

# Synthesis and Structure of Piano Stool Complexes Derived from the Tetrakis(pentafluorophenyl)cyclopentadienyl Ligand

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The reaction of NaCp (Cp = C<sub>5</sub>H<sub>5</sub>) with excess C<sub>6</sub>F<sub>6</sub> and excess NaH in refluxing diglyme afforded a 57% yield of 1,2,3,4-tetrakis(pentafluorophenyl)cyclopentadiene (**1**). Treatment of **1** with NaH in THF afforded sodium tetrakis(pentafluorophenyl)cyclopentadienide (**2**) in 89% yield. Reactions of **2** with M(CO)<sub>5</sub>Br (M = Mn, Re) yielded [(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>C<sub>5</sub>H]M(CO)<sub>3</sub> complexes (**3**, M = Mn, 33%, and **4**, M = Re, 28%). Reactions of **2** with various iron(II) salts and with CoBr<sub>2</sub> however failed to afford the corresponding octaarylated metallocenes. Infrared spectroscopic analysis of **3** and **4** revealed an increase of 16(1) cm<sup>-1</sup> relative to CpM(CO)<sub>3</sub> in the A-symmetric C–O stretching frequency, suggesting that the C<sub>6</sub>F<sub>5</sub> groups have a highly electron-withdrawing effect on the coordinated M(CO)<sub>3</sub> moieties. Crystal structures of **1**, **1**·½C<sub>6</sub>D<sub>6</sub>, **2**, and **3** display a propeller-like arrangement of the C<sub>6</sub>F<sub>5</sub> groups. Complexes **2** and **3** show elongation of the C<sub>5</sub>(centroid)–M bond distances relative to CpMn(CO)<sub>3</sub> and CpRe(CO)<sub>3</sub>, which is attributed to steric effects.

## Introduction

Substituent effects on transition metal cyclopentadienyl (Cp) complexes have been studied extensively. Changes in the size, shape, and electron-donating character of ring substituents influence molecular structure and crystal packing,<sup>1</sup> physical and spectroscopic properties,<sup>2</sup> and fundamental aspects of inner coordination sphere reactivity.<sup>3</sup> The wide-ranging influences of Cp ligand substituents have been exploited in catalysis<sup>4</sup> and in mechanistic studies.<sup>5</sup> We have noted,<sup>6</sup> however, that the effects of highly electron-withdrawing substituents are much less thoroughly studied than either electron-donating substituent effects or steric effects.<sup>7,8</sup> Nevertheless, electron-withdrawing substituents may offer advantages for some catalytic applications.<sup>9</sup>

We are exploring the electron-withdrawing extreme of substituent effects in Cp complexes. We showed

previously that up to three pentafluorophenyl (C<sub>6</sub>F<sub>5</sub>) groups are readily attached to cyclopentadiene and that up to two C<sub>6</sub>F<sub>5</sub> groups may be attached to indene by one-pot procedures involving nucleophilic aromatic substitution of hexafluorobenzene.<sup>6,10</sup> C<sub>6</sub>F<sub>5</sub>-substituted Cp and indenyl anions are stable as sodium salts and can

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Table 1. Crystallographic Data

	1	1·1/2C <sub>6</sub> D <sub>6</sub>	3	4
empirical formula	C <sub>29</sub> H <sub>2</sub> F <sub>20</sub>	2 C <sub>29</sub> H <sub>2</sub> F <sub>20</sub> ·C <sub>6</sub> D <sub>6</sub>	C <sub>32</sub> HF <sub>20</sub> MnO <sub>3</sub>	C <sub>32</sub> HF <sub>20</sub> ReO <sub>3</sub>
fw	730.31	1544.72	868.27	999.54
diffractometer	Nonius Kappa CCD	Nonius Kappa CCD	Siemens P4	Nonius Kappa CCD
cryst dimens (mm)	0.23 × 0.32 × 0.38	0.18 × 0.20 × 0.30	0.13 × 0.29 × 0.48	0.08 × 0.20 × 0.20
cryst syst	triclinic	monoclinic	triclinic	triclinic
a (Å)	11.1190(2)	10.6760(4)	10.515(2)	8.1450(2)
b (Å)	14.7360(3)	10.8820(5)	11.345(3)	13.1900(4)
c (Å)	15.6200(3)	24.4400(12)	13.910(3)	14.4900(3)
α (deg)	82.1670(13)		93.097(16)	75.9910(18)
β (deg)	80.2890(11)	94.266(3)	97.264(18)	81.0610(16)
γ (deg)	79.7970(15)		117.174(17)	79.9430(18)
V (Å <sup>3</sup> )	2467.78(8)	2831.5(2)	1452.6(6)	1476.73(7)
space group	P-1 (No. 2)	P2 <sub>1</sub> /n (No. 14)	P-1 (No. 2)	P-1 (No. 2)
Z	4	2	2	2
D <sub>calc</sub> (Mg m <sup>-3</sup> )	1.966	1.812	1.985	2.248
abs coeff (mm <sup>-1</sup> )	0.221	0.199	0.622	4.3
F <sub>000</sub>	1424	1508	844	944
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
temp (K)	100	150	293	120
θ range for collection	1.4–27.9	2.7–27.5	2.0–27.5	2.5–32.6
no. of reflns colld	18 771	10 584	7744	15 805
no. of indep reflns	11 729	6259	6649	10 352
abs corr method	none	none	ψ scans	multiscan
max, min transm			0.550, 0.487	0.726, 0.521
no. of data/restrnts/params	11 729/0/884	6259/0/470	6649/0/509	10 352/0/506
R [I > 2σ(I)]	0.068	0.036	0.041	0.031
R <sub>w</sub> [I > 2σ(I)]	0.184	0.082	0.077	0.063
GoF on I <sup>2</sup>	1.56	0.84	0.81	1.00
peak, hole (e Å <sup>-3</sup> )	0.61, -0.44	0.21, -0.21	0.26, -0.22	1.28, -1.71

be used in various standard synthetic procedures to prepare complexes of both early and late transition metals.

