture **1** may be stored for 1−2 days at −20 °C. Recrystallization of the crude mixture of dienes **1** from hot ethanol afforded the monoisomeric dimer **2** in 60% yield. Flash vacuum thermolysis of the dimer **2** regenerated the dienes **1**, which were treated immediately with NaH in THF to afford sodium cyclopentadienide **3**. Alternatively, the anionic ligand **3** may be synthesized directly by carrying out the reaction of NaCp and C_6F_6 in the presence of NaH (1.1 equiv). This modification traps the dienes **1** by deprotonation *in situ* to afford **3** in one step, while avoiding the formation of the byproduct, dicyclopentadiene. However, the crude product from the latter one-pot procedure contains 5−10% of unreacted NaCp as determined by ^{1}H NMR.

The structure proposed for the dimer **2** was verified by single-crystal X-ray diffraction analysis. The thermal ellipsoid plots shown in Figure 1 demonstrate the *endo* stereochemistry of the tricyclic core and the regiochemistry of the double bonds, as well as the regiochemistry and conformational disposition of the pentafluorophenyl substituents on the tricyclo[5.2.1.0^{2,6}]deca-3,8-diene skeleton. These structural features were confirmed by location and isotropic refinement of all the hydrogen atoms in the molecule. The supporting information contains complete crystal data and metric parameters for **2**.

As shown in Scheme 2, the reaction of NaCp with an excess of C_6F_6 and 2 equiv of NaH in THF at reflux afforded, after aqueous workup, the disubstituted diene **4** in 54% yield. The diene **4** reacted with sodium hydride in THF to form sodium 1,3-bis(pentafluorophenyl)cyclopentadienide **5**.

As shown in Figure 2, common ligand-substitution procedures[6] for the syntheses of the corresponding

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[5] (Pentafluorophenyl)cyclopentadiene was previously reported as a product of the photolysis of $Cp_2Ti(C_6F_5)_2$. (a) Kligert, B.; Roloff, A.; Urwyler, B.; Wirz, J. *Helv. Chim. Acta* **1988**, *71*, 1858. (b) Wahren, R. *J. Organometal. Chem.* **1973**, *57*, 415. (c) Finter, J.; Riediker, M.; Rohde, O.; Rotzinger, B. *Makromol. Chem., Macromol. Symp.* **1989**, *24*, 177.

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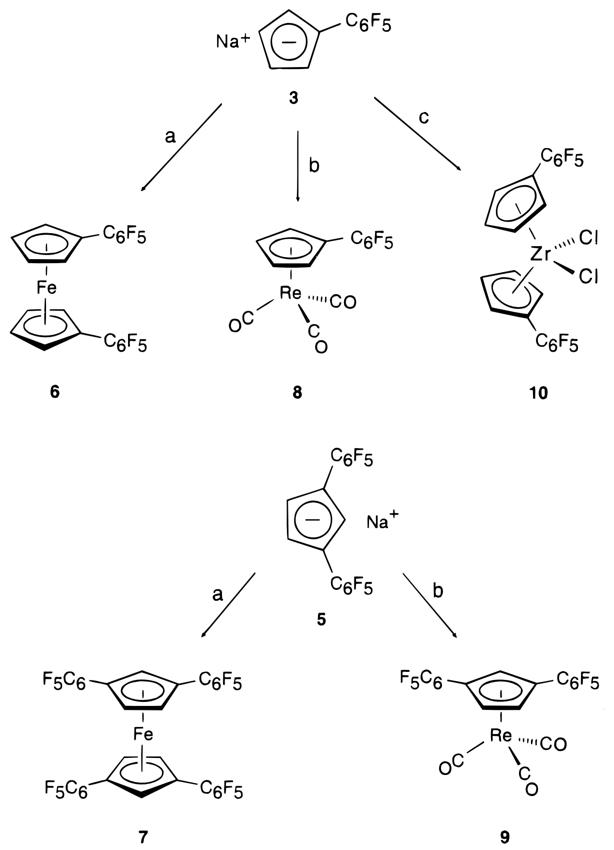

Figure 2. Synthesis of C_6F_5-substituted cyclopentadienyl-metal complexes. Reagents and conditions: (a) 0.5 $FeBr_2$, THF, reflux, 6 h. (b) $Re(CO)_5Br$, THF, reflux, 15 h. (c) 0.5 $ZrCl_4(THF)_2$, toluene, 100 °C, 1 h.

unsubstituted Cp complexes were readily adapted to the new pentafluorophenyl-substituted ligands. The disubstituted ferrocene **6** forms hydrocarbon-soluble red-orange flake crystals, while the tetrasubstituted ferrocene **7** is a sparingly soluble red-orange microcrystalline solid. The mono- and disubstituted tricarbonylrhenium(I) complexes **8** and **9** form colorless, air-stable, hydrocarbon-soluble crystalline solids. The disubstituted zirconocene dichloride **10** forms very fine pale yellow needles and is sparingly soluble in common solvents.

