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Transition metal cyclopentadienyl complexes bearing perfluoro-4-tolyl substituents

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Abstract

Depending on the ratio of starting materials and the reaction conditions, perfluorotoluene ($C_6F_5CF_3$) reacts with sodium cyclopentadienide (NaCp; Cp = C_5H_5) and excess sodium hydride to afford, after acidic aqueous workup, moderate to high yields of mono-, bis-, tris-, and tetrakis(perfluoro-4-tolyl)cyclopentadiene (**1**, **2**, **3**, and **4**, respectively). Treatment of **1** with excess NaH in THF afforded sodium (perfluoro-4-tolyl)cyclopentadienide (**5**) in 90% yield. Reaction of $FeBr_2$ with 2 equiv. of **5** afforded a 68% yield of $(\eta^5\text{-}C_5H_4C_7F_7)_2Fe$ (**6**). Reaction of $ZrCl_4(THF)_2$ with 2 equiv. of **5** afforded a 58% yield of $(\eta^5\text{-}C_7F_7C_5H_4)_2ZrCl_2$ (**7**). Reaction of $Mn(CO)_5Br$ with **5** afforded a 74% yield of $(\eta^5\text{-}C_7F_7C_5H_4)Mn(CO)_3$ (**8**). Treatment of **3b** with NaH and then with $Mn(CO)_5Br$ in DME afforded a 26% yield of $[\eta^5\text{-}1,2,4\text{-}(C_7F_7)_3C_5H_2]Mn(CO)_3$ (**9**). Treatment of **3b** with NaH and then with $FeBr_2$ in DME afforded a trace yield of $[\eta^5\text{-}1,2,4\text{-}(C_7F_7)_3C_5H_2]_2Fe$ (**10**), which was not fully characterized. Dienes **2a**, **3a**, and **3b** and metal complexes **7**, **8**, and **9** were structurally characterized by single-crystal X-ray diffraction. Infrared spectroscopic analysis of the substituted $CpMn(CO)_3$ complexes showed a linear increase of 5 cm^{-1} in the *A*-symmteric stretching frequency for each C_7F_7 substituent, compared to the analogous value of 4 cm^{-1} reported earlier for each pentafluorophenyl (C_6F_5) substituent. Solution voltammetric analysis of the substituted ferrocene **6** revealed a shift in the $E_{1/2}$ of 465 mV relative to ferrocene, compared to the analogous value of about 340 mV for 1,1′-bis(pentafluorophenyl)ferrocene.

Keywords: Cyclopentadienyl complexes; Metallocenes; Ferrocene; Fluorous; Fluoroaromatic; Electronic effects; Ligand effects

1. Introduction

Ring substituents bring about interesting and useful changes in the chemical reactivity, spectroscopic features, and physical properties of transition metal cyclopentadienyl (Cp) complexes. Systematic analyses of *electron-withdrawing* substituents on metal-centered reactivity are still relatively sparse, however, mainly because "standard" electron-withdrawing groups such as acetyl, nitro, or trifluoromethyl can engage in undesirable reactions of their own. We showed previously that up to four pentafluorophenyl (C_6F_5) groups are readily attached to cyclopentadiene in one-pot procedures involving nucleophilic aromatic substitution of hexafluorobenzene [1–5]. C_6F_5-substituted Cp anions are stable as sodium salts and can be used in standard synthetic procedures to prepare complexes of both early and late transition metals. C_6F_5-substituted ferrocenes and cobaltocenes exhibit reversible electrochemical $M^{II}|M^{III}$ couples. The C_6F_5 substituents attached to zirconocene dichloride are stable under the conditions of methylalumoxane-cocatalyzed coordination polymerization of ethylene [6,7]. Yet, in some reactions, such as the conversion of $(\eta^5\text{-}C_6F_5C_5H_4)_2ZrCl_2$ to the corresponding zirconium dimethyl [8], we have observed side reactions in which a *para* fluorine of a C_6F_5 group undergoes a nucleophilic substitution. Although these problems can often be minimized by careful control of reaction conditions, another approach would be to replace the *para* fluorine with a less nucleophilically susceptible group. We chose CF_3 to retain the strongly electron-withdrawing effect of the aryl

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substituent. We now report the preparation of perfluoro-4-tolyl (C_7F_7) substituted cyclopentadienes and Cp complexes. We find that the C_7F_7 substituent is slightly more electron-withdrawing than C_6F_5.

2. Experimental

2.1. General procedures

Standard inert-atmosphere techniques were used for all reactions. $C_6F_5CF_3$ was used as received from Matrix Scientific. $FeBr_2$ and $Mn(CO)_5Br$ were used as received from Aldrich. $ZrCl_4(THF)_2$ was prepared by the method of Manzer [9]. NaH was purchased as a 60% mineral oil dispersion from Aldrich, washed repeatedly with hexanes, dried under vacuum, and stored in a glove box. NaCp was prepared by the method of Roesky et al. [10]. Reaction solvents were purified by the method of Pangborn et al. [11], except diglyme, which was distilled from CaH_2 under reduced pressure. THF-d_8 (Isotec) was vacuum-transferred from NaK_2 alloy. Infrared spectra were recorded on a Midac M-series transmission instrument operating at $1\ cm^{-1}$ resolution, using dilute *n*-tetradecane solutions and KBr-windowed cells. NMR experiments used Varian Unity 400 and Varian Inova 400 instruments. ^{19}F NMR spectra were referenced to external C_6F_6 in $CDCl_3$ (−163 ppm). Elemental analyses were performed by Desert Analytics (Tucson, Arizona) or Oneida Research Services (Whitesboro, New York).

2.2. Electrochemical measurements

Single-sweep cyclic (CV) and Osteryoung square-wave (OSWV) voltammograms were obtained for **6** at nominal concentrations of about 1 mM in CH_2Cl_2 using 0.10 M tetra(*n*-butylammonium) hexafluorophosphate at the electrolyte, activated alumina as an internal desiccant, and ferrocene as an internal standard. The apparatus was a CH Instruments 620B digital potentiostat with a platinum disk working electrode, a platinum wire auxiliary electrode, and an [Ag|AgCl] reference electrode. The cell was purged thoroughly with nitrogen prior to measurement. CV sweeps were initialized at 0 mV, scanned to +1500 mV, and reversed to 0 mV, at a scan rate of $100\ mV\ s^{-1}$. Wave parameters ($|E_{ox} - E_{red}|$, I_c/I_a) similar to internal ferrocene suggested substantially reversible $Fe^{II}|Fe^{III}$ couples for **6**. Shifts in oxidation potential relative to internal ferrocene were obtained using OSWV. The cell voltage was swept from 0 to 1500 mV with a step resolution of 4 mV, a square-wave amplitude of 25 mV, a frequency of 15 Hz, and 256 samples per point. Voltammograms were analyzed using the CH Instruments software package.

2.3. Crystallographic studies

Crystallographic data are presented in Table 1. Samples were prepared as follows. Colorless blocks ($0.16 \times 0.25 \times 0.27\ mm^3$) of **2a** were obtained by cooling a concentrated hexane solution from 60 to 25 °C and allowing the supersaturated solution to stand at 25 °C overnight. Colorless plates ($0.030 \times 0.182 \times 0.231\ mm^3$) of **3a** were crystallized from hexanes by cooling a concentrated hexane solution from 60 to 25 °C and allowing the supersaturated solution to stand at 25 °C overnight. Colorless blocks ($0.17 \times 0.26 \times 0.30\ mm^3$) of **3b** were crystallized from hexane by cooling a concentrated hexane solution from 60 to 25 °C and allowing the supersaturated solution to stand at 25 °C overnight. Pale yellow rods ($0.06 \times 0.14 \times 0.42\ mm^3$) of **7** were crystallized from toluene by cooling a warm, Celite-filtered toluene solution to 25 °C. Large yellow chunks of **8** crystallized from a concentrated hexanes solution in a freezer at −10 °C. Cutting afforded a single-crystalline block ($0.25 \times 0.25 \times 0.43\ mm^3$). Yellow rods ($0.16 \times 0.17 \times 0.29\ mm^3$) of **9** were crystallized from hexanes/toluene (10:1) by dissolving a sample at 60 °C and cooling to −10 °C.