This contribution reports our extension of these studies to the tetrakis(pentafluorophenyl)cyclopentadienyl ligand. We first present an efficient synthesis of 1,2,3,4-tetrakis(pentafluorophenyl)cyclopentadiene, and we characterize its molecular structure using two crystal structures, one of which contains a "stacked" benzene solvate molecule. The syntheses and characterization of the corresponding sodium salt as well as two complexes, [(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>C<sub>5</sub>H]M(CO)<sub>3</sub> (M = Mn and Re), are reported. We also briefly discuss our failure to prepare either [(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>C<sub>5</sub>H]<sub>2</sub>Fe or [(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>C<sub>5</sub>H]<sub>2</sub>Co using methods that were successful for the corresponding triarylated Cp ligands.<sup>6</sup>

## Experimental Section

**General Procedures.** Standard inert-atmosphere techniques were used for all reactions. C<sub>6</sub>F<sub>6</sub> (99% purity), FeBr<sub>2</sub>, Mn(CO)<sub>5</sub>Br, Re(CO)<sub>5</sub>Br, KH, and 18-crown-6 were used as received from Aldrich. NaH was purchased as a 60% mineral oil dispersion from Aldrich, washed with hexanes, dried under vacuum, and stored in a glovebox. Anhydrous CoBr<sub>2</sub> was prepared by heating the red commercial hydrate (from Fisher) under vacuum to obtain a bright green powder. NaCp was prepared from freshly distilled cyclopentadiene and excess NaH in THF. Fe(acac)<sub>2</sub> was prepared by a published method.<sup>11</sup> Melting points were obtained using a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Midac M-series instrument operating at 1 cm<sup>-1</sup> resolution, using dilute hexane or octane solutions and KBr-windowed cells. NMR experiments used JEOL ECP500, Varian U400, and Bruker EM360 instruments. THF-*d*<sub>6</sub> (Isotec) was vacuum-transferred from NaK<sub>2</sub> alloy. <sup>19</sup>F NMR spectra were referenced to external C<sub>6</sub>F<sub>6</sub> in CDCl<sub>3</sub> (-163.00 ppm) at 25 °C. C-F coupling constants were approximated from apparent splittings. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Version 5.19 of the Cambridge Structural

Database (CSD) was searched using ConQuest software (version 1.0) from the Cambridge Crystallographic Data Centre.

**Crystallographic Studies.** Crystals of **1** were obtained by allowing a solution of **1** in ethyl acetate/hexane to evaporate completely. Crystals of **1** were also obtained serendipitously during NMR-scale experiments in which **1** was reacted with (C<sub>6</sub>F<sub>5</sub>C<sub>5</sub>H<sub>4</sub>)CpZr(CH<sub>3</sub>)<sub>2</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in benzene-*d*<sub>6</sub>. The reaction afforded a red, viscous oil that we were unable to characterize and a few colorless crystals. X-ray diffraction analysis of the colorless crystals found **1**·1/2C<sub>6</sub>D<sub>6</sub>. These crystals were found to be highly unstable toward solvent loss, so crystals were removed quickly from the mother liquor, mounted on a fiber under oil, and transferred to the cold stream of the diffractometer. Crystals of **3** and **4** were grown by cooling warm, concentrated toluene solutions to 25 °C. Crystallographic data are assembled in Table 1.

**1,2,3,4-Tetrakis(pentafluorophenyl)cyclopentadiene (1).** A mixture of NaCp (2.00 g, 22.7 mmol), NaH (3.27 g, 136 mmol), and diglyme (250 mL) was stirred at reflux. Using a syringe, C<sub>6</sub>F<sub>6</sub> (25.6 g, 138 mmol) was added cautiously to the refluxing reaction mixture over a period of 5 min. The mixture was stirred at reflux for 2 days. The diglyme was then removed by heating the dark mixture under vacuum. The black residue was taken up in 200 mL of THF and added, using a cannula, to an aqueous solution of NH<sub>4</sub>Cl (10.0 g in 400 mL). The biphasic mixture was evaporated, and the resulting dark, oily residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>, filtered through Celite, and evaporated to yield a brown, oily solid. The crude solid was triturated with warm hexane, collected on a filter, and dried under vacuum to afford 9.44 g (12.9 mmol, 57%) of a brown powder, which was found by <sup>1</sup>H and <sup>19</sup>F NMR analysis to be about 95% pure. An analytically pure sample was obtained by sublimation (125 °C, 5 × 10<sup>-6</sup> Torr): mp 196–197 °C (open capillary). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.17 (s, 2 H). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -140.02 (dd, <sup>3</sup>J = 22 Hz, <sup>5</sup>J = 8 Hz, 4 F), -140.29 (dd, <sup>3</sup>J = 23 Hz, <sup>5</sup>J = 8 Hz, 4 F), -151.10 (t, <sup>3</sup>J = 21 Hz, 2 F), -152.00 (t, <sup>3</sup>J = 21 Hz, 2 F), -160.18 (m, 4 F), -160.62 (m, 4 F). {<sup>19</sup>F}<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 144.1 (s, CF), 144.0 (s, CF), 141.8 (s, CF), 141.7 (s, CF), 138.1 (s, CF), 137.7 (s, CF), 136.1 (t, J = 6 Hz, C-C<sub>6</sub>F<sub>5</sub>), 134.5 (t, J = 4 Hz, C-C<sub>6</sub>F<sub>5</sub>), 109.3 (s, C<sub>ipso</sub>), 108.3 (s, C<sub>ipso</sub>), 48.1 (t, J = 132 Hz, CH<sub>2</sub>). {<sup>1</sup>H}<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 144.1 (d, <sup>1</sup>J<sub>CF</sub> = 240 Hz, CF), 141.6 (d, <sup>1</sup>J<sub>CF</sub> = 250 Hz, CF), 138.1 (d, <sup>1</sup>J<sub>CF</sub> = 260 Hz, CF), 137.7 (d, <sup>1</sup>J<sub>CF</sub> = 260 Hz, CF), 136.1 (s, C-C<sub>6</sub>F<sub>5</sub>), 134.5 (s, C-C<sub>6</sub>F<sub>5</sub>), 109.3 (m, C<sub>ipso</sub>), 108.3 (m,

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$C_{ipso}$ , 48.1 (s,  $CH_2$ ). Anal. Calcd for  $C_{29}H_2F_{20}$ : C, 47.70; H, 0.28. Found C, 48.01; H, 0.29.

