

## “HALF-OPEN COBALTOCENE” CHEMISTRY: DIENE REPLACEMENT VS. HYDRIDE ABSTRACTION BY THE TRIPHENYLMETHYL CATION

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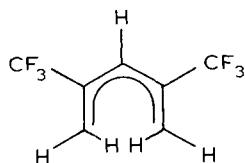
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### Summary

Cyclopentadienyl( $\eta^4$ -2,4-bis(trifluoromethyl)-1,3-pentadiene)cobalt has been prepared by the reaction of the fluorinated diene with (cyclopentadienyl)bis(ethylene)cobalt. An attempt to bring about hydride abstraction from the former compound using the triphenylmethyl cation has instead led to a replacement of the fluorinated diene by an  $\eta^5$ -( $C_6H_5$ ) $_3C^+$  ligand.

As part of our efforts to add to our understanding of pentadienyl metal chemistry, we have become interested in studying the effects brought about by the addition of various substituents to pentadienyl ligands. Even though we have reported a variety of complexes containing methylated pentadienyl ligands [1], it appeared worthwhile to attempt the preparation of complexes containing more radically substituted pentadienyl ligands. While pentadienyl anions containing cyano [2], siloxy [3], and silyl [4] substituents are known, we were particularly interested in  $CF_3$  substituents, which would provide a predominately inductive electron-withdrawing influence. Perhaps especially favorable for bonding to a transition metal would be a 2,4-bis(trifluoromethyl)pentadienyl ligand, 2,4-( $CF_3$ ) $_2C_5H_5$  (I). The primary reason for this notion is that the carbon atoms in the 2 and 4 positions are those which are formally uncharged, and hence should be



(I)

involved mostly in  $M \rightarrow L$   $\delta$  (back)bonding, as opposed to the atoms in the 1, 3, and 5 positions, which should be involved mostly in  $L \rightarrow M$   $\pi$ -bonding. Hence,  $CF_3$  substitution at the 2 and 4 positions should primarily lead to an enhancement of  $\delta$  bonding, while incorporation at the 1, 3, and 5 positions should lead primarily to a loss in  $\pi$  bonding. In order to evaluate the effect of  $CF_3$  substitution, we have therefore prepared  $Co(C_3H_5)(\eta^4\text{-}2,4\text{-bis(trifluoromethyl)-}1,3\text{-pentadiene})$  as a candidate for conversion to a pentadienyl complex via hydride ion abstraction with the triphenylmethyl cation. Herein we report our observations concerning these complexes, including the unexpected course followed by the latter reaction.

## Experimental

All operations involving organometallics were carried out under nitrogen in prepurified Schlenk apparatus or in a glovebox. Nonaqueous solvents were thoroughly dried and deoxygenated in a manner appropriate to each and were distilled immediately before use. Mass spectra were recorded on a Varian MAT 112 spectrometer at 70 eV. Except for the parent fragment, peaks are only quoted if their relative intensities are at least 10% of the intensity of the strongest peak. NMR spectra were recorded on Varian XL-300 and XL-400 spectrometers. Infrared spectra were recorded with a Perkin-Elmer 298 spectrophotometer. Mulls were prepared in a glovebox using dry, degassed Nujol. Elemental analyses were performed by MicAnal Laboratories (Tucson).

*4-Methyl-1,1,1,5,5,5-hexafluoro-3-penten-2-one.* This compound was prepared in a fashion similar to that previously reported [5], with the following differences. Most of the crude condensation product (2-methyl-2-hydroxy-1,1,1,5,5,5-hexafluoro-4-pentanone) from 1,1,1-trifluoroacetone was collected as a liquid ether extract. Relatively little solid hydrate was collected from filtration of the aqueous layer. After most of the ether was removed by distillation through an 8" Vigreux column, the remaining liquid was combined with the solid hydrate and vacuum distilled from 100 ml of concentrated sulfuric acid to remove excess water. This compound was then dehydrated by three successive distillations from 30 ml portions of 20% oleum, by which time GC analysis indicated that less than 1% of the alcohol remained. The product was carefully distilled once more (without acid), the fraction coming over between 50–85°C being collected. GC analysis indicated a composition of 96% 4-methyl-1,1,1,5,5,5-hexafluoro-3-penten-2-one and 4% ether. A yield of 55 g (60%) was obtained.  $^1H$  NMR:  $\delta$  6.70 (s, 1H), 1.95 (s, 3H) ppm.