The general crystallographic procedure was as follows. Each chosen crystal was mounted on a nylon CryoLoop™ (Hampton Research) with Krytox® Oil (DuPont) and centered on the goniometer of an Oxford Diffraction Xcalibur™ diffractometer equipped with a Sapphire 3™ CCD detector. The data collection routine, unit cell refinement, and data processing were carried out with the program CRYSALIS. The structure was solved by direct methods and refined using the SHELXTL NT software package. Except where noted in the following paragraph, the final refinement model involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all hydrogen atoms. Molecular graphics generation used SHELXTL NT software.

Noteworthy details of the structure determinations are as follows. For the diene **2a**, the asymmetric unit of the structure comprises two crystallographically independent molecules. For the diene **3a**, the asymmetric unit of the structure comprises two crystallographically independent cyclopentadiene molecules and 0.5 hexane molecules. For the diene **3b**, the asymmetric unit of the structure comprises two crystallographically independent molecules. Redisual electron density suggested disorder in all three CF_3 groups, each modeled over two positions, with relative occupancies of 71.3%/28.7%; 85.2%/14.8%, and 67.8%/32.2%. The hydrogen atom positions and isotropic thermal parameters were refined independently. For the zirconocene dichloride complex **7**, the Laue symmetry and systematic absences were consistent with the monoclinic space groups *C2/c* and *Cc*; the centric space group *C2/c* was chosen. The asymmetric unit of the structure comprises 0.5 crystallographically independent molecules. There was substantial rotational disorder in the sole crystallographically independent CF_3 group, which was modeled as a threefold disorder with relative occupancies refining to 36.9%, 34.9%, and 28.2%. The C–F distances, C⋯F (CCF_3) distances, and F⋯F (F–C–F) distances were restrained to 1.32(1), 2.35(1), and 2.09(1) Å, respectively, for each of the three

Table 1
Crystallographic data

Compound	**2a**	**3a**	**3b**	**7**	**8**	**9**
Empirical formula	$C_{19}H_4F_{14}$	$C_{26}H_3F_{21} \cdot 0.25(C_6H_{14})$	$C_{26}H_3F_{21}$	$C_{24}H_8Cl_2F_{14}Zr$	$C_{15}H_4F_7MnO_3$	$C_{29}H_2F_{21}MnO_3$
FW	498.22	735.83	735.83	724.42	420.12	852.25
Crystal dimensions (mm)	0.27 × 0.25 × 0.16	0.23 × 0.18 × 0.030	0.30 × 0.26 × 0.17	0.42 × 0.14 × 0.060	0.43 × 0.25 × 0.25	0.29 × 0.17 × 0.16
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
a (Å)	8.7178(13)	12.5475(18)	10.4204(18)	27.528(4)	10.3003(14)	11.9406(15)
b (Å)	17.724(3)	19.713(3)	11.3004(19)	6.7256(7)	17.129(2)	14.6514(19)
c (Å)	21.561(3)	21.690(4)	21.345(3)	14.347(2)	8.0472(10)	15.6930(19)
α (°)	90	90	86.110(13)	90	90	90
β (°)	93.201(12)	99.103(14)	83.263(13)	120.41(2)	91.331(11)	94.756(10)
γ (°)	90	90	84.913(14)	90	90	90
V (Å)^3	3326.3(9)	5297.2(14)	2482.1(7)	2290.7(5)	1419.4(3)	2736.0(6)
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P2_1/n$
Z	8	8	4	4	4	4
D_{calc} (Mg m^{-3})	1.990	1.845	1.911	2.101	1.966	2.069
Absorption coefficient (mm^{-1})	None	None	None	0.843	1.029	0.663
$F(000)$	1952	2884	1392	1408	824	1656
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
θ Collection range	3.93 to 25.09	4.12 to 25.06	3.99 to 27.56	3.35 to 30.08	4.38 to 30.08	4.09 to 30.10
Number of reflections collected	14536	23855	15316	8512	9632	18805
Number of independent reflections	5889	9336	11431	3363	4162	8027
Absorption correction method	None	None	None	Analytical	Analytical	None
Maximum and minimum transmission	None	None	None	0.952 and 0.799	0.8740 and 0.7388	None
Data/restraints/parameters	5889/0/595	9336/0/875	11431/0/955	3363/28/198	4162/0/235	8027/0/487
R [$I > 2\sigma$(I)]	0.0684	0.1080	0.0590	0.0658	0.0364	0.0469
R_w [$I > 2\sigma$(I)]	0.1545	0.2021	0.1489	0.1560	0.0978	0.1213
GoF on F^2	0.961	1.210	0.908	1.074	1.119	1.032
Peak and hole (e Å^{-3})	0.828 and −0.420	0.454 and −0.285	0.598 and −0.347	1.791 and −0.991	0.807 and −0.364	0.887 and −0.445

orientations. The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms, except the fluorine atoms of the disordered CF_3 group; a riding model was used for all hydrogen atoms. The manganese complexes **8** and **9** each comprised a single independent molecule per unit cell without disorder in the CF_3 groups.

*2.4. Synthesis of (perfluoro-4-tolyl)cyclopentadiene (**1**)*

To a mixture of NaCp (2.2 g, 25 mmol), NaH (1.2 g, 50 mmol), and THF (75 mL) maintained at about −10 °C (salt-ice bath) was added $C_6F_5CF_3$ (4.72 g, 20 mmol) in small portions over 15 min using a syringe. With the first few drops of $C_6F_5CF_3$, the mixture turned bright yellow, and with each addition gas (H_2) was evolved. After stirring for 1 h, the mixture had turned a tan color. The cooling bath was removed and the mixture was stirred at room temperature for 15 h; during this interval the reaction turned a tarry brown-black color, whether shielded from light or not. TLC analysis (silica with fluorescent indicator, developed with hexanes) showed, under UV irradiation, a brown spot at $R_f = 0.65$ and a poorly-resolved pair of smaller spots (one brown and one blue) at $R_f = 0.40$. The solvent was then thoroughly evaporated at 25 °C. Pentane (100 mL, not hexanes) was added, and a spatula was inserted under a nitrogen counterstream to break up the residue. After restarting the stirrer, ice-water (50 mL) was added (cautiously at first – hydrogen is evolved) followed by 10 mL of ice-cold concentrated hydrochloric acid. The biphasic mixture was capped again with a septum and stirred for 30 min with ice cooling to ensure complete hydrolysis of the numerous small black lumps. The aqueous layer was separated and extracted with 100 mL of pentane. The combined organic layers (orange to red) were washed with water (2 × 50 mL), dried over $MgSO_4$, filtered, and evaporated using a rotary evaporator with equipped with aspirator suction, an ice-water bath, and a solvent collection bulb chilled with liquid nitrogen. The latter conditions ensure efficient solvent evaporation without significant loss or dimerization of the product. About 5.4 g (95% crude yield) of an orange residue was obtained. The product was purified by flash chromatography on a 6 cm × 20 cm column of silica, eluting with pentane. After the forerun (about 300 mL), a colorless band (about 250 mL of eluent) was collected and evaporated, using the same rotary evaporator setup as before, to afford 4.2 g (75%) of a white solid. Yields ranged from 4.0 to 4.5 g in triplicate experiments. ^1H NMR (400 MHz, $CDCl_3$): Major isomer (1-arylcyclopentadiene, ca. 80% of product) δ 7.43 (m, 1H), 6.78 (m, 1H), 6.73 (m, 1H), 3.59 (m, 2H); minor isomer (2-arylcyclopentadiene, ca. 20% of product) δ 7.02 (m, 1H), 6.85 (m, 1H), 6.63 (m, 1H), 3.27 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): Major isomer δ −56.5 ($^4J = 21$ Hz, 3F), −139.6 (m, 2F), −142.7 (m, 2F); minor isomer δ −56.7 ($^4J = 21$ Hz, 3F), −139.8 (m, 2F); −142.0 (m, 2F). Storage of this compound at room temperature results in rapid decomposition (over several hours) to a sticky, hexane-insoluble gum. Satisfactory elemental analysis was not obtained. ^1H and ^{19}F NMR spectra are provided in the supporting information as evidence of substantial bulk purity.