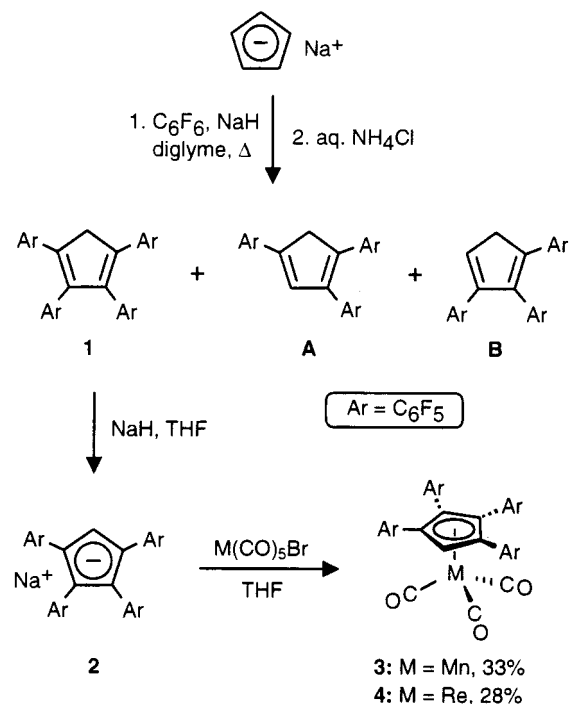
**Sodium 1,2,3,4-tetrakis(pentafluorophenyl)cyclopentadienide (2).** A mixture of 1,2,3,4-tetrakis(pentafluorophenyl)cyclopentadiene (**1**, 2.05 g, 2.81 mmol), NaH (0.17 g, 7.08 mmol), and THF (50 mL) was stirred at 25 °C for 1 day and then filtered to remove unreacted NaH. The filtrate was evaporated, and the residue was triturated with hexane, collected on a fritted filter, and dried under vacuum to afford 1.88 g (2.50 mmol, 89%) of a tan powder. (The potassium salt can be prepared analogously by using KH in place of NaH).  $^1H$  NMR (THF- $d_6$ ):  $\delta$  6.43 (p,  $^5J = 1.6$  Hz, 1 H).  $^{19}F$  NMR (THF- $d_6$ ):  $\delta$  -143.95 (dd,  $^3J = 25$  Hz,  $^5J = 7$  Hz, 4 F), -144.86 (d,  $^3J = 25$  Hz,  $^5J = 6$  Hz, 4 F), -165.00 (t,  $^3J = 21$  Hz, 2 F), -167.52 (m, 6 F, two unresolved signals), -167.83 (m, 4 F).  $\{^{19}F\}^{13}C$  NMR (THF- $d_6$ ):  $\delta$  144.3 (s, CF), 143.8 (s, CF), 138.0 (s, CF), 137.8 (s, CF), 137.5 (s, CF), 137.1 (s, CF), 117.7 (s,  $C_{ipso}$ ), 117.6 (s,  $C_{ipso}$ ), 115.5 (d,  $J = 165$  Hz, CH), 106.6 (d,  $J = 4.2$  Hz,  $C-C_6F_5$ ), 106.4 (d,  $J = 8.3$  Hz,  $C-C_6F_5$ ).  $\{^1H\}^{13}C$  NMR (THF- $d_6$ ):  $\delta$  144.3 (d,  $J = 243$  Hz, CF), 143.8 (d,  $J = 241$  Hz, CF), 137.7 (d,  $J = 243$  Hz, three unresolved CF), 137.1 (d,  $J = 233$  Hz, CF), 117.6 (m, two unresolved  $C_{ipso}$ ), 115.5 (s, CH), 106.6 (s,  $C-C_6F_5$ ), 106.4 ( $C-C_6F_5$ ). Satisfactory microanalytical data were not obtained.  $^1H$  and  $^{19}F$  NMR spectra of **2** are provided in the Supporting Information as evidence of substantial bulk purity.

**Tricarbonyl[ $\eta^5$ -1,2,3,4-tetrakis(pentafluorophenyl)cyclopentadienyl]manganese(I) (3).** A mixture of  $Mn(CO)_5Br$  (0.223 g, 0.811 mmol), sodium 1,2,3,4-tetrakis(pentafluorophenyl)cyclopentadienide (**2**, 0.597 g, 0.794 mmol), NaH (20 mg), and toluene (50 mL) was stirred under reflux for 1 day. The mixture was then filtered while still warm, and the filtrate was evaporated. The resulting residue was triturated with hexane, collected on a filter, and dried under vacuum to afford 0.197 g (0.259 mmol, 33%) of a yellow solid. An analytically pure sample was obtained by recrystallization from toluene. Mp (sealed, nitrogen-filled capillary): 190–192 °C. IR (octane)  $\nu_{CO} = 2044, 1980, 1970$   $cm^{-1}$ .  $^1H$  NMR (THF- $d_6$ ):  $\delta$  6.29 (s, 1 H).  $^{19}F$  NMR (THF- $d_6$ ):  $\delta$  -131.53 (m, 2 F), -135.82 (d,  $^3J = 21$  Hz, 4 F), -140.30 (d,  $^3J = 21$  Hz, 2 F), -151.57 (t,  $^3J = 24$  Hz, 2 F), -153.27 (t,  $^3J = 22$  Hz, 2 F), -161.51 (m, 2 F), -162.04 (m, 2 F), -162.47 (m, 4 F). Anal. Calcd for  $C_{32}HF_{20}MnO_3$ : C, 44.27; H, 0.12. Found: C, 44.09; H, 0.05.

**Tricarbonyl[ $\eta^5$ -1,2,3,4-tetrakis(pentafluorophenyl)cyclopentadienyl]rhenium(I) (4).** A mixture of  $Re(CO)_5Br$  (0.325 g, 0.800 mmol), sodium 1,2,3,4-tetrakis(pentafluorophenyl)cyclopentadienide (**2**, 0.603 g, 0.802 mmol), NaH (20 mg), and toluene (50 mL) was refluxed for 1 day and then filtered while still warm. The filtrate was evaporated, and the resulting residue was triturated with hexane, collected on a filter, and dried under vacuum to afford 0.196 g (0.220 mmol, 28%) of an off-white solid. An analytically pure sample was obtained by recrystallization from toluene. Mp (sealed, nitrogen-filled capillary): 205–207 °C. IR (hexane)  $\nu_{CO} = 2047, 1970, 1959$   $cm^{-1}$ .  $^1H$  NMR (THF- $d_6$ ):  $\delta$  6.95 (s, 1 H).  $^{19}F$  NMR (THF- $d_6$ ):  $\delta$  -131.89 (d,  $^3J = 24$  Hz, 2 F), -135.88 (m, 4 F), -140.94 (d,  $^3J = 22$  Hz, 2 F), -151.30 (t,  $^3J = 21$  Hz, 2 F), -153.23 (t,  $^3J = 22$  Hz, 2 F), -161.21 (m, 2 F), -161.93 (m, 2 F), -162.34 (m, 4 F). Anal. Calcd for  $C_{32}HF_{20}O_3Re$ : C, 38.45; H, 0.10. Found: C, 38.60; H, 0.05.

**Reactions of Iron Salts and  $CoBr_2$  with **2**.** Several reactions were attempted in order to prepare metallocenes using 2 equiv of **2** and either (a) 1 equiv of  $FeBr_2$  in THF at 25 °C, (b) 1 equiv of  $FeBr_2$  in THF at 65 °C, (c) 1 equiv of  $FeBr_2$  in DME at 85 °C, (d) 1 equiv of  $Fe(acac)_2$  in toluene at 110 °C with catalytic 18-crown-6 (the potassium congener of **2** was used), or (e) 1 equiv of  $CoBr_2$  in THF at 65 °C. Crude product mixtures, obtained after cooling the reactions to 25 °C and removing the solvents under reduced pressure, were analyzed by  $^1H$  and  $^{19}F$  NMR spectroscopy. These spectra showed only unreacted ligand.