Infrared data (neat): 3460 w, 3090 w, 3015 vw, 2970 vw, 2930 vw, 1740 s, 1658 s, 1440 m, 1376 m, 1329 ms, 1280 vs, 1220–1130 vs, 1112 ms, 1070 s, 1037 sh, 975 ms, 892 ms, 860 m, 738 m, 630  $m\text{ cm}^{-1}$ .

*2,4-Bis(trifluoromethyl)-1,3-pentadiene.* After conversion of the previous ketone to 2,4-dimethyl-1,1,1,5,5,5-hexafluoro-2-penten-4-ol by the reported procedure [5], the crude product was vacuum distilled from 100 ml of concentrated sulfuric acid in order to remove most of the excess water. The alcohol was then dehydrated by successive distillations from 20–30 ml portions of 20% oleum. Several such distillations were required to assure that less than 1% of the alcohol remained. A final distillation (without acid) was carried out, during which the fraction coming over at 72–98°C (650 torr) was collected. GC analysis indicated a composition of at least 97% diene, with approximately 2% ether and 0.2% starting alcohol.

Anal. Found: C, 41.17; H, 2.95.  $C_7H_6F_6$  calcd.: C, 41.19; H, 2.96%.  $^1H$  NMR ( $CDCl_3$ , TMS reference):  $\delta$  6.51 (possible pseudo-sextet, 1 H,  $J$  1.4 Hz), 6.07 (q, 1H,  $J$  1.5 Hz), 5.58 (possible pseudo-quintet, 1 H,  $J$  1.4 Hz), 1.96 (d, 3H,  $J(CH)$  1.5 Hz) ppm.  $^{19}F$  NMR ( $CDCl_3$ ,  $CFCl_3$  reference, 0.00 ppm):  $\delta$  -69.0, -70.9 ppm.  $^{13}C$  NMR ( $CDCl_3$ , TMS reference):  $\delta$  134.0 (C, q,  $J(CF)$  30 Hz), 133.2 (C, q of q of d,  $J(CF)$  30\* Hz,  $J(CH)$  7, 3 Hz), 124.4 ( $CF_3$ , q of d of q,  $J(CF)$  272 Hz,  $J(CH)$  7, 5 Hz), 123.7 (CH, d of m,  $J(CH)$  159 Hz,  $J(CH)$  5, 10 Hz (both from  $CH_2$ ),  $J(CH)$  5 Hz (from  $CH_3$ ),  $J(CF)$  6\*, 1.5 Hz), 123.2 ( $CF_3$ , q of d of d,  $J(CF)$  272\* Hz,  $J(CH)$  14, 7 Hz), 123.2 ( $CH_2$ , t of d of q (t of pseudo-quintets),  $J(CH)$  160, 5 Hz,  $J(CF)$  5 Hz), 12.3 ppm ( $CH_3$ , q of d,  $J(CH)$  130, 7 Hz). Resonances denoted with asterisks are those for which the fluorine coupling derives from the fluorine atoms which resonate at -70.9 ppm. The coupling pattern for the CH carbon atom (at 123.7 ppm) was particularly complex. In the fully proton decoupled spectrum, the resonance appeared as a clear quartet of quartets. In the fully fluorine decoupled spectrum, a doublet of seven-line multiplets resulted, which seemed to match a 1/4/7/8/7/4/1 pattern that would result for the given assignments above. Selective decoupling of the fluorine resonance at -69.1 ppm led to a doublet of multiplets, each of which seemed to be an apparent ten-line pattern (eight lines of the 1/7/22/42/56/56/42/22/7/1 pattern clearly resolvable, the other two questionable), due to the similarity of the  $J(CF)$  to some of the  $J(CH)$  values.

Infrared data (neat): 3006 w, 2974 w, 2938 w, 2878 vw, 2305 vw, 2130 vw, 1914 w, 1784 vw, 1676 w, 1451 m, 1416 ms, 1395 w, 1370 ms, 1343 s, 1292 vs, 1182 vs, 1129 vs, 1099 s, 1044 w, 1011 ms, 956 ms, 934 mw, 893 m, 813 mw, 789 w, 733 mw, 715 m, 683 w, 637 m  $cm^{-1}$ .