*2.5. Synthesis of bis(perfluoro-4-tolyl)cyclopentadiene isomers (**2a**, **2b**, **2c**, and **2d**)*

To a stirred mixture of NaCp (0.44 g, 5.0 mmol), NaH (0.60 g, 25 mmol), and THF (50 mL) maintained under nitrogen at 0 °C was added perfluorotoluene (2.6 g, 11 mmol) slowly using a syringe. The mixture turned yellow and then brown. After stirring at 0 °C for 1 h, the cooling bath was removed and the mixture was stirred at room temperature for 24 h. TLC analysis of the reaction mixture showed a faint spot ($R_f \sim 0.55$, brown under UV irradiation) assigned to the monoarylated cyclopentadiene **1**, a pair of intense spots ($R_f \sim 0.38$ and 0.32, respectively, brown and blue under UV irradiation), faint spots ($R_f \sim 0.20$ and 0.1) assigned to the triarylated cyclopentadienes **3a** and **3b**, and a dark brown spot on the baseline. The THF was removed in vacuo, and ether (50 mL) was added, followed by water (10 mL, cautiously at first because of the vigorous H_2 evolution) and aqueous sulfuric acid (10%, 5 mL). The biphasic mixture was stirred for 15 min to ensure complete hydrolysis of the reaction mixture. The aqueous phase was separated and extracted with ether (10 mL). The combined organic layers were washed with water (3 × 10 mL), dried over anhydrous $MgSO_4$, filtered, and evaporated to afford 2.63 g of a dark, sticky residue. TLC analysis of the residue was consistent with the product mixture. The residue was subjected to flash chromatography on silica gel (6 cm × 20 cm column), eluting with hexanes. After a forerun of 300 mL, 50-mL fractions were collected. Fractions 1–5 afforded about 100 mg of **1**. Fractions 7–20 afforded 1.61 g (3.2 mmol, 64%) of a colorless oil, which solidified to a pale yellow waxy solid containing a few well-formed crystals. The crystals were found by NMR spectroscopy to be nearly pure **2a**. One of the crystals was selected for single-crystal X-ray diffraction. The waxy bulk solid was found by ^1H NMR spectroscopic analysis to contain a mixture of diarylated cyclopentadiene isomers **2a** (24%), **2b** (4%), **2c** (63%), and **2d** (9%). ^1H NMR data ($CDCl_3$): for **2a**, δ 7.54 (m, 2H), 4.18 (m, 2H); for **2b**, δ 7.65 (m, 1H), 7.27 (m, 1H), 3.87 (br s, 2H); for **2c**, δ 6.90 (m, 1H), 6.74 (m, 1H), 3.70 (br s, 2H); and for **2d**, δ 6.93 (m, 2H), 3.54 (m, 2H). The ^{19}F NMR spectrum of the isomeric mixture showed signals for the CF_3 groups (relative integration 3F) centered around −56.7 ppm and signals for the aromatic CF groups (relative integration 4 F) between −137 and −143 ppm. An analytical sample of **2a**/**2b** was obtained as a byproduct of the synthesis of **3a**/**3b**. Analysis calcd. (Found) for $C_{19}H_4F_{14}$ C, 45.80 (45.54); H, 0.81 (0.90).

2.6. Synthesis of tris(perfluoro-4-tolyl)cyclopentadiene isomers (**3a** and **3b**)

To a stirred mixture of NaCp (0.44 g, 5.0 mmol), NaH (0.60 g, 25 mmol), and THF (50 mL) maintained under nitrogen was added perfluorotoluene (5.0 g, 21 mmol). The solution turned bright yellow and then brown in color, initially with vigorous gas (H_2) evolution. The mixture was stirred at 60 °C for 2 days. TLC analysis (silica, hexanes) showed a spot corresponding to **2a/2b** and two intense spots corresponding to **3a** and **3b** as well as a dark spot on the baseline of the chromatogram. (In other experiments the reaction temperature was increased to a gentle reflux and extended for one more day, or until TLC analysis showed that **2a/2b/2c/2d** was no longer present, however, no significant improvements in the isolated yields of **3a** and **3b** were realized.) The THF was removed in vacuo, and ether (60 mL) was added, followed by water (10 mL, cautiously at first because of the vigorous H_2 evolution) and aqueous sulfuric acid (10%, 5 mL). The biphasic mixture was stirred for 15 min to ensure complete hydrolysis of the reaction mixture. The aqueous phase was separated and extracted with ether (20 mL). The combined organic layers were washed with water (3 × 10 mL), dried over anhydrous $MgSO_4$, filtered, and evaporated to afford 4.2 g of a dark, sticky residue. The residue was subjected to flash chromatography on silica, loading with 5 mL of toluene and eluting with hexanes. A 6 cm × 25 cm column clearly resolved the major products. After a long forerun (about 1.1 L), 50-mL fractions were collected. Based on TLC analysis, fractions 1–10 were combined and evaporated to obtain 200 mg (0.40 mmol, 8%) of **2a/2b**; fractions 12–32 were combined to afford 1.3 g (1.8 mmol, 36%) of **3b**; and fractions 36–75 were combined to afford 1.2 g (1.7 mmol, 34%) of **3a**. Analytical samples of both **3a** and **3b** (including crystals suitable for single-crystal X-ray diffraction) were obtained by recrystallization from *n*-hexane. Data for **3a**: ^{1}H NMR ($CDCl_3$) d ^{1}H NMR ($CDCl_3$) d 7.16 (s, 1H), 3.93 (s, 2H). ^{19}F NMR ($CDCl_3$) d −56.30 (t, $^4J_{FF} = 20$ Hz, 3F, CF_3), −56.33 (t, $^4J_{FF} = 22$ Hz, 3F, CF_3), −56.36 (t, $^4J_{FF} = 22$ Hz, 3F, CF_3), −138.3 (m, 6F), −138.9 (m, 4F), −139.2 (m, 2F). Anal calcd. (Found) for **3a** C, 43.72 (43.58); H, 0.42 (0.73). Data for **3b** 7.53 (s, 1H), 4.26 (s, 2H). ^{19}F NMR ($CDCl_3$) d −56.26 (t, 3F, $^4J_{FF} = 22$ Hz, CF_3), −56.35 (t, 3F, $^4J_{FF} = 21$ Hz, 3F, CF_3), −56.37 (t, $^4J_{FF} = 22$ Hz, 3F, CF_3) −137.6 (m, 2F), −137.9 (m, 2F), −138.1 (m, 2F), −138.8 (m, 4F), −140.4 (m, 2F). Anal calcd. (Found) for **3b** C, 43.72 (44.06); H, 0.42 (0.73).