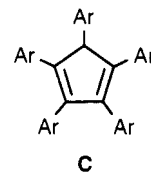
Scheme 1



## Results and Discussion

**Ligand Synthesis.** Sodium cyclopentadienide (NaCp) reacts with a large excess of hexafluorobenzene ( $C_6F_6$ ) and excess sodium hydride (NaH) under forcing conditions (Scheme 1) to afford, after aqueous workup, a 57% yield of 1,2,3,4-tetrakis(pentafluorophenyl)cyclopentadiene (**1**). Initially, we had failed to detect **1** as a minor impurity in the synthesis of the triarylated cyclopentadienes (**A** and **B**),<sup>10b</sup> simply because **1** does not elute from silica gel with hexanes, a procedure used in the purification of **A** and **B**. Subsequent adjustment of the reaction conditions and isolation procedures enabled us to obtain **1** directly, with **A** and **B** as minor impurities.

We have attempted unsuccessfully to prepare the corresponding pentaarylated cyclopentadiene (**C**) by using longer reaction times, by using solvents with higher boiling points, and by carrying out the reactions under pressure in a stirred autoclave. We have found that  $C_6F_5$ -substituted cyclopentadienes exclusively adopt regiochemical arrangements in which all of the  $C_6F_5$  groups are conjugated with the diene moiety (e.g., **A** and **B**). Conjugation of a fifth  $C_6F_5$  group is not possible in the neutral cyclopentadiene. Steric effects<sup>12</sup> may also impede the formation of **C**. Finally, each added  $C_6F_5$  group renders the cyclopentadienyl anion less nucleophilic in the subsequent arylation.



Treatment of the diene (**1**) with either NaH or KH in THF (Scheme 1) affords high yields of the corresponding

(12) Burkey, D. J.; Alexander, E. K.; Hanusa, T. P. *Organometallics* 1994, 13, 2773.

**Table 2. Carbonyl Stretching Wavenumbers of Piano Stool Complexes**

entry	complex	wavenumbers (cm <sup>-1</sup> ) <sup>a</sup>	
		$\nu_{\text{CO}}$ (A)	$\nu_{\text{CO}}$ (E)
1	CpMn(CO) <sub>3</sub> <sup>b</sup>	2028	1944
2	(C <sub>6</sub> F <sub>5</sub> C <sub>5</sub> H <sub>4</sub> )Mn(CO) <sub>3</sub> <sup>c</sup>	2032	1954
3	[(1,3-C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> ]Mn(CO) <sub>3</sub> <sup>c</sup>	2035	1966, 1960
4	[(1,2,4-C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> C <sub>5</sub> H <sub>2</sub> ]Mn(CO) <sub>3</sub> <sup>c</sup>	2040	1973, 1965
5	[(1,2,3-C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> C <sub>5</sub> H <sub>2</sub> ]Mn(CO) <sub>3</sub> <sup>c</sup>	2041	1975, 1963
6	[(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> C <sub>5</sub> H]Mn(CO) <sub>3</sub> ( <b>3</b> )	2044	1980, 1970
7	CpRe(CO) <sub>3</sub> <sup>b</sup>	2031	1939
8	(C <sub>6</sub> F <sub>5</sub> C <sub>5</sub> H <sub>4</sub> )Re(CO) <sub>3</sub> <sup>c</sup>	2034	1947
9	[(1,3-C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> ]Re(CO) <sub>3</sub> <sup>c</sup>	2038	1953
10	[(1,2,4-C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> C <sub>5</sub> H <sub>2</sub> ]Re(CO) <sub>3</sub> <sup>c</sup>	2042	1963, 1957
11	[(1,2,3-C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> C <sub>5</sub> H <sub>2</sub> ]Re(CO) <sub>3</sub> <sup>c</sup>	2043	1965, 1954
12	[(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> C <sub>5</sub> H]Re(CO) <sub>3</sub> ( <b>4</b> )	2047	1970, 1959

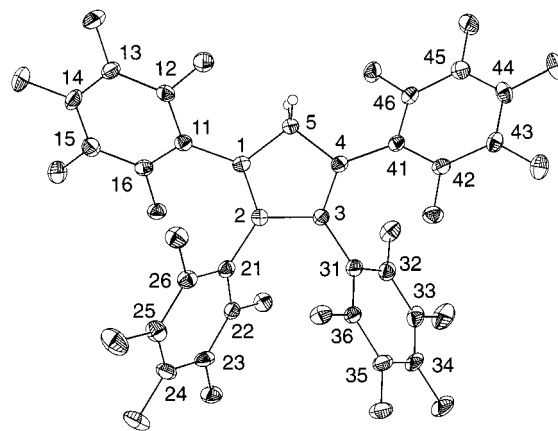
<sup>a</sup> Recorded in octane or hexane solution. Reproducibility is within 1 cm<sup>-1</sup>. <sup>b</sup> Values of 2030 and 1946 cm<sup>-1</sup> for CpMn(CO)<sub>3</sub> and 2032 and 1940 for CpRe(CO)<sub>3</sub> were reported elsewhere.<sup>23</sup> We re-prepared these complexes for direct comparisons with our compounds. <sup>c</sup> Prior results from our laboratories.<sup>6,10</sup>

sodium or potassium tetrakis(pentafluorophenyl)cyclopentadienide (**2**). Both the diene (**1**) and the anion (**2**) are characterized by a single <sup>1</sup>H NMR resonance and six signals in the <sup>19</sup>F NMR assigned to the *ortho*, *meta*, and *para* fluorine atoms of the “inner” and “outer” C<sub>6</sub>F<sub>5</sub> groups, clear indicators of time-averaged C<sub>2v</sub> symmetry in solution.

**Synthesis of Piano Stool Complexes.** The tetra-arylated ligand (**2**) reacts with either Mn(CO)<sub>5</sub>Br or Re(CO)<sub>5</sub>Br (Scheme 1) to afford moderate yields of the corresponding [(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>C<sub>5</sub>H]M(CO)<sub>3</sub> complexes (**3**, M = Mn, 33%; and **4**, M = Re, 28%). Both complexes are relatively thermally stable, crystalline solids. The major difficulty in the synthesis of these complexes is that in small-scale experiments moisture must be rigorously excluded, otherwise **2** is converted to **1**, which is the most significant side-product observed. Unlike previous syntheses of related compounds, we find that the use of THF as a reaction solvent affords **3** and **4** in low yields. Using toluene as the reaction solvent and a small amount of added NaH to scavenge adventitious moisture affords the reported yields, which we consider optimized.