Infrared (IR) spectroscopic analysis of the mono- and disubstituted tricarbonylrhenium(I) complexes **8** and **9**, respectively, and cyclic voltammetric analysis of the substituted ferrocenes **6** and **7**, respectively, were carried out in order to quantify the electronic effects of the pentafluorophenyl substituents in a manner that could be compared to published data obtained with other substituents. The IR analysis of **8** and **9** showed a stepwise increase in the wavenumber of symmetric CO stretch of 4 cm^{-1} for each C_6F_5 group relative to the parent complex, $(\eta^5\text{-}C_5H_5)Re(CO)_3$. These data show that the pentafluorophenyl substitutent has a strong electron-withdrawing effect on the electronic properties of the complexed $Re(CO)_3$ fragment. The effect of the C_6F_5 group is therefore comparable to that of an acetyl substituent, which increases ν_{CO} by 3 cm^{-1} relative to $(\eta^5\text{-}C_5H_5)Re(CO)_3$.[6b,c]

$E_{1/2}$ of oxidation values of 345(5) mV and 678(5) mV (relative to Cp_2Fe^+/Cp_2Fe) for the disubstituted and tetrasubstituted ferrocenes **6** and **7**, respectively, were obtained by cyclic voltammetry. As $(\eta^5\text{-}C_5H_4CF_3)_2Fe$ was previously shown to have an $E°$ of oxidation 640 mV positive of ferrocene,[7] we learned that the C_6F_5 group exerts an electron-withdrawing influence about half that of the CF_3 group on ferrocene. Another noteworthy aspect of both the infrared spectroscopic and electrochemical data is that the effect of four C_6F_5 groups is exactly twice the effect of two C_6F_5 groups, within experimental errors, relative to the unsubstituted parent complex.

Experimental Section

General Considerations. All manipulations were carried out using standard nitrogen-atmosphere techniques. Hexafluorobenzene was purchased from PCR (Gainesville, FL). NaCp was made by the reaction of freshly distilled cyclopentadiene and NaH in THF or purchased from Aldrich as a 2.0 M solution in THF. NMR spectra were recorded on a Varian Unity 400 MHz instrument. Melting points were obtained in open capillaries and are uncorrected. Elemental analyses were performed by Oneida Research Services (Whitesboro, NY). For infrared spectroscopic measurements, a MIDAC M-Series FT-IR operating at 0.5-cm^{-1} resolution was used to examine *n*-octane solutions of the tricarbonylrhenium(I) complexes **7** and **8** in a NaCl-windowed cell.

Electrochemical Measurements. Single-sweep cyclic voltammetric data were obtained for substituted ferrocenes **6** and **7** at nominal concentrations of 5 μM in CH_2Cl_2 using 0.10 M $[n\text{-}Bu_4N][PF_6]$ as the electrolyte and activated alumina as an internal desiccant. The apparatus was a BAS 100B potentiostat with a glassy Pt working electrode, a Pt wire auxiliary electrode, and a Ag/AgCl reference electrode. The sweep was initialized at 0 V, scanned to +2.0 V, reversed to −1.8 V, and returned to 0 V, at a scan rate of 100 mV s^{-1}. Reported $E_{1/2}$ values represent the average of three experiments. $|E_{ox} - E_{red}|$ ranged from 58 to 72 mV, and I_c/I_a was within 7% of unity, both indicators of substantially reversible oxidation. Increases in scan rate did not improve reversibility.

Crystallographic Studies. Colorless prisms of diene dimer (**2**) were grown by cooling a concentrated hexanes solution to −20 °C. Relevant crystal data are summarized in Table 1. Hydrogen atoms were located and isotropically refined. Data were collected in a $P2_1/a$ setting. Superlattice reflections (with doubled *a*) exist, but refinement with $Z = 8$, $A = 30.1192$ Å, was unsucessful. Complete details of the crystallographic experiment, structure solution and refinement, and metric and thermal parameters are provided in the supporting information.