2.7. Synthesis of tetrakis(perfluoro-4-tolyl)cyclopentadiene (**4**)

Under a nitrogen atmosphere, perfluorotoluene (7.1 g, 0.030 mol) was added over 5 min to a mixture of NaCp (0.44 g, 5.0 mmol), NaH (0.72 g, 0.030 mol), and anhydrous diglyme (40 mL). An exothermic reaction occurred ($T_{rxn} \sim 70$ °C), during which gas (H_2) was evolved and the mixture turned a dark yellow-brown color. After the initial exotherm subsided (about 15 min), TLC analysis showed that the reaction mixture contained di- and triarylated cyclopentadienes (**2** and **3**). The mixture was lowered into an oil bath maintained at 115 °C. After 18 h, a small aliquot was worked up and analyzed by ^{1}H NMR spectroscopy (the methylene region at 4.0–4.5 ppm is diagnostic and well resolved from the diglyme signals in the region 3.3–3.7 ppm), which revealed a roughly 50:50 mixture of **3b** and **4** (30:70, respectively, after 36 h; 15:87 after 60 h, 5:95 after 84 h). The reaction was allowed to proceed (typically for 3 or 4 days at 115 °C) until **3b** was no longer observed. After cooling, water (10 mL) was added under a nitrogen counterstream to quench the unreacted sodium hydride. Then 10 mL of 10% aqueous sulfuric acid was added to acidify the mixture. The mixture was then diluted with ether (300 mL). The layers were separated, and the organic layer was washed with water (15 × 25 mL) and brine (3 × 25 mL), dried over anhydrous $MgSO_4$, filtered, and evaporated. The crude yield at this point was 5.0 g, but ^{1}H NMR spectroscopic analysis revealed the presence of residual diglyme. A 1.0-g sample of the residue was taken up in 10 mL of ether. The insoluble portion was triturated with cold methanol (5 mL) and collected on a filter to afford 140 mg of **4** (98+% pure by ^{1}H NMR spectroscopic analysis). The soluble portion was subjected to flash chromatography on silica gel (4 cm × 10 cm). A forerun was eluted with ether and evaporated to afford a yellow-orange residue (100 mg) that was mostly diglyme according to ^{1}H NMR spectroscopic analysis. A second band was eluted with 10% acetic acid in ether and evaporated to afford 380 mg of a brown solid. A third band was eluted with 20% acetic acid in methanol and evaporated to afford about 150 mg of a violet solid. The brown and violet residues were found by ^{1}H NMR spectroscopy to contain nearly pure **4**, ostensibly contaminated by small amounts of highly colored impurities. Thus, the total amount of **4** (95% purity) isolated from the ether trituration and chromatographic separation of the 1.0-g sample was 670 mg (67%). The remaining 4.0 g of crude product was triturated with 10 mL of methanol at 0 °C for 1 h, collected on a filter, washed with cold methanol (2 × 5 mL) and pentane (2 × 5 mL) and dried to afford 2.2 g (55%) of a gray solid that was found to contain 0.5% by weight of diglyme. Subsequent trituration with methanol and pentane affords analytical (rigorously diglyme-free) samples at a recovery level of about 50%. ^{1}H NMR ($CDCl_3$) δ 4.33 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −56.78 (t, $^4J_{FF} = 22$ Hz, 6F), −56.84 (t, $^4J_{FF} = 22$ Hz, 6F), −138.0 (m, 4F), −138.1 (m, 4F), −138.3 (m, 4F), −138.5 (m, 4F). Analysis calcd. (Found) for $C_{33}H_2F_{28}$ C, 42.60 (42.36); H, 0.22 (0.33).

2.8. Synthesis of sodium (perfluoro-4-tolyl) cyclopentadienide (**5**)

A suspension of NaH (600 mg, 25 mmol) in THF (50 mL) was prepared and cooled to 0 °C using an ice bath.

With continued cooling and stirring, (perfluoro-4-tolyl)cyclopentadiene (**1**, 4.10 g, 14.5 mmol) dissolved in 10 mL of THF was added using a cannula. Gas (H_2) evolved, and the solution turned yellow and then a drab green color with continued stirring. After stirring 30 min, the mixture was filtered through a medium fritte. The filtrate was evaporated, and the residue was heated at 60 °C under vacuum for 15 h. The resulting purple solid was triturated with pentane (2 × 50 mL), collected on a filter, and dried under vacuum to afford 4.10 g (13.5 mmol, 93%) of a purple solid. ^{1}H NMR (THF-d_8) δ 6.62 (m, 2H), 6.00 (m, 2H). ^{19}F NMR (THF-d_8) δ −55.3 (t, $^4J = 20$ Hz, 3F, CF_3), −147.1 (m, 2F), −149.0 (m, 2F). ^{1}H NMR spectroscopic analysis revealed the presence of about 5% of residual THF.

2.9. Synthesis of $[\eta^5\text{-}(C_7F_7)C_5H_4]_2Fe$ (**6**)

A mixture of sodium (perfluoro-4-tolyl)-cyclopentadienide (**5**, 670 mg, 2.2 mmol), $FeBr_2$ (216 mg, 1.0 mmol) and THF (15 mL) was stirred under reflux for 15 h. After cooling, the solvent was evaporated, and the residue was transferred to a column of silica gel (5 cm × 10 cm). A dark red band eluted with dichloromethane. Evaporation followed by recrystallization of the residue from hexane/chloroform afforded 420 mg (0.68 mmol, 68%) of a brick-red micro-crystalline solid. ^{1}H NMR ($CDCl_3$) d 4.93 (m, 2H), 4.54 (m, 2H). ^{19}F NMR ($CDCl_3$) d −56.6 (t, $^4J_{FF} = 22$ Hz, 6F), −138.6 (m, 4F), −142.3 (m, 4F). Analysis calcd. (Found) for $C_{24}H_8F_{14}Fe$ C, 46.63 (46.83); H, 1.30 (1.48).

2.10. Synthesis of $[\eta^5\text{-}(C_7F_7)C_5H_4]_2ZrCl_2$ (**7**)

A mixture of sodium (perfluoro-4-tolyl)cyclo-pentadienide (**5**, 640 mg, 2.1 mmol), $ZrCl_4(THF)_2$ (380 mg, 1.0 mmol), and toluene (50 mL) was stirred at 100 °C for 1 h. The initial purple color gradually turned to a deep orange. Using a heat gun, the mixture was boiled and then quickly filtered through a bed of Celite. Fine orange needles separated as the filtrate cooled to room temperature. The crystals were collected on a filter, washed with pentane (20 mL), and dried in vacuo to obtain 410 mg (5.8 mmol, 58%) of orange crystals subsequently found suitable for single-crystal X-ray diffraction. Cooling the mother liquor in a freezer (−10 °C) afforded no additional crystals. ^{1}H NMR (THF-d_8) δ 7.11 (m, 4H), 6.86 (m, 4H). ^{19}F NMR (THF-d_8) δ −57.6 (t, $J = 21$ Hz, 6F), −138.6 (m, 4F), −143.8 (m, 4F). Analysis calcd. (Found) for $C_{24}H_8Cl_2F_{14}Zr$ C, 39.79 (39.89); H, 1.11 (0.92).