**Infrared Spectroscopic Analysis.** The trend that we have established (Table 2),<sup>10</sup> whereby the symmetric (A) stretching mode increases in frequency by 4 cm<sup>-1</sup> per C<sub>6</sub>F<sub>5</sub> group, continues with complexes **3** and **4**. We have long been curious about the possibility of reaching a substituent effect “limit” in which so many electron-withdrawing groups are attached to a Cp ligand that the M(CO)<sub>3</sub> moiety can no longer “adjust” to their combined effects. The nearly linear trends implied by the data in Table 2 suggest that we are *not* approaching such a “limit” in the CpM(CO)<sub>3</sub> system. The principle of “additivity” therefore is reliable even when the complexes are as electronically “stressed” as **3** and **4**.

**Crystal Structures of 1.** Figure 1 shows a diagram of the molecular structure of **1**. The compound crystallizes with two independent but substantially isostructural molecules in the asymmetric unit. We also obtained a crystal structure of **1** in which a molecule of benzene is included in the lattice. Metric data for these three molecular structures are provided in Table 3. A comparison (Table 4) of the bond lengths in the cyclopentadiene “core” with corresponding data from cyclo-



**Figure 1.** Thermal ellipsoid plot of **1** 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.

pentadiene<sup>13</sup> and 1,2,3,4-tetra(isopropyl)cyclopentadiene<sup>12</sup> reveals only one significant feature, an elongation of the C2–C3 bond in the tetra(isopropyl)cyclopentadiene, which we ascribe to steric congestion.

The C<sub>6</sub>F<sub>5</sub> groups of **1** are splayed in a propeller-like array relative to the C<sub>5</sub> ring. The “outer” C<sub>6</sub>F<sub>5</sub> groups (C11–C16 and C41–C46) tend to show greater coplanarity with the C<sub>5</sub> ring than the “inner” groups (C21–C26 and C31–C36), reflecting the greater congestion of the latter. The value of 64° for  $\beta_1$  in 1·1/2C<sub>6</sub>D<sub>6</sub> (Table 3) was therefore surprising. Our efforts to rationalize this angle by examining the packing diagrams for specific intermolecular interactions were inconclusive. Although the unfluorinated counterpart (1,2,3,4-tetraphenylcyclopentadiene) does not show a propeller-like structure,<sup>14</sup> that feature is found in both tetraphenylcyclopentadienone<sup>15</sup> and tetraphenylcyclopentadienyl anion.<sup>16</sup>

The benzene solvate in 1·1/2C<sub>6</sub>D<sub>6</sub> is incorporated in a C<sub>6</sub>F<sub>5</sub>–C<sub>6</sub>D<sub>6</sub>–C<sub>6</sub>F<sub>5</sub> “stacking” motif (Figure 2). The stacking is defined by a C<sub>6</sub>F<sub>5</sub>-centroid to C<sub>6</sub>D<sub>6</sub>-centroid distance of 3.558(4) Å, a C<sub>6</sub>F<sub>5</sub>-centroid to C<sub>6</sub>D<sub>6</sub>-plane distance of 3.456(4) Å, a C<sub>6</sub>D<sub>6</sub>-centroid to C<sub>6</sub>F<sub>5</sub>-plane distance of 3.360(4) Å, and an interplanar angle of 5.2°. The stacking motif involves the C41–C46 C<sub>6</sub>F<sub>5</sub> group. The relative orientations of the two six-membered rings are nearly eclipsed. These parameters are nearly identical to the observations we reported earlier for [1,2,4-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]Mn(CO)<sub>3</sub>·1/2C<sub>6</sub>D<sub>6</sub>.<sup>6</sup>

**Crystal Structures of Piano Stool Complexes 3 and 4.** Figures 3 and 4 present the molecular structures of **3** and **4**. Metric data are presented in Table 5. Both complexes adopt similar M(CO)<sub>3</sub> conformations ( $\alpha$  values in Table 5) despite having crystallized in qualitatively different unit cells and in different packing arrangements (see below). Neither complex exhibits a significantly “slipped” Cp ligand,<sup>17</sup> and the carbonyl ligands are substantially linear, with relatively uniform

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(14) Evrard, G.; Piret, P.; Germain, G.; Van Meerssche, M. *Acta Crystallogr.* **1971**, *B27*, 661.

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(16) Bock, H.; Hauck, T.; Nather, C.; Haulas, Z. *Z. Naturforsch.* **1997**, *B52*, 524.

**Table 3. Selected Metric Data for 1 and 1-<sup>1/2</sup>C<sub>6</sub>D<sub>6</sub>**

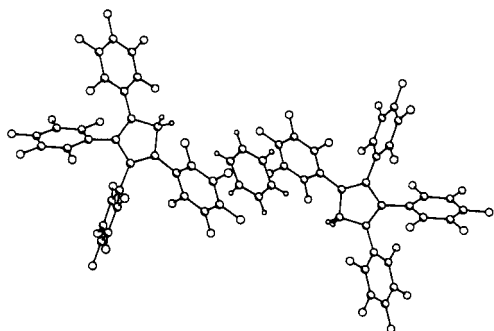
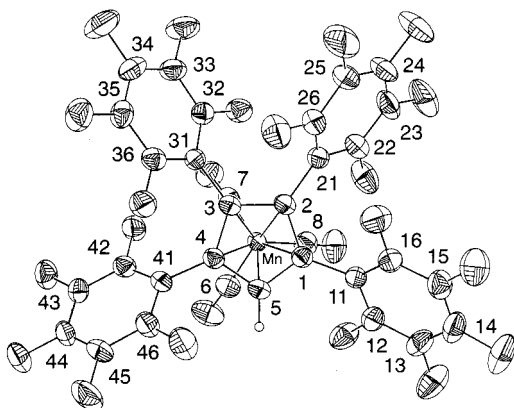
distance (Å)	1 <sup>a</sup>		1- <sup>1/2</sup> C <sub>6</sub> D <sub>6</sub>	angle (deg) <sup>b</sup>	1 <sup>a</sup>		1- <sup>1/2</sup> C <sub>6</sub> D <sub>6</sub>
C1–C2	1.355(4)	1.349(4)	1.349(3)	C1–C2–C3	108.6(3)	109.3(3)	109.2(2)
C2–C3	1.481(5)	1.472(4)	1.476(3)	C2–C3–C4	109.8(3)	109.3(3)	109.0(2)
C3–C4	1.358(5)	1.359(4)	1.354(3)	C3–C4–C5	107.8(3)	108.6(3)	109.0(2)
C4–C5	1.499(4)	1.498(4)	1.506(3)	C4–C5–C1	104.9(3)	104.0(3)	103.5(2)
C5–C1	1.495(5)	1.505(4)	1.502(3)	C5–C1–C2	108.8(3)	108.8(3)	109.3(2)
C1–C11	1.479(4)	1.505(4)	1.502(3)	β1	39.7(5)	40.0(5)	64.0(3)
C2–C21	1.475(5)	1.485(4)	1.472(3)	β2	53.7(5)	58.5(5)	57.5(3)
C3–C31	1.487(4)	1.483(5)	1.478(3)	β3	53.3(5)	55.7(5)	58.8(3)
C4–C41	1.464(5)	1.470(4)	1.475(3)	β4	41.2(5)	45.9(5)	47.4(3)