1,4-Bis(pentafluorophenyl)tricyclo[5.2.1.0^{2,6}]deca-3,8-diene (2). Under nitrogen, 3.7 g (0.020 mol) of C_6F_6 was slowly added to a solution of NaCp (3.5 g, 0.040 mmol) in 20 mL of THF. The mixture was stirred at 25 °C for 15 h. The solvent was removed under reduced pressure, and the residue was washed with pentane (3 × 10 mL) to remove the dicyclopentadiene byproduct. ^1H NMR (THF-d_8) analysis of the residue found mainly $Na(C_6F_5Cp)$ containing about 10% of NaCp and a variable amount of THF. The residue was then taken up in 20 mL of pentane, and the slurry was hydrolyzed with 10 mL of ice−water. The layers were separated, and the organic layer was dried over $MgSO_4$ at 0 °C, filtered through neutral alumina, and evaporated at 0 °C to afford 3.65 g (0.016 mol, 80%) of the complex diene mixture **1** as a sweet-smelling white solid. Recrystallization twice from hot ethanol or hexanes afforded an analytical sample of the dimer, $C_{22}H_{10}F_{10}$ (**2**): ^1H NMR (400 MHz, $CDCl_3$) δ 6.31 (d, $J = 5.8$ Hz, 1H), 6.20 (m, 1 H), 6.05 (m, 1 H), 3.64 (m, 1H), 3.12 (m, 2 H), 2.69 (m, 1 H), 2.11 (m, 3 H). $\{^1H\}^{13}C$ NMR ($CDCl_3$) δ 146.8 (d), 143.5 (d), 140.5 (d), 138.4 (d), 137.3, 137.2 (d), 135.8, 132.6, 131.3, 116.1 (t), 112.2 (t), 62.0, 56.4, 55.1, 45.8, 43.0, 37.7. Anal. Calcd for $C_{22}H_{10}F_{10}$ C, 56.91; H, 2.17. Found: C, 56.81; H, 1.93.

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(7) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4228.

Table 1. Crystal Data for $C_{22}H_{10}F_{10}$ (2)

formula	$C_{22}H_{10}F_{10}$
formula weight	464.3
crystal system	monoclinic
space group	$P2_1/c$
a, Å	15.0596(10)
b, Å	11.0688(13)
c, Å	10.9452(7)
β, deg	93.112(5)
V, Å^3	1821.8(10)
Z	4
cryst dimens, mm	0.28 × 0.18 × 0.15
cryst color, habit	colorless rectangular prism
D_{calc}, g cm^{-3}	1.693
μ(Cu Kα), cm^{-1}	15.1
temp, K	295
diffractometer	Enraf-Nonius CAD-4
monochromator	graphite
radiation	Cu Kα ($\lambda = 1.54184$ Å)
2θ scan range, deg	2−75
index ranges	$-13 \le h \le 0, -13 \le k \le 0, -37 \le l \le 37$
no. of collcd rflns	8324
no. of ind rflns	3747
no. of ind obsd rflns	2747
solution	direct methods (MULTAN)[7]
refinement software	MolEN
$R(F)$	0.043
$R(wF)$	0.047
GOF	2.092

[a] Scattering factors and anomalous dispersion ($\Delta f'$, $\Delta f''$) data were from (a) International Tables for X-ray Crystallography; Lonsdale, K., Ed.; Reidel: Boston, 1985. For a discussion of anomalous dispersion effects, see: (b) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