2.11. Synthesis of $[\eta^5\text{-}(C_7F_7)C_5H_4]Mn(CO)_3$ (**8**)

A mixture of sodium (perfluoro-4-tolyl)-cyclopentadienide (**5**, 310 mg, 1.02 mmol), $Mn(CO)_5Br$, and DME (8 mL) was stirred at 75 °C for 15 h. The resulting dark residue was evaporated, the residue was triturated with hexanes (3 × 20 mL) and filtered through a 5-cm pad of silica gel, eluting with additional hexanes. The yellow filtrate was evaporated to afford 310 mg (74%) of the cryde product as a dark yellow solid. An analytical sample (also suitable for single-crystal X-ray diffraction) was obtained by preparing a warm, concentrated hexanes solution and cooling it overnight in a freezer at −10 °C. ^{1}H NMR ($CDCl_3$) δ 5.53 (m, 2H), 4.93 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −56.7 (t, $^4J_{FF} = 21$ Hz, 3F, CF_3), −137.3 (m, 2F), −140.7 (m, 2F). IR (tetradecane) $\nu_{CO} = 2034$, 1957 cm^{-1}. Analysis calcd. (Found) for $C_{15}H_4F_7MnO_3$ C, 42.88 (42.56); H, 0.96 (0.96).

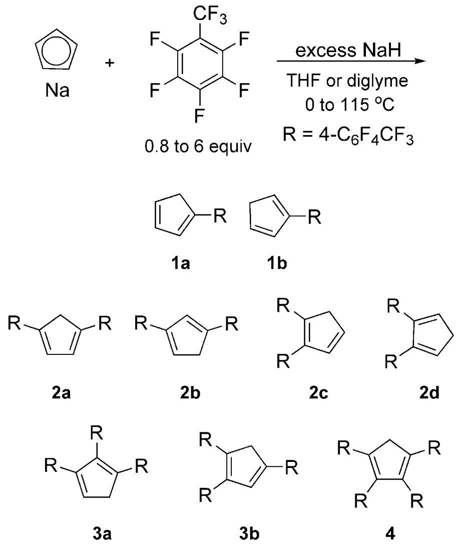
2.12. Synthesis of $[\eta^5\text{-}1,2,4\text{-}(C_7F_7)_3C_5H_2]Mn(CO)_3$ (**9**)

To a suspension of NaH (72 mg, 3.0 mmol) in anhydrous DME (25 mL), the diene **3b** (715 mg, 1.00 mmol) was added as a solid under a nitrogen counterstream. The mixture turned a deep yellow color and gas (H_2) evolved. After stirring several hours at room temperature, the mixture was filtered to remove unreacted NaH. To the filtrate was added $Mn(CO)_5Br$ (250 mg, 0.91 mmol) as a solid under a nitrogen counterstream. The mixture was stirred at 75 °C for 15 h. After evaporating the solvent, the dark residue was triturated for 15 min with 20 mL of 5% ethyl acetate in hexanes. The yellow supernatant was transferred to a column of silica (4 cm × 10 cm). A yellow band eluted with 5% ethyl acetate in hexanes. Evaporation afforded 205 mg (0.24 mmol, 26% based on $Mn(CO)_5Br$) of a yellow solid. An analytical sample (also suitable for single-crystal X-ray diffraction) of yellow crystals was obtained by recrystallization from a warm 10:1 hexanes:toluene solution at −10 °C. ^{1}H NMR ($CDCl_3$) δ 6.01 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −56.7 (t, $^4J_{FF} = 21$ Hz, 3F, CF_3), −56.8 (t, $^4J_{FF} = 21$ Hz, 6F, 2 CF_3), −134.1 (m, 4F), −137.0 (m, 2F), −138.6 (m, 4F), −139.2 (m 2F). IR (tetradecane) $\nu_{CO} = 2044$, 1979, 1972 cm^{-1}. Analysis calcd. (Found) for $C_{15}H_4F_7MnO_3$ C, 40.87 (40.79); H, 0.24 (0.52).

3. Results and discussion

3.1. Cyclopentadiene arylation

As shown in Scheme 1, perfluorotoluene ($C_6F_5CF_3$) reacts with an excess of sodium cyclopentadienide (NaCp) and excess sodium hydride (NaH) to afford, after aqueous workup, a 75% yield of (perfluoro-4-tolyl)cyclopentadiene (**1**). The use of limiting $C_6F_5CF_3$ in the synthesis of **1** is required to prevent diarylation (**2**), in contrast to the synthesis of (pentafluorophenyl)cyclopentadiene, where NaCp was treated with *excess* C_6F_6 at 0 to 25 °C. The CF_3 group has an activating effect on the nucleophilic susceptibility of the arene. The enhanced reactivity of perfluorotoluene relative to hexafluorobenzene has been noted elsewhere [12]. The diene **1** is formed as a mixture of tautomers (**1a** and **1b**) which are not separated on silica gel. The monoarylated diene **1** also undergoes significant decomposition over several hours in solution at 25 °C. Like other nucleophilic substitution reactions of $C_6F_5CF_3$, these reactions are



Scheme 1.

completely regioselective for attack at the 4-position [12], although the formation of black, tarry substances during the reactions suggests the possibility of various oligomerization or coupling pathways.

The diarylated product **2** was isolated as a mixture of regioisomers, **2a–d**. Isomers **2a** and **2b** are tautomers of the vicinal skeleton, whereas isomers **2c** and **2d** are tautomers of the distal skeleton. The two skeletal isomers are obtained in approximately equal amounts, in contrast to our observations with C_6F_5-substituted cyclopentadienes, where the distal isomer predominates and the vicinal isomer is only isolated from reaction mixtures in small amounts and even then not reproducibly. The skeletal isomers of **2** could not be separated efficiently by silica gel chromatography. However, the ^{1}H NMR signals for the four isomers were well resolved and readily assigned on the basis of chemical shift and integration data. As described below, a small sample of **2a/2b** was obtained another way. Unequivocal assignment of the skeletal isomers (**2a/2b** versus **2c/2d**) was accomplished by the crystallographic analysis of **2a**.

Under more vigorous reaction conditions, the arylation proceeds to the triarylated products **3a** and **3b**, which are formed in roughly equal amounts. Using TLC analysis, we found that **2c/2d** was depleted from the reaction faster than **2a/2b**. We speculate that **2c/2d** is more reactive as a nucleophile because it has one ring carbon that does not have a C_7F_7 group in a vicinal position. This observation allowed us to stop the reaction after **2c/2d** was depleted but while **2a/2b** was still present. Subsequent workup and chromatographic separation on silica gel afforded a small yield (8%) of "skeletally pure" **2a/2b**. The separation of the two triarylated cyclopentadienes **3a** and **3b** was much easier than with their C_6F_5-substituted counterparts, largely because the C_7F_7-substituted species are more soluble in the preferred chromatography solvent (hexanes). Thus, a relatively short silica column resolves the two isomers easily.

Under more severe conditions we obtain the tetraarylated diene **4**. Crude yields of **4** are high (about 90%) but removal of residual reaction solvent (diglyme) from the reaction mixture is difficult and inefficient, leading to somewhat lower yields (about 50%) of the purified diene **4**. Following the reaction leading to diene **4** by ^{1}H NMR spectroscopic analysis of small, worked-up aliquots reveal that the 1,2,3-triarylated diene **3a** is depleted from the reaction mixture relatively quickly (in less than 24 h) but the isomeric 1,2,4-triarylated diene **3b** is consumed more slowly (after about 100 h) at a reaction temperature of 115 °C. We speculate that this difference in reactivity arises because **3a** has two ring carbons having only one C_7F_7 substituent in a vicinal position, while both reactive ring carbons in **3b** have two C_7F_7 groups in vicinal positions. Although consistent with the reactivity trends observed for the diarylated cyclopentadienes **2a/2b** versus **2c/2d**, is not clear whether these effects are steric or electronic in origin. Attempts to prepare the pentaarylated homologue under forcing conditions (e.g., diglyme, reflux) led only to intractable black tar.