<sup>a</sup> Two independent molecules in the unit cell. <sup>b</sup> β angles are interplanar torsion angles (0–90°) between the (C1–C5) least-squares planes and the least-squares planes of C11–C16 (β1), C21–C26 (β2), C31–C36 (β3), and C41–C46 (β4).

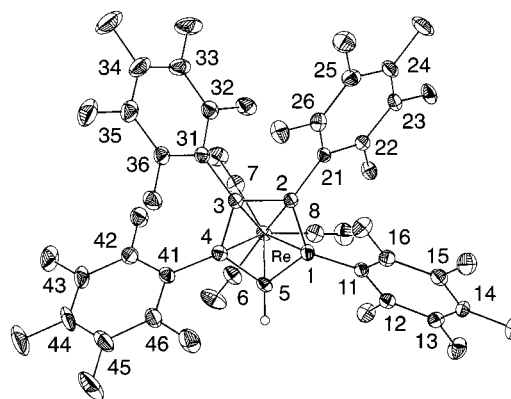
**Table 4. Comparison of Metric Data for 1,2,3,4-Tetrasubstituted Cyclopentadienes**

	average for 1 <sup>a</sup>	average for C <sub>5</sub> H <sub>6</sub> <sup>b</sup>	average for C <sub>5</sub> H <sub>2</sub> ( <i>i</i> Pr) <sub>4</sub> <sup>c</sup>
C1–C2, C3–C4	1.354	1.344	1.351
C2–C3	1.476	1.460	1.502
C4–C5, C5–C1	1.501	1.498	1.489

<sup>a</sup> Both independent molecules of crystalline 1 as well as 1-<sup>1/2</sup>C<sub>6</sub>D<sub>6</sub> were included in the average. <sup>b</sup> Ref 13. <sup>c</sup> Ref 12.

**Figure 2. Stacking of benzene solvate in 1-<sup>1/2</sup>C<sub>6</sub>D<sub>6</sub>.****Figure 3. Thermal ellipsoid plot of 3 shown at 50% probability. Hydrogen, fluorine, and oxygen atoms are numbered the same as the carbon atoms to which they are attached.**

M–C and C–O distances in both M(CO)<sub>3</sub> tripods. The Cp–Mn distance of 1.812(3) Å in 3 is relatively long compared to the values of 1.762 and 1.766 Å obtained for CpMn(CO)<sub>3</sub><sup>18</sup> as well as the Cp–Mn distance of

**Figure 4. Thermal ellipsoid plot of 4 shown at 50% probability. Hydrogen, fluorine, and oxygen atoms are numbered the same as the carbon atoms to which they are attached.****Table 5. Selected Metric Data for Piano Stool Complexes (3 and 4)**

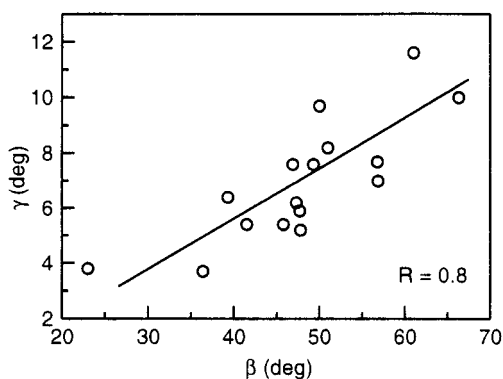
distance (Å)	3		4		bond angle <sup>a</sup> (deg)	3		4	
	3	4	3	4		3	4	3	4
M–C1	2.193(3)	2.343(2)	M–C6–O6	176.8(3)	178.0(3)				
M–C2	2.196(3)	2.345(2)	M–C7–O7	175.9(3)	175.8(3)				
M–C3	2.191(3)	2.332(3)	M–C8–O8	176.9(3)	178.8(3)				
M–C4	2.159(3)	2.309(3)	α	34.0(3)	36.1(3)				
M–C5	2.158(3)	2.317(3)	β1	50.0(3)	61.0(3)				
M–Cp <sup>b</sup>	1.812(3)	1.983(3)	β2	56.9(3)	56.8(3)				
M–C6	1.770(3)	1.893(3)	β3	46.9(3)	49.3(3)				
M–C7	1.787(3)	1.919(3)	β4	47.8(3)	45.8(3)				
M–C8	1.797(3)	1.921(3)	γ1	9.7(3)	11.6(3)				
C6–O6	1.158(4)	1.151(3)	γ2	7.0(3)	7.7(3)				
C7–O7	1.150(4)	1.147(4)	γ3	7.6(3)	7.6(3)				
C8–O8	1.150(4)	1.148(5)	γ4	5.2(3)	5.4(3)				

<sup>a</sup> α is the smallest C<sub>CO</sub>–M–Cp<sup>b</sup>–C<sub>5</sub> torsion angle, defining the disposition of the M(CO)<sub>3</sub> group relative to the Ar<sub>4</sub>C<sub>5</sub>H ligand. β angles are interplanar torsion angles (0–90°) between the (C1–C5) least-squares planes and the least-squares planes of C11–C16 (β1), C21–C26 (β2), C31–C36 (β3), and C41–C46 (β4). γ angles are the angle formed between the C1–C5 least-squares plane and the Cp–C<sub>6</sub>F<sub>5</sub> bonds: C1–C11 (γ1), C2–C21 (γ2), C3–C31 (γ3), and C4–C41 (γ4). <sup>b</sup> Cp is the C1–C5 centroid.