Mass spectrum:  $m/e$  (rel. intensity): 39 (51), 51 (18), 57 (14), 63 (12), 65 (19), 69 (37), 75 (15), 77 (15), 85 (13), 89 (13), 95 (27), 114 (11), 115 (100), 121 (13), 135 (52), 140 (12), 145 (11), 165 (11), 204 (50).

(Cyclopentadienyl)( $\eta^4$ -2,4-bis(trifluoromethyl)-1,3-pentadiene)cobalt,  $Co(C_5H_5)(\eta^4$ -2,4-( $CF_3$ )<sub>2</sub>-1,3- $C_5H_6$ ). A preliminary study of the reaction between  $Co(C_5H_5)(C_2H_4)_2$  [6] (0.38 M) and the diene (0.76 M) in an NMR tube indicated a half-life of ca. 90 min at room temperature. For preparative purposes, a hexane solution (20 ml) containing 0.34 g (1.9 mmol) of  $Co(C_5H_5)(C_2H_4)_2$  and 1.22 g (2.7 mmol) of 2,4-bis(trifluoromethyl)-1,3-pentadiene was stirred under nitrogen at room temperature for 16 to 24 h. The solution was stored overnight at -90°C to crystallize out any remaining  $Co(C_5H_5)(C_2H_4)_2$ , after which the liquid portion was removed by syringe. After most of the solvent was removed in vacuo, the remaining red oil was eluted through a florisil column (2.5 × 20 cm) with hexanes. Solvent was removed in vacuo from the eluent until the solution contained only ca. 30% solvent. On cooling this solution to -90° overnight, red crystals were obtained, which melted to an oil below room temperature. If desired, the red oil may be sublimed onto a dry-ice cooled cold finger by heating the oil to 35–50°C in vacuo. A yield of 0.50 g (80%) was obtained.

Anal. Found: C, 43.82; H, 3.23.  $C_{12}H_{11}CoF_6$  calcd.: C, 43.92; H, 3.38%.  $^1H$  NMR:  $\delta$  5.64 (s, 1H), 4.52 (s, 5H), 2.27 (d of d, 1H,  $J$  1, 3 Hz), 0.70 (d, 1H,  $J$  3 Hz), 0.45 (s, 3H) ppm. The 1 Hz coupling for the 2.27 ppm resonance was found from selective decoupling to result from interaction with the 5.64 ppm resonance. The splitting of the 5.64 ppm resonance could not be observed presumably due to its broadness resulting from weak fluorine couplings.  $^{19}F$  NMR ( $CDCl_3$ ,  $CFCl_3$

reference):  $\delta$  -63.2, -63.6 ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS reference):  $\delta$  129.3 ( $\text{CF}_3$ , q,  $J(\text{CF})$  271 Hz), 125.8 ( $\text{CF}_3$ , q,  $J(\text{CF})$  269 Hz), 87.5 (C, q,  $J(\text{CF})$  35 Hz), 82.4 (CH (Cp), d of quintets (from 4 Cp H's),  $J(\text{CH})$  178, 7 Hz), 78.7 (CH, d of m,  $J(\text{CH})$  171 Hz), 46.6 (C, q,  $J(\text{CF})$  30 Hz), 29.7 ( $\text{CH}_2$ , t,  $J(\text{CH})$  160 Hz), 13.2 ppm ( $\text{CH}_3$ , q,  $J(\text{CH})$  129 Hz).

Infrared data (neat): 2962 w, 2925 sh, 2880 sh, 2850 sh, 1484 w, 1465 sh, 1440 vw, 1410 vw, 1383 mw, 1363 m, 1342 m, 1278 m, 1259 vs, 1150 s, 1131 s, 1100 s, 1062 s, 1012 ms, 931 w, 909 sh, 857 vw, 820 ms, 797 m, 731 w, 713 w, 677 m, 622 sh  $\text{cm}^{-1}$ .

Mass spectrum (70 eV):  $m/e$  (rel. intensity): 39 (12), 40 (100), 44 (14), 59 (14), 65 (11), 77 (13), 78 (20), 110 (10), 124 (100), 142 (15), 145 (13), 165 (14), 185 (13), 198 (12), 328 (42).