Sodium (Pentafluorophenyl)cyclopentadienide (3). A solution of 1-(pentafluorophenyl)cyclopentadiene dimer (**2**, 2.5 g, 5.4 mmol) in pentane (10 mL) was subjected to flash vacuum thermolysis in a 20-cm Pyrex tube at 200 °C to afford 2.1 g (9.1 mmol, 84%) of an approximately 1:1 mixture of 1- and 2-(pentafluorophenyl)cyclopentadienes, as determined by ^{1}H NMR. This colorless oil was dissolved in THF (10 mL) and added to a stirred suspension of NaH (500 mg, 0.021 mol) in THF (20 mL) maintained at 0 °C. After stirring for 2 h, during which the mixture warmed to 25 °C, the solvent was evaporated, and the residue was triturated with several 10-mL portions of pentane to obtain 2.2 g (8.7 mmol, 96%) of $Na(C_6F_5C_5H_5)$ (**3**) as a violet solid: ^{1}H NMR (THF-d_8) δ 6.45 (m, 2 H), 5.93 (m, 2 H). $\{^1H\}^{13}C$ NMR (THF-d_8) δ 146.2 (d, $^1J_{CF} = 240$ Hz, *C*F), 141.4 (d, $^1J_{CF} = 244$ Hz, *C*F), 137.0 (d, $^1J_{CF} = 228$ Hz, *C*F), 121.7 (t, $^2J_{CF} = 17$ Hz, C_6F_5 ipso *C*), 111.3 (t, $^4J_{CF} = 7$ Hz, *C*H), 110.3 (t, $^5J_{CF} = 2$ Hz, *C*H), 105.8 ($^3J_{CF} = 3$ Hz, *C*C_6F_5). ^{19}F NMR (THF-d_8) δ −144.51 (d, $^3J_{FF} = 23$ Hz, 2 F), −166.43 (t, $^3J_{FF} = 24$ Hz, 2 F), −172.51 (tt, $^3J_{FF} = 21$ Hz, $^4J_{FF} = 5$ Hz, 1 F). Variable small quantities of THF in the product (as determined by ^{1}H NMR) prevented us from obtaining satisfactory elemental analysis. Heating the product under vacuum to remove residual THF leads to slow decomposition.

1,4-Bis(pentafluorophenyl)cyclopentadiene (4). A mixture of NaCp (2.0 g, 0.023 mmol), NaH (1.1 g, 0.046 mol), C_6F_6 (42 g, 0.23 mol), and THF (100 mL) was stirred at reflux under nitrogen for 3 d. The solvent was then removed under reduced pressure, and the residue was washed with pentane (3 × 50 mL). Pentane (100 mL) and water (20 mL) were added, the layers were separated, and the organic layer was dried over $MgSO_4$, filtered through neutral alumina, and evaporated to afford 4.9 g (54% based on NaCp) of the **4**. An analytical sample was obtained by recrystallization from hot ethanol or hexanes: mp 104−106 °C; ^{1}H NMR (CDCl$_3$) δ 7.31 (tt, $^4J_{HH} = 1.3$ Hz, $^5J_{HF} = 0.9$ Hz, 2 H), 4.05 (tp, $^5J_{HF} = 1.8$ Hz, $^4J_{HH} = 1.3$ Hz, 2 H). $\{^1H\}^{13}C$ NMR (CDCl$_3$) δ 144.5 (d, $^1J_{CF} = 253$ Hz, *C*F), 139.5 (d, $^1J_{CF} = 253$ Hz, *C*F), 138.0 (d, $^1J_{CF} = 251$ Hz, *C*F), 136.3 (t, $^4J = 8$ Hz, *C*H), 133.7 (m, *C*C_6F_5), 110.9 (td, $^2J_{CF} = 14$ Hz, $^4J_{CF} = 4$ Hz, C_6F_5 ipso *C*), 46.5 (p, $^4J_{CF} = 5$ Hz, *C*H$_2$). ^{19}F NMR (CDCl$_3$) δ −140.99 (d, $^3J_{FF} = 22$ Hz, 4 F), −157.44 (t, $^3J_{FF} = 21$ Hz, 2 F), −163.66 (m, 4 F). Anal. Calcd for $C_{17}H_4F_{10}$: C, 51.28; H, 1.01. Found: C, 51.30; H, 0.93.

Sodium 1,3-Bis(pentafluorophenyl)cyclopentadienide (5). A mixture of the 1,4-bis(pentafluorophenyl)cyclopentadiene (**4**) and a 10% molar excess of NaH in THF was stirred at room temperature for 3 h. Filtration to remove unreacted sodium hydride and evaporation of the filtrate afforded the crude product as a $(THF)_x$ solvate in yields exceeding 90%. Heating the product at 80 °C under high vacuum (10^{-5} torr) for several hours affords a THF-free sample: ^{1}H NMR (THF-d_8) δ 6.99 (m, 1 H), 6.44 (m, 2 H). $\{^1H\}^{13}C$ NMR (THF-d_8) δ 144.0 (d, $^1J_{CF} = 241$ Hz, *C*F), 138.9 (d, $^1J_{CF} = 245$ Hz, *C*F), 135.0 (d, $^1J_{CF} = 241$ Hz, *C*F), 118.5 (t, $^2J_{CF} = 16$ Hz, C_6F_5 ipso *C*), 113.2 (m, *C*C_6F_5), 111.6 (*C*H), 106.9 (*C*H). ^{19}F NMR (THF-d_8) δ −143.9 (d, $^3J_{FF} = 20$ Hz, 4 F), −166.03 (m, 4 F), −170.86 (tt, $^3J_{FF} = 21$ Hz, $^4J_{FF} = 5$ Hz, 2 F). Anal. Calcd for $C_{17}H_3F_{10}Na$ C, 48.59; H, 0.72. Found: C, 48.12; H, 0.65.