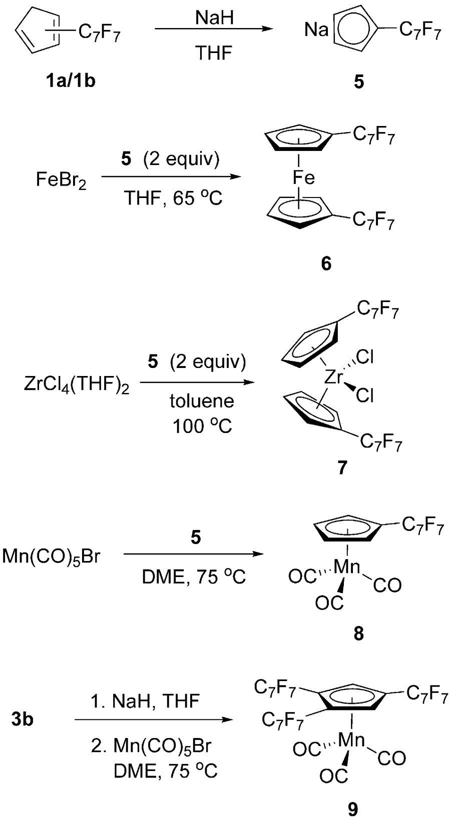
Whereas **1a/1b**, **2a/2b**, **3a**, and **3b** are colorless solids, **4** is obtained as an off-white or tan solid. Hexane solutions of all of these dienes are essentially colorless, whereas aqueous acetone or aqueous THF solutions go from a very pale straw color (**1a/1b**) to a deep yellow color (**4**). We ascribe these colors to autoionization of the increasingly acidic dienes in the more polar solvents. Efforts are underway in our laboratories to measure the acidity constants of these dienes on Streitwieser's lithium ion-pair acidity-indicator scale [13].

3.2. Synthesis of organometallic complexes

Scheme 2 presents the synthesis of several organometallic complexes containing cyclopentadienyl ligands bearing perfluoro-4-tolyl substituents. As the monoarylated diene **1** was readily prepared on a large scale but rather unstable toward decomposition, we found it convenient to prepare and store the corresponding sodium salt (**5**). Simple substitution reactions of **5** and transition metal halides gave the ferrocene **6**, the zirconocene dichloride **7**, and the manganese tricarbonyl complex **8** in moderate to high yields. Yields of analogous reactions of the triarylated diene **3b** were somewhat lower, perhaps due to the low nucleophilicity of the corresponding anion. The triarylated manganese tricarbonyl complex **9** was obtained in 26% yield. Attempts to synthesize the hexaarylated ferrocene **10** largely failed. One of three reactions afforded a trace yield, and the identity of the product was confirmed only by a relatively poor-quality X-ray crystal structure determination ($R = 0.14$ with intractible disorder in the CF_3 groups). Transannular steric strain may impede the formation of this hexaarylated ferrocene.

3.3. Analysis of substituent effects

Table 2 presents data obtained from infrared spectra of the two manganese tricarbonyl complexes (**8** and **9**). of



Scheme 2.

Table 2
Carbonyl stretching wavenumbers (cm^{-1}) of Piano Stool complexes[a]

Entry	Complex	ν_{CO} (A)	ν_{CO} (E)
1	$CpMn(CO)_3$[b,c]	2028	1944
2	$(\eta^5\text{-}C_6F_5C_5H_4)Mn(CO)_3$[b]	2032	1954
3	$[\eta^5\text{-}1,2,4\text{-}(C_6F_5)_3C_5H_2]Mn(CO)_3$[b]	2040	1973, 1965
4	$[\eta^5\text{-}(4\text{-}F_3CC_6F_4)C_5H_4]Mn(CO)_3$	2034	1957
5	$[\eta^5\text{-}1,2,4\text{-}(4\text{-}F_3CC_6F_4)_3C_5H_2]Mn(CO)_3$	2044	1979, 1972

[a] Recorded in *n*-alkane solution. Reproducibility is within 1 cm^{-1}.
[b] Prior results from our laboratories [2].
[c] Lit.: 2030 and 1946 cm^{-1} for $CpMn(CO)_3$ [18].

results. Comparing entries 1–3, the, the value for ν_{CO}(A) increases by 4 cm^{-1} per C_6F_5 substituent [2]. Entries 1, 4, and 5 show that the effect of each perfluoro-4-tolyl substituent is an increase of about 5–6 cm^{-1} in ν_{CO}(A). We also used solution voltammetry to evaluate the electronic effect of the C_7F_7 groups in the substituted ferrocene **6**. Square-wave voltammetric measurements gave a shift in the $E_{1/2}$(ox) of 465(5) mV relative to ferrocene. The corresponding shift for 1,1′-bis(pentafluorophenyl)ferrocene is 345(5) mV. From these results we conclude that the perfluoro-4-tolyl group is about 1.2–1.4 times as electron-withdrawing as the perfluorophenyl (C_6F_5) group when attached to cyclopentadienyl ligands.

3.4. Structures of dienes

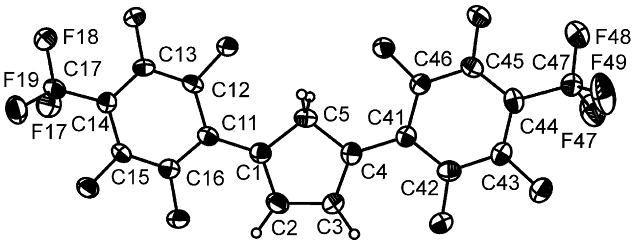


Fig. 1. Thermal ellipsoid plot of **2a** shown at 50% probability. One of two nearly identical independent molecules is shown. Unlabeled fluorine atoms are numbered the same as the carbon atoms to which they are attached. Selected bond lengths (Å): C(1)–C(2), 1.363(5); C(2)–C(3), 1.442(5); C(3)–C(4), 1.357(5); C(4)–C(5), 1.492(5); C(1)–C(5), 1.486(5). Selected bond angles (°): C(2)–C(1)–C(5), 108.1(3); C(1)–C(2)–C(3), 109.4(3); C(4)–C(3)–C(2), 109.9(3); C(3)–C(4)–C(5), 107.9(3); C(1)–C(5)–C(4), 104.6(3). Selected torsional angles (°): C(2)–C(1)–C(11)–C(12), 172.8(3); C(3)–C(4)–C(41)–C(42), −6.7(5).