(Cyclopentadienyl)( $\eta^5$ -triphenylmethyl)cobalt(III) tetrafluoroborate,  $\text{Co}(\text{C}_5\text{H}_5)(\eta^5\text{-C}_{19}\text{H}_{15})^+ \text{BF}_4^-$ . A stirred solution of 0.73 g (2.2 mmol) of the diene complex in 20 ml  $\text{CH}_2\text{Cl}_2$  under nitrogen was cooled to  $-78^\circ\text{C}$ , after which a solution of 0.73 g (2.2 mmol) of triphenylmethyl tetrafluoroborate in 10 ml  $\text{CH}_2\text{Cl}_2$  was added dropwise over a period of 0.5 h. The mixture was allowed to warm slowly to room temperature, after which stirring was continued for 1–2 h, at which time 10 ml of ether was added to decompose any excess triphenylmethyl cation. After stirring for 2 h, the reaction mixture was cooled to  $-20^\circ\text{C}$  until no more precipitation seemed to occur, at which time the product was isolated by filtration on a medium frit, and washed with several 5 ml portions of cold ether. A yield of 0.49 g (61%) of the brick-red product was obtained.

Anal. Found: C, 63.20; H, 4.34.  $\text{C}_{24}\text{H}_{20}\text{BCoF}_4$  calcd.: C, 63.47; H, 4.44%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{NO}_2$ , 4.30 ppm reference):  $\delta$  7.84 (t, 1H,  $J$  5 Hz), 7.3–7.45 (m, 6H), 7.2–7.25 (m, 4H), 5.98 (d of d, 2H,  $J$  6, 8 Hz), 5.65 (s, 5H), 5.63 (d of d, 2H,  $J(\text{CH})$  8, 1 Hz).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{NO}_2$ , 57.3 ppm reference):  $\delta$  135.2 (2C, t,  $J(\text{CH})$  8 Hz), 128.7 (1C), 125.0 (4CH, d of t,  $J(\text{CH})$  159, 7 Hz), 124.5 (4CH, d of d,  $J(\text{CH})$  161, 7 Hz), 123.9 (2CH, d of t,  $J(\text{CH})$  162, 8 Hz), 119.7 (1C, t,  $J(\text{CH})$  6 Hz), 87.6 (2CH, d of d,  $J(\text{CH})$  178, 7 Hz), 85.2 (1CH, d of m,  $J(\text{CH})$  172 Hz), 82.2 (5CH, d of quintets (from 4 Cp H's),  $J(\text{CH})$  183, 7 Hz), 70.5 (2CH, d,  $J(\text{CH})$  172 Hz).

Infrared data (Nujol mull): 3130 w, 3110 w, 3070 w, 1407 m, 1357 m, 1337 sh, 1286 w, 1189 w, 1160 m, 1143 sh, 1110 sh, 1084 sh, 1070 vs, 1049 s, 1019 sh, 978 sh, 970 sh, 934 mw, 850 mw, 838 w, 832 mw, 776 ms, 767 ms, 712 ms, 703 s, 678 m  $\text{cm}^{-1}$ .

Mass spectrum (fast atom bombardment, *m*-nitrobenzyl alcohol matrix):  $m/e$  (rel. intensity): 367 (28), 243 (21), 176 (12), 165 (13), 139 (14), 138 (31), 137 (60), 136 (85), 124 (11), 120 (15), 107 (33), 105 (11), 91 (19).

## Results and discussion

The reaction of  $\text{Co}(\text{C}_5\text{H}_5)(\text{C}_2\text{H}_4)_2$  with 2,4-bis(trifluoromethyl)-1,3-pentadiene (2,4-( $\text{CF}_3$ ) $_2\text{C}_5\text{H}_6$ ) leads to the formation of  $\text{Co}(\text{C}_5\text{H}_5)(\eta^4\text{-2,4-(CF}_3)_2\text{C}_5\text{H}_6)$  (II) in high yield at a readily measurable rate (see Experimental). This liquid compound is much more thermally stable than either  $\text{Co}(\text{C}_5\text{H}_5)(\text{C}_2\text{H}_4)_2$  or  $\text{Co}(\text{C}_5\text{H}_5)(\eta^4\text{-2,4-(CH}_3)_2\text{C}_5\text{H}_6)$  [7], presumably as a result of electronic influences. The complex could be characterized analytically and spectroscopically. The two expected resonances were observed in the  $^{19}\text{F}$  NMR spectrum ( $-63.2$  and  $-63.6$  ppm), and the  $^1\text{H}$  NMR spectrum contained the expected five resonances in a 1/5/1/1/3 ratio.