1.780(4) Å observed in [1,2,4-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]Mn(CO)<sub>3</sub>.<sup>6</sup> The Cp–Re distance of 1.983(3) Å in 4 is long compared to the values of 1.955(8) Å observed in [1,3-(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>]-Re(CO)<sub>3</sub> and of 1.968(6) Å observed in [1,2,4-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]-Re(CO)<sub>3</sub>.<sup>6</sup> Ordinarily, electron-deficient carbocyclic ligands are closer to the metal than their electron-rich counterparts.<sup>19</sup> However, no clear substituent effects were

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(18) (a) Fitzpatrick, P. J.; LePage, Y.; Sedman, J.; Butler, I. S. *Inorg. Chem.* **1981**, *20*, 2852. (b) Cowie, J.; Hamilton, E. J. M.; Laurie, J. C. V.; Welch, A. J. *J. Organomet. Chem.* **1990**, *394*, 1. (c) A value of 1.794 was found earlier: Berndt, A. F.; Marsh, R. E. *Acta Crystallogr.* **1963**, *16*, 118.



**Figure 5.** Correlation of  $\beta$  and  $\gamma$  for  $C_6F_5$ -substituted  $CpM(CO)_3$  complexes ( $M = Mn, Re$ ). Parameters are defined in Table 5. Additional data are taken from ref 6.

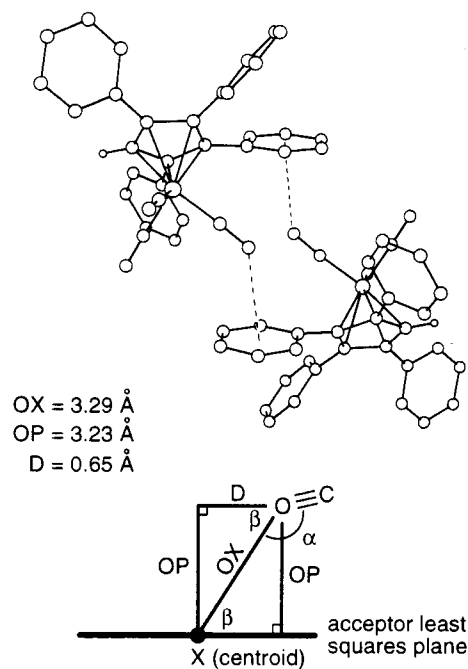
evident from an examination of the 120 substituted  $CpMn(CO)_3$  compounds ( $Cp-Mn$  distances ranging from 1.749–1.795 Å) or the 12 substituted  $CpRe(CO)_3$  compounds ( $Cp-Re$  distance ranging from 1.944–1.982 Å) retrieved from the Cambridge Structural Database.<sup>20</sup> The trends observed here may be due simply to weak steric interactions of the  $C_6F_5$  groups with the  $M(CO)_3$  moieties.

As in the diene **1**, both piano stool complexes **3** and **4** hold the  $C_6F_5$  groups in propeller-like arrays relative to their respective Cp rings; however, all the torsion angles ( $\beta_1$ – $\beta_4$ ) fall into the range 45–61°, with no pronounced tendency for the “inner”  $C_6F_5$  groups to adopt more perpendicular conformations. A search of the Cambridge Structural Database showed that all of the crystallographically characterized transition metal complexes of the  $\eta^5$ -tetrakis(pentafluorophenyl)cyclopentadienyl ligand adopt propeller-like conformations also.

The  $C_6F_5$  *ipso* carbon lies slightly out of the  $C_5$  least-squares plane of the cyclopentadienyl ligand and is directed away from the  $M(CO)_3$  fragment (*exo*). The angle between the  $C-C_6F_5$  bond and the  $C_5$  least-squares plane is reported as the angle  $\gamma$  in Table 5. We noticed that  $\gamma$  appears to correlate with the  $Cp-C_6F_5$  torsion angle ( $\beta$ ). This prompted us to reexamine the crystal structures of  $[1,3-(C_6F_5)_2C_5H_3]Re(CO)_3$ ,  $[1,2,4-(C_6F_5)_3C_5H_2]Mn(CO)_3 \cdot \frac{1}{2}C_6D_6$ , and  $[1,2,4-(C_6F_5)_3C_5H_2]Re(CO)_3$ <sup>6</sup> in order to double the number of points in our correlation. The result of this analysis is presented in Figure 5. The  $\beta$ – $\gamma$  plot shows a correlation coefficient of 0.8, which is surprisingly high considering the softness of the  $Cp-C_6F_5$  conformational potentials and the likely susceptibility of  $\beta$  to deformation by weak intermolecular (packing) interactions. The positive  $\beta$ – $\gamma$  correlation could arise from the same steric interactions proposed to account for the elongated  $Cp-M$  bonds in **3** and **4**. As  $\beta$  increases, interactions between the *endo ortho* fluorine atoms and the  $M(CO)_3$  moiety push the  $C_6F_5$  groups in the *exo* direction.

The packing diagram of the manganese complex **3** (but not of **4**) reveals that the oxygen atom of one of the CO ligands (a Lewis-basic “donor”) interacts with a  $C_6F_5$  “acceptor” in a pairwise fashion (Chart 1). The  $C\equiv O$

**Chart 1**



bond length and  $Mn-C\equiv O$  angles, however, are identical to those of the other carbonyl ligands, suggesting that the donor–acceptor interaction is just a weak packing interaction.

**Dynamic NMR Studies.** Figure 6 shows several  $^{19}F$  NMR spectra of **4** obtained at temperatures ranging from –100 to +25 °C. In the room-temperature (top) spectrum, the two signals at –132 and –141 ppm are assigned to the *ortho* fluorines of the “inner”  $C_6F_5$  groups, for which the *exo* and *endo* positions ( $Cp-C_6F_5$ ) are in slow exchange at all temperatures. In contrast, the signal at –135 ppm, which we assign to the *ortho* fluorines of the “outer”  $C_6F_5$  groups, is in fast exchange at 25 °C but decoalesces at –75 °C. Application of eqs 1–3 enables the measurement of first-order *exo*–*endo* exchange rate constants across a wide temperature range.<sup>21</sup> These rates lead to the construction of an Eyring plot (Figure 7), from which activation parameters are determined to be  $\Delta H^\ddagger = 7(1)$  kcal mol<sup>–1</sup> and  $\Delta S^\ddagger = -5(5)$  cal mol<sup>–1</sup> K<sup>–1</sup>. A similar analysis of **3** generates exactly the same activation parameters. These values are consistent with activation parameters for  $Cp-C_6F_5$  rotation of the vicinal pair of  $C_6F_5$  groups in  $[1,2,4-(C_6F_5)_3C_5H_2]Re(CO)_3$  that we obtained earlier.<sup>6</sup> Details of the Eyring analyses are deposited in the Supporting Information. In neither **3** nor **4** did we find evidence for “restricted” rotation of the  $M(CO)_3$  groups,<sup>22</sup> which could result in loss of time-averaged  $C_s$  symmetry of the complexes.