Bis[η^5-(pentafluorophenyl)cyclopentadienyl]iron(II) (6). A mixture of FeBr$_2$ (216 mg, 1.00 mmol), sodium (pentafluorophenyl)cyclopentadienide (**3**, 533 mg, 2.10 mmol), and THF (25 mL) was stirred under reflux for 6 h. The solvent was then removed under reduced pressure, water (50 mL) was added, and the crude product was extracted with benzene (50 mL). Evaporation of the organic layer gave an orange residue, from which the analytically pure product (**6**, 445 mg 0.86 mmol, 86%) was obtained as three crops of red-orange flakes by crystallization from hexanes: mp 183−185 °C. ^{1}H NMR (CDCl$_3$) δ 4.78 (tt, $^3J_{HH} = 2.0$ Hz, $^5J_{FF} = 2.0$ Hz, 4 H), 4.42 (t, $^3J_{HH} = 2.0$ Hz, 4 H). $\{^1H\}^{13}C$ NMR (CDCl$_3$) δ 144.2 (d, $^1J_{CF} = 251$ Hz), 138.9 (d, $^1J_{CF} = 252$ Hz), 137.8 (d, $^1J_{CF} = 252$ Hz), 112.53 (t, $^2J_{CF} = 15$ Hz), 72.7 (t, $^3J_{CF} = 6$ Hz), 71.1 (t, $J_{CF} = 2$ Hz), 70.8 (t, $J_{CF} = 6.0$ Hz). ^{19}F NMR (CDCl$_3$) δ −140.67 (d, $^3J_{FF} = 22$ Hz, 4 F), −159.17 (t, $^3J_{FF} = 21$ Hz, 2 F), −164.07 (m, 4 F). Anal. Calcd for $C_{22}H_8F_{10}Fe$: C, 51.00; H, 1.56. Found: C, 51.12; H, 1.60.

Bis[η^5-1,3-bis(pentafluorophenyl)cyclopentadienyl]iron(II) (7). A mixture of sodium 1,3-bis(pentafluorophenyl)cyclopentadienide (**5**, 105 mg, 0.25 mmol) and FeBr$_2$ (27 mg, 0.12 mmol) in THF (20 mL) was stirred at reflux under nitrogen for 12 h. Removal of the solvent under reduced pressure, extraction of the residue with hot benzene, and evaporation of the solvent afforded 90 mg (0.11 mmol, 88%) of (**7**) as a red-orange solid. An analytical sample was obtained by sublimation (80 °C, 0.050 torr): mp 237−241 °C. ^{1}H NMR (CDCl$_3$) δ 5.41 (br s, 2 H), 5.04 (br s, 4 H). The compound was not sufficiently soluble for ^{13}C NMR analysis. ^{19}F NMR (CDCl$_3$) δ −139.96 (d, $^3J_{FF} = 22$ Hz, 8 F), −156.88 (t, $^3J_{FF} = 21$ Hz, 4 F), −162.98 (m, 8 F). Anal. Calcd for $C_{34}H_6F_{20}Fe$: C, 48.03; H, 0.71. Found: C, 48.36; H, 0.76.

Tricarbonyl[η^5-(pentafluorophenyl)cyclopentadienyl]rhenium(I) (8). A mixture of Re(CO)$_5$Br (Aldrich, 203 mg, 0.500 mmol), sodium (pentafluorophenyl)cyclopentadienide (**3**, 140 mg, 0.55 mmol), and THF (25 mL) was stirred at reflux under nitrogen for 2 h. After the solvent was removed under reduced pressure, the brown residue was extracted with hexanes (50 mL). The solution was eluted through neutral alumina and evaporated to afford 180 mg (0.36 mmol, 72%) of crude **8**. Crystallization from hexanes at −20 °C afforded an analytical sample: mp 66.0−66.5 °C; IR (octane) $\nu_{CO} = 2034$, 1947 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 6.00 (tt, $^3J_{HH} = 2.4$ Hz, $^3J_{HF} = 1.6$ Hz, 2 H), 5.47 (t, $^3J = 2.4$ Hz, 2 H). $\{^1H\}^{13}C$ NMR (CDCl$_3$) δ 192.6 (*C*O), 144.1 (d, $^1J_{CF} = 251$ Hz, *C*F), 140.3 (d, $^1J_{CF} = 251$ Hz, *C*F), 138.0 (d, $^1J_{CF} = 252$ Hz, *C*F), 108.2 (t, $^2J_{CF} = 16$ Hz, C_6F_5 ipso *C*), 87.8 (m, *C*C_6F_5), 87.4 (t, $^4J_{CF} = 6$ Hz, *C*H), 84.05 (s, *C*H). ^{19}F NMR (CDCl$_3$) δ −138.95 (m, 2 F), −155.47 (tt, $^3J_{FF} = 21$ Hz, $^4J_{FF} = 2$ Hz, 1 F), −162.15 (m, 2 F). IR (octane) $\nu_{CO} = 2038$, 1954 cm^{-1}. Anal. Calcd for $C_{14}H_4F_5O_3Re$ C, 33.54; H, 0.80. Found: C, 33.50; H, 0.63.