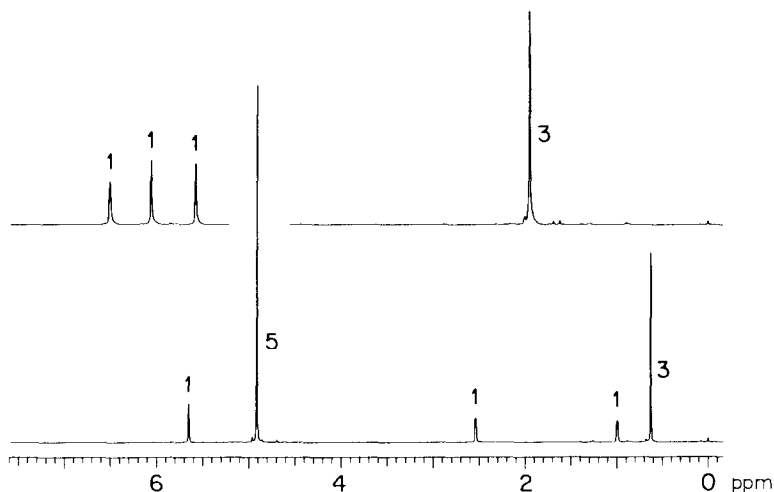
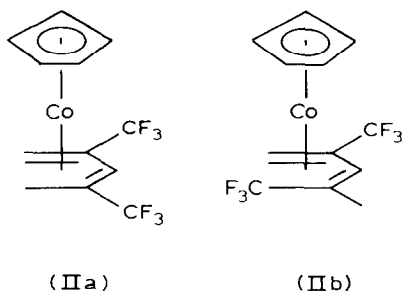
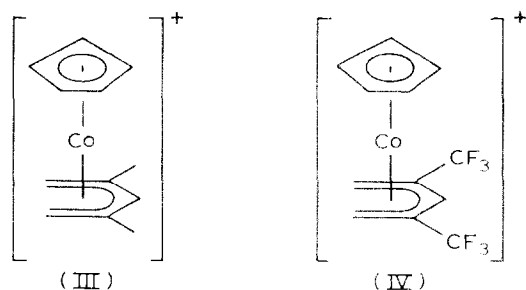


Fig. 1.  $^1\text{H}$  NMR Spectra of 2,4-bis(trifluoromethyl)-1,3-pentadiene ( $2,4-(\text{CF}_3)_2\text{C}_5\text{H}_6$ ) (top) and  $\text{Co}(\text{C}_5\text{H}_5)(2,4-(\text{CF}_3)_2\text{C}_5\text{H}_6)$ . From single frequency proton decoupling studies, the proton resonance for the central  $\text{CH}$  group can be assigned as the furthest downfield resonance for both spectra.

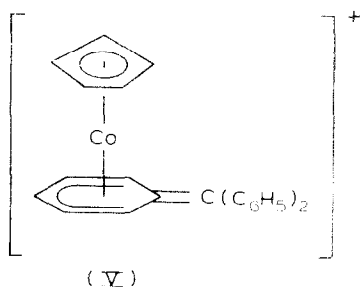
Quite notably, two of the single proton resonances have shifted dramatically upfield from their locations in the free diene (see Fig. 1). In all likelihood these are the two vinylic protons on the terminal  $\text{CH}_2$  group. While it should be possible for the diene complex to exist as a pair of isomers, IIa and IIb, the  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{13}\text{C}$  NMR spectra demonstrate that only one isomer is present in detectable quantities [8]. Isomer IIa is the logical choice on steric grounds, and the very large upfield shift experienced by the methyl group in the diene complex, as well as the two nearly identical  $^{19}\text{F}$  resonances, fairly certainly establish the nature of the observed isomer as IIa. It should be noted, however, that the free diene compound also was isolated as a single isomer, and it may be that this circumstance is actually more responsible for the isolation of only one metal complex isomer.