The molecular structure of the diarylated diene **2a** is shown in Fig. 1. The asymmetric unit contains two nearly identical molecules. The cyclopentadiene and aryl groups are nearly coplanar (torsional angles are 6–8° among both independent molecules). The molecular structure of the triarylated diene **3a** is shown in Fig. 2. The asymmetric unit contains two nearly identical diene molecules and one molecule of hexane. Vicinal aryl–aryl interactions give rise to a propellar arrangement with cyclopentadiene–aryl torsion angles in the range 44–55°. The molecular structure of the isomeric triarylated diene **3b** is shown in Fig. 3. The asymmetric unit contains two nearly identical diene molecules. The cyclopentadiene–aryl torsion angles for the vicinal aryl groups are in the range 45–60°, while the isolated aryl groups lie more in the cyclopentadiene plane (torsion angles of 19.0° and 35.6° for the two independent molecules). The variations in these angles suggest that, aside from the obvious trend for vicinal interactions to drive the torsional angles away from 0°, deformation of these angles are relatively soft and probably influenced

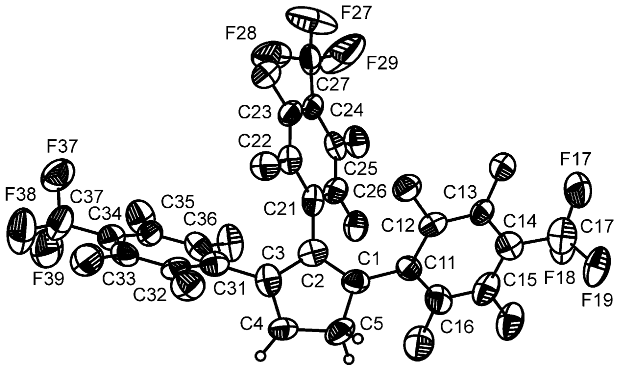


Fig. 2. Thermal ellipsoid plot of **3a** shown at 50% probability. One of two nearly identical independent molecules is shown. The solvent of crystallization (0.5 hexane) is omitted. Fluorine atoms are numbered the same as the carbon atoms to which they are attached. Selected bond lengths (Å): C(1)–C(2), 1.362(11); C(2)–C(3), 1.429(11); C(3)–C(4), 1.399(11); C(4)–C(5), 1.466(11); C(1)–C(5), 1.465(11). Selected bond angles (°): C(2)–C(1)–C(5), 107.6(7); C(1)–C(2)–C(3), 110.1(8); C(4)–C(3)–C(2), 109.0(7); C(3)–C(4)–C(5), 106.5(7); C(1)–C(5)–C(4), 106.7(7). Selected torsional angles (°): C(2)–C(1)–C(11)–C(12), 49.0(13); C(3)–C(2)–C(21)–C(22), 51.4(11); C(4)–C(3)–C(31)–C(32); 48.0(12).

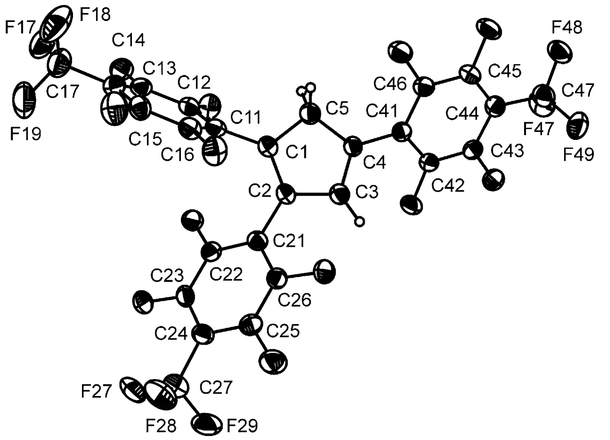


Fig. 3. Thermal ellipsoid plot of **3b** shown at 50% probability. One of two nearly identical independent molecules is shown. Fluorine atoms are numbered the same as the carbon atoms to which they are attached. Selected bond lengths (Å): C(1)–C(2), 1.356(4); C(2)–C(3), 1.468(4); C(3)–C(4), 1.382(4); C(4)–C(5), 1.462(4); C(1)–C(5), 1.495(4). Selected bond angles (°): C(2)–C(1)–C(5), 108.6(2); C(1)–C(2)–C(3), 109.3(2); C(4)–C(3)–C(2), 108.1(2); C(3)–C(4)–C(5), 109.1(2); C(4)–C(5)–C(1); 104.9(2). Selected torsional angles (°): C(2)–C(1)–C(11)–C(12), −120.7(3); C(1)–C(2)–C(21)–C(22); 45.0(4); C(3)–C(4)–C(41)–C(42), 35.6(4).

significantly by crystal packing forces. Packing diagrams of **2a**, **3a**, and **3b** do not reveal any arene stacking interactions and no compelling evidence for CH–FC hydrogen bonding.

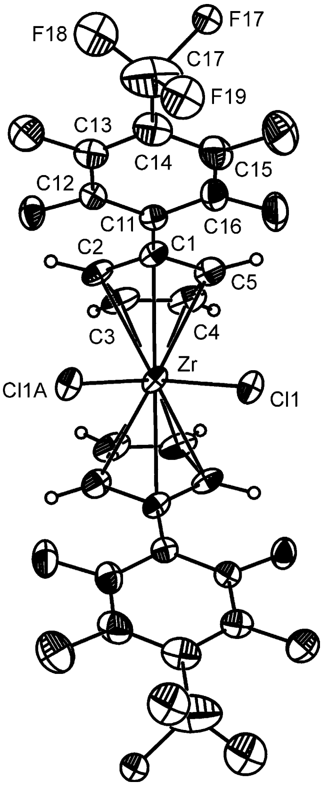


Fig. 4. Thermal ellipsoid plot of **7** shown at 50% probability. Unlabeled fluorine and hydrogen atoms are numbered the same as the carbon atoms to which they are attached. Selected bond lengths (Å): Zr–Cl(1), 2.4260(12); Zr–Cp(centroid), 2.211(5). Zr–C(1), 2.549(5); Zr–C(2), 2.527(4); Zr–C(3), 2.487(5); Zr–C(4), 2.491(5); Zr–C(5), 2.537(5); C(1)–C(2), 1.421(7); C(2)–C(3), 1.415(7); C(3)–C(4), 1.405(9); C(4)–C(5), 1.411(9); C(1)–C(5), 1.430(7). Selected bond angles (°): Cl(1)–Zr–Cl(1A), 94.56(6); Cp(centroid)–Zr–Cp(centroid), 107.1(1). Selected torsional angles (°): Cp(least-squares plane)–aryl(least-squares plane), 7.1.

3.5. Structures of organometallic complexes

The molecular structure of the substituted zirconocene dichloride **6** is shown in Fig. 4. The overall molecular structure (with the two aryl groups occupying positions directly above and below the metallocene wedge) as well as key aspects of the packing arrangement (molecules lined up head-to-tail) are analogous to those reported for 1,1′-diphenylzirconocene dichloride [7]. The perfluoro-4-tolyl substituent effects subtle but interesting changes in certain bond lengths of the complex. First, the Zr–Cl bonds of **7** are somewhat contracted at 2.426(1) Å, compared to 2.445(2) Å for Cp_2ZrCl_2 [14], consistent with the electron-withdrawing character of the perfluoro-4-tolyl group. The Cl–Zr–Cl bond angle of **7** is also contracted by about 2.5° compared to Cp_2ZrCl_2. Second, the Zr–Cp(centroid) distances of both **7** and Cp_2ZrCl_2 are essentially identical at 2.21 Å, but the individual Zr–C bond lengths of **7** are slightly (about 0.02 Å) longer. This finding is consistent with the observed lengthening of the Cp C–C bonds in **7** (1.41–1.43 Å) compared to Cp_2ZrCl_2 (1.37–1.39 Å). Electron-withdrawl from the pi system of the Cp ligand should increase the C–C bond lengths. The individual Zr–C bond lengths reveals a slight ring-slip distortion in which the C(1) (Cp *ipso*) carbon is about 0.06 Å farther from the Zr atom than the C(3) and C(4) carbons. A similar distortion of similar magnitude is observed in Cp_2ZrCl_2 [14], suggesting that the distortion is intrinsic to the bent-metallocene framework and not the result of a substituent effect. However, it is interesting that in 1,1′-diphenylzirconocene dichloride this distortion is much more pronounced: the C(1) carbon is nearly 0.16 Å farther from Zr than C(3) [7].