$$k_{\text{coal}} = (\pi/\sqrt{2})\Delta v = 2.22\Delta v \quad (1)$$

$$k(T) = \pi[\text{fwhm}(T) - \text{fwhm}(\text{natural})] \quad (2)$$

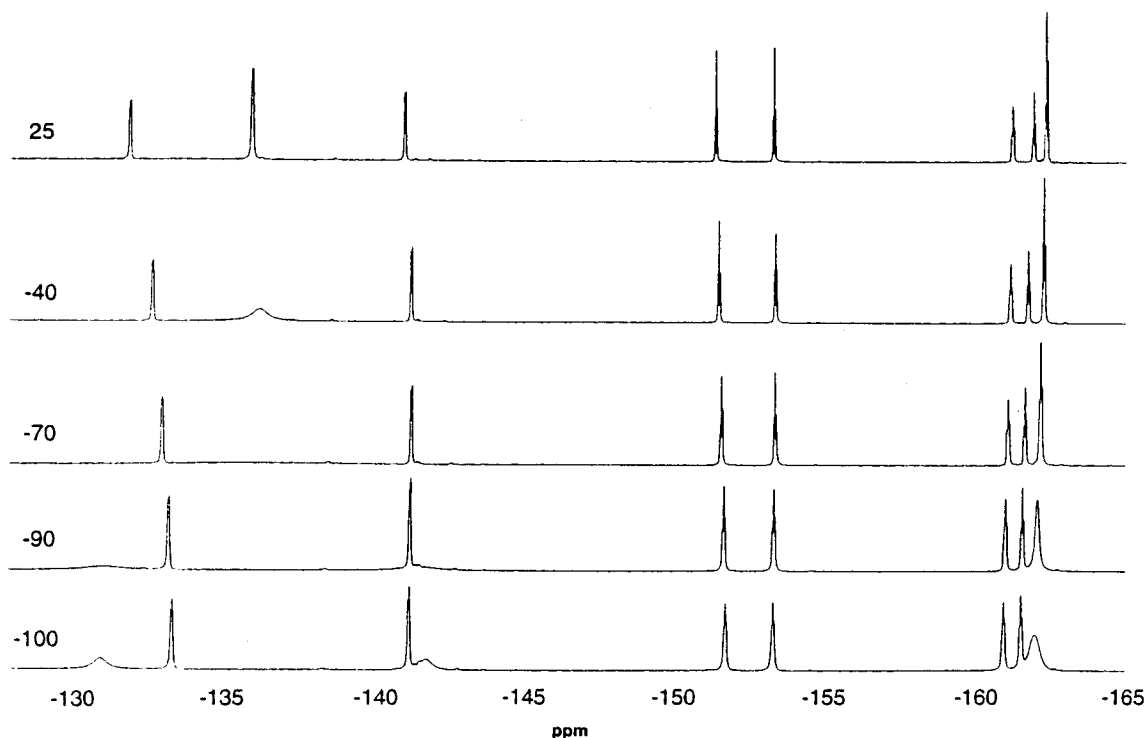
$$k(T) = \pi(\Delta v)^2/[\text{fwhm}(T) - \text{fwhm}(\text{natural})] \quad (3)$$

**Conclusions.** Tetrakis(pentafluorophenyl)cyclopent-

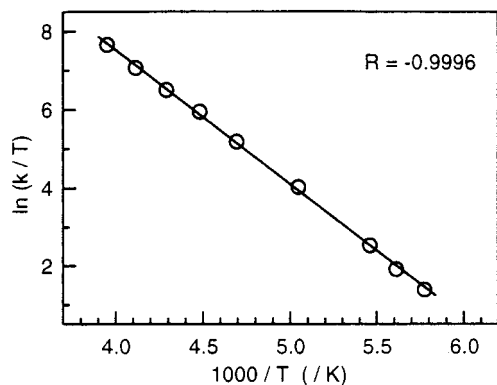
(19) (a) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 6130. (b) Gassman, P. G.; Deck, P. A. *Organometallics* **1994**, *13*, 1934. (c) Gassman, P. G.; Winter, C. H. *Organometallics* **1991**, *10*, 1592.

(20) Compounds having additional rings fused to the Cp ligand (such as indenyl complexes) were excluded from the CSD search.

(21) Hore, P. J. *Nuclear Magnetic Resonance*; New York: Oxford, 1995; pp 44–47.



**Figure 6.**  $^{19}\text{F}$  NMR spectra of **4** at several temperatures ( $^{\circ}\text{C}$ ).



**Figure 7.** Eyring plot of  $\text{Cp-C}_6\text{F}_5$  rotation rates in **4**.

tadiene (**1**) may be prepared in one pot from sodium cyclopentadienide, excess hexafluorobenzene, and excess  $\text{NaH}$  in diglyme. The corresponding sodium salt **2** is a useful ligand for the formation of  $\text{Mn}(\text{CO})_3$  and  $\text{Re}(\text{CO})_3$  complexes **3** and **4**, although attempts to form the

(22) (a) Hardcastle, K.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 6138. (b) Kilway, K. V.; Siegel, J. S. *Organometallics* **1992**, *11*, 1426.

(23) (a) Benson, I. B.; Knox, S. A. R.; Stansfield, R. F. D.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 51. (b) Casey, C. P.; Rutter, E. W. *Inorg. Chem.* **1990**, *29*, 2333.

corresponding ferrocene by standard methods failed. The effect of four  $\text{C}_6\text{F}_5$  groups on the carbonyl stretching wavenumbers is linearly additive. Compounds **1**, **3**, and **4** adopt propeller-like conformations in the solid state. A correlation between  $\text{Cp-C}_6\text{F}_5$  torsion angle and the angular displacement of the  $\text{C}_6\text{F}_5$  group from the  $\text{C}_5$  least-squares plane of the  $\text{CpM}(\text{CO})_3$  core in  $\text{C}_6\text{F}_5$ -substituted  $\text{CpM}(\text{CO})_3$  complexes ( $\text{M} = \text{Mn}, \text{Re}$ ) is ascribed to steric interaction between the *endo ortho* fluorine atoms and the  $\text{M}(\text{CO})_3$  tripod.  $\text{Cp-C}_6\text{F}_5$  rotation barriers are identical to those observed in homologous  $\text{C}_6\text{F}_5$ -substituted  $\text{CpM}(\text{CO})_3$  complexes.

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**Supporting Information Available:** Crystallographic data for **1** (Tables S1–S8),  $1\text{-}^{1/2}\text{C}_6\text{D}_6$  (Tables S9–S16), **3** (Tables S17–S24), and **4** (Tables S25–S32).  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra of **2** (Figures S1 and S2) showing bulk purity of the sample. Variable-temperature  $^{19}\text{F}$  NMR spectra of **3** (Figure S3) and **4** (Figure S4). Eyring analysis of dynamic NMR data for **3** (Chart S1) and **4** (Chart S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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