As  $\text{Co}(\text{C}_5\text{H}_5)(2,4-\text{C}_7\text{H}_{12})$  ( $\text{C}_7\text{H}_{12}$  = dimethylpentadiene) readily undergoes a formal hydride abstraction reaction on treatment with the triphenylmethyl cation, yielding the "half-open cobalticinium" complex,  $\text{Co}(\text{C}_5\text{H}_5)(2,4-\text{C}_7\text{H}_{11})^+$  (III,  $\text{C}_7\text{H}_{11}$  = dimethylpentadienyl), the analogous reaction was likewise attempted with IIa, in the hope of isolating  $\text{Co}(\text{C}_5\text{H}_5)(2,4-(\text{CF}_3)_2\text{C}_5\text{H}_5)^+$  (IV).





Indeed, a product with similar appearance and physical properties to those of III was isolated, and its <sup>1</sup>H NMR spectrum contained the expected set of resonances for IV in a 1/2/2/5 ratio. However, also present were aromatic resonances, which might have been ascribed to a complex incorporating (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CH, or some similar species. In fact, integration of the <sup>1</sup>H NMR spectrum fitted a formulation such as Co(C<sub>5</sub>H<sub>5</sub>)(2,4-(CF<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>) · n(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CH, where n = 0.67. However, analytical data could only fit such a formulation for n = ca. 1.6 [9], and a <sup>19</sup>F NMR spectrum contained only one resonance, in a location consistent with the BF<sub>4</sub><sup>-</sup> counter-ion [10]. In addition, the mass spectrum also provided no evidence for the presence of the expected CF<sub>3</sub>-containing fragments, and the highest observed peak (m/e = 367) corresponded well with the molecular fragment Co(C<sub>5</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>C<sup>+</sup>. As the analytical data and <sup>1</sup>H NMR integration were in agreement with the stoichiometry Co(C<sub>5</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub><sup>+</sup> BF<sub>4</sub><sup>-</sup>, it became clear that rather than abstracting a hydride ion from IIa to yield IV, the triphenylmethyl cation had actually just replaced the diene ligand in IIa to yield V. Not surprisingly, therefore, it was found that complex V could also be prepared by simply substituting the appropriate molar quantity of Co(C<sub>5</sub>H<sub>5</sub>)(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> for Co(C<sub>5</sub>H<sub>5</sub>)(2,4-(CF<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>6</sub>). Experimental conditions and yield were essentially identical. In view of the fact that the fluorodiene complex IIa is thermally more robust than the analog III, the observed replacement of the fluorodiene ligand was completely unexpected. However, the relative thermal stabilities and differing chemical reactivities are not incompatible, and it may well be that the inductive effects of the CF<sub>3</sub> groups on the diene have greatly impeded the abstraction of a hydride ion, leading to the observed reaction [11].



While the observed formation of an  $\eta^5$ -triphenylmethyl ligand was unexpected, it can be noted that somewhat similar modes of bonding have been observed in  $\eta^5$ -phenoxide [12],  $\eta^5$ -benzyl [13],  $\eta^5$ -amide [14], and  $\eta^6$ -tetraphenylborate [15] complexes. Quite possibly, a wide variety of  $\eta^5$ -benzyl and related species may be obtained through reactions similar to that observed herein. It does not appear that the failure to bring about a hydride abstraction indicates something unfavorable about  $\text{CF}_3$ -substituted pentadienyl ligands, as some of these have been reported, through somewhat unusual reactions [16]. It can be noted, however, that both the expected and the observed products are very similar in that they can be regarded as "half-open cobalticinium" cations. Other attempts to probe the effects of varying substituents on pentadienyl skeletons are in progress.

### Acknowledgment

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- The  $^{13}\text{C}$  NMR spectra for both the free hexafluorodiene and its cobalt compound were particularly complex due to coupling from both hydrogen and fluorine nuclei. Nevertheless, nearly all if not all observed couplings could be assigned with the aid of a variety of single frequency and broad band proton and fluorine decoupled spectra.
- Calcd. for  $n = 1.6$ , C, 63.27; H, 4.46%.
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- If hydride abstraction became much slower, a direct replacement of the diene might become favored. However, the relatively slow rate of replacement of even ethylene in  $\text{Co}(\text{C}_5\text{H}_5)(\text{C}_2\text{H}_4)_2$  by the fluorodiene suggests that a one-electron oxidation of the cobalt complex may be involved, at which point the presumably weakly bound fluorodiene ligand could come off. This possibility was also favored by one referee.

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