The molecular structures of the manganese tricarbonyl complexes **8** and **9** are shown in Figs. 5 and 6, respectively. The isolated aryl substituents adopt Cp–aryl torsional angles close to 0°, while the two vicinal aryl groups adopt Cp–aryl torsional angles of about 40°. The nearly coplanar arrangement of the Cp and isolated aryl groups was somewhat unexpected based on our earlier work with C_6F_5-substituted $CpMn(CO)_3$ and $CpRe(CO)_3$ complexes; isolated C_6F_5 substituents adopt Cp–aryl torsional angles of 20–40°. Cp–aryl torsional deformations are fairly soft, probably allowing this parameter some flexibility as the molecule adapts to crystal packing forces. The C–C bond lengths in **8** are lengthened (1.41–1.44 Å) compared to the unsubstituted $CpMn(CO)_3$, and they also show a slight Mills-Nixon type alternation [15], with the C(1)–C(2) and C(1)–C(5) distances adjacent to the aryl group the longest at 1.442(2) and 1.443(2) Å, the C(3)–C(4) bond opposite the aryl group slightly shorter at

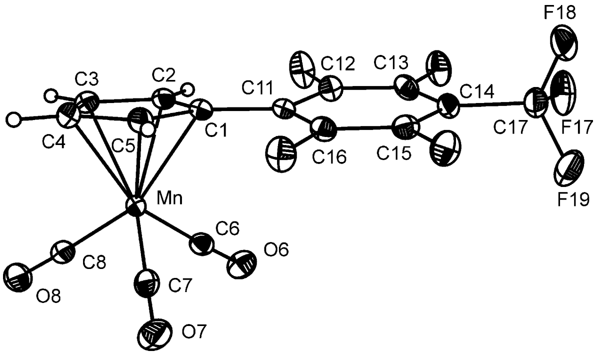


Fig. 5. Thermal ellipsoid plot of **8** shown at 50% probability. Fluorine and hydrogen atoms are numbered the same as the carbon atoms to which they are attached. Selected bond lengths (Å): Mn–Cp(centroid), 1.764(2), Mn–C(6), 1.798(2); Mn–C(8), 1.800(2); Mn–C(7), 1.808(2); Mn–C(2), 2.134(2); Mn–C(3), 2.141(2); Mn–C(1), 2.141(2); Mn–C(5), 2.141(2); Mn–C(4), 2.147(2); C(1)–C(2), 1.442(2); C(2)–C(3), 1.411(2); C(3)–C(4), 1.420(3); C(4)–C(5), 1.415(2); C(5)–C(1), 1.443(2); C(6)–O(6), 1.151(2); C(7)–O(7), 1.139(2); C(8)–O(8), 1.141(2). Selected bond angles (°): C(6)–Mn–C(8), 92.00(8); C(6)–Mn–C(7), 92.57(7); C(8)–Mn–C(7), 92.58(8); O(6)–C(6)–Mn, 177.61(15); O(7)–C(7)–Mn, 178.51(17); O(8)–C(8)–Mn, 177.11(17). Selected torsional angles (°): C(2)–C(1)–C(11)–C(12), 7.6(2).

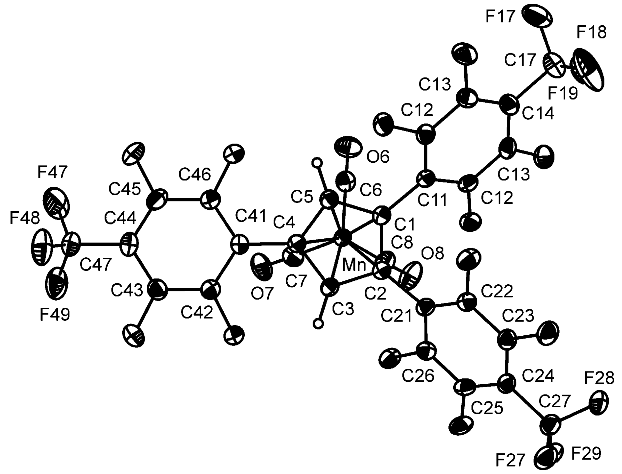


Fig. 6. Thermal ellipsoid plot of **9** shown at 50% probability. Fluorine and hydrogen atoms are numbered the same as the carbon atoms to which they are attached. Selected bond lengths (Å): Mn–Cp(centroid) 1.782(2); Mn–C(1), 2.157(2); Mn–C(2) 2.173(2); Mn–C(3), 2.146(2); Mn–C(4), 2.157(2); Mn–C(5), 2.138(2); Mn–C(6), 1.802(2); Mn–C(7), 1.800(3); Mn–C(8), 1.807(2); C(1)–C(5), 1.421(3); C(1)–C(2), 1.432(3); C(2)–C(3), 1.417(3); C(3)–C(4), 1.428(3); C(4)–C(5), 1.421(3); C(6)–O(6), 1.136(3); C(7)–O(7), 1.144(3); C(8)–O(8), 1.143(3). Selected bond angles (°): C(7)–Mn–C(6), 90.75(11); C(7)–Mn–C(8), 91.36(11); C(6)–Mn–C(8), 89.03(11); O(6)–C(6)–Mn, 179.0(2); O(7)–C(7)–Mn, 177.0(2); O(8)–C(8)–Mn, 178.3(2). Selected torsional angles (°): C(2)–C(1)–C(11)–C(16), 43.0(3); C(1)–C(2)–C(21)–C(22), 40.9(3); C(5)–C(4)–C(41)–C(46), 3.0(3).

1.420(3) Å, and the C(2)–C(3) and C(4)–C(5) bonds the shortest at 1.411(2) and 1.415(2) Å, respectively. A search of the Cambridge Structural Database (CSD) for monometallic, monosubstituted $CpMn(CO)_3$ complexes shows that such a pronounced structural effect occurs only when the substituent is clearly electron-withdrawing. For example, a comparable distortion was observed when the substituent was the cationic cycloheptatrienyl (C_7H_6) moiety [16], and an even more severe distortion was observed when the substituent was the cationic Ph_2C group [17]. In the latter case, Helmchen, Gleiter, and co-workers rationalized the observed distortions (including a significant displacement of the α-carbon toward the metal) by designating the ligand as an η^5-(6,6-diphenylfulvene) with the formal positive charge shifted to Mn. In complex **8**, however, the α-carbon is actually deflected slightly away from the Mn center; a fulvene formulation is clearly inappropriate in our case. There is no further lengthening of the Cp ring C–C distances upon going from the monoarylated complex **8** to the triarylated complex **9**, and in fact the ring C–C bond lengths in **9** are somewhat more uniform. In other respects both **8** and **9** have structural parameters very similar to $CpMn(CO)_3$.

4. Conclusions

Nucleophilic arylation is an efficient approach to the synthesis of cyclopentadienes bearing one, two, three, or four perfluoro-4-tolyl substituents. These compounds, when deprotonated by sodium hydride, are varied in their utility to serve as ligands for early and late transition metals. In general the more highly arylated homologues give lower yields of the desired metal complexes. Perfluoro-4-tolyl substituents impart an electron-withdrawing effect slightly stronger than that of pentafluorophenyl substituents.

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Appendix A. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 294056–294061 for compounds **2a**, **3a**, **3b**, **8**, **9**, and **7**, respectively. Copies of this information may be obtained free of charge by writing The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Alternatively one may contact CCDC by telefax on +44 1223 336 033, by e-mail at deposit@ccdc.cam.ac.uk, or on the internet at www: http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.12.056.

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