Tricarbonyl[η^5-1,3-bis(pentafluorophenyl)cyclopentadienyl]rhenium(I) (9). This complex was prepared from Re(CO)$_5$Br and **5**, following the same method as for the monosubstituted complex (**8**); a 78% yield of [η^5-1,3-C_5H_3-$(C_6F_5)_2$]$Re(CO)_3$ (**9**) was obtained: mp 107.0−107.5 °C. IR (octane) ν_{CO} = 2038, 1953 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.56 (br s, 1 H), 6.08 (br s, 2 H). $\{^1H\}^{13}C$ NMR ($CDCl_3$) δ 191.6 (s, *C*O), 144.1 (d, $^1J_{CF}$ = 251 Hz, *C*F), 140.6 (d, $^1J_{CF}$ = 250 Hz, *C*F), 138.0 (d, $^1J_{CF}$ = 251 Hz, *C*F), 107.4 (td, $^2J_{CF}$ = 13 Hz, $^4J_{CF}$ = 4 Hz, C_6F_5 ipso), 89.1 (t, $^4J_{CF}$ = 5 Hz, *C*H), 87.6 (s, *C*C_6F_5), 86.5 (t, $^4J_{CF}$ = 5 Hz, *C*H). ^{19}F NMR ($CDCl_3$) δ −138.80 (d, $^3J_{FF}$ = 23 Hz, 4 F), −151.40 (tt, $^3J_{FF}$ = 21 Hz, $^4J_{FF}$ = 3 Hz, 2 F), −161.60 (m, 4 F). Anal. Calcd for $C_{20}H_3F_{10}O_3Re$: C, 35.99; H, 0.45. Found: C, 36.17; H, 0.44.

Dichlorobis[η^5-(pentafluorophenyl)cyclopentadienyl]zirconium(IV) (10). A mixture of $ZrCl_4(THF)_2$ (350 mg, 0.93 mmol), sodium (pentafluorophenyl)cyclopentadienide (**3**, 320 mg, 1.00 mmol), and toluene (50 mL) was stirred at 100 °C for 1 h. The *hot* mixture was filtered through Celite, which was washed with additional hot toluene. Fine needles separated from the yellow filtrate upon cooling to room temperature. The crystalline product was collected by filtration and washed with pentane to afford 427 mg (0.68 mmol, 73%) of pure **10**: ^1H NMR (C_6D_6) δ 6.48 (m, 4 H), 5.81 (t, $^3J_{HH}$ = 3.2 Hz, 4 H). The complex was not sufficiently soluble for ^{13}C NMR analysis. ^{19}F NMR (C_6D_6) δ −140.52 (d, $^3J_{FF}$ = 20 Hz, 4 F), −155.21 (tt, $^3J_{FF}$ = 22 Hz, $^4J_{FF}$ = 3 Hz, 2 F), −163.50 (m, 4 F). Anal. Calcd for $C_{22}H_8Cl_2F_{10}Zr$ C, 42.32; H, 1.29. Found: C, 42.58, H, 1.01.

Conclusions

Formal nucleophilic aromatic substitution of fluoride with cyclopentadienyl anions in hexafluorobenzene provides a simple route to new Cp ligands for use in preparing transition metal complexes with electron-deficient metal centers. We are presently exploring the scope of this method with respect to other cyclopentadienes, fluoroarenes, and transition metal fragments.

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Supporting Information Available: Crystal data for $C_{22}H_{10}F_{10}$ (**2**) (10 pages). Ordering information is given on any current masthead page.

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