Selective Solubility of Organometallic Complexes in Saturated Fluorocarbons. Synthesis of Cyclopentadienyl Ligands with Fluorinated Ponytails

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Cyclopentadienes bearing varying length fluorinated "ponytails", $C_5H_5[(CH_2)_n(CF_2)_mF]$ ($[n.m]$ = [0.8], [0.10], [0.12], [2.6], [2.8], and [2,10]) have been prepared by reaction of the corresponding fluoroalkyl iodides and triphenylphosphine with nickelocene. From these, the 1,1′-bis[2.6]-, 1,1′-bis[2.8]-, and 1,1′-bis[2.10]-disubstituted ferrocenes and [2.10]-substituted $[Mn(CO)_3L]$, $[Re(CO)_3L]$, and $[Co(CO)_2L]$ derivatives ($L = \eta^5$-C_5H_4[2.10]) were prepared. Although the anions of the [0.m] compounds were thermally unstable, the corresponding [0.8], [0.10], and [0.12] cobalt dicarbonyl complexes were prepared directly from the cyclopentadienes. The solubilities of these compounds in both saturated fluorocarbon (fluorous) and conventional solvents was found to depend strongly on the length of the fluoroalkyl tail and on the temperature. These compounds all dissolve in fluorous solvents, and the 1,1′-bis[2.10]ferrocene partitions *selectively* into the fluorous layer of a biphasic perfluoro(methylcyclohexane)/toluene system. The oxidation potentials of the 1,1′-, bis[2.6]-, and 1,1′-bis[2.10]ferrocenes are only very slightly more positive than ferrocene itself, demonstrating that the C_2H_4 spacer effectively insulates the electron-withdrawing effect of the fluoroalkyl part of the ponytail from the metal. A similar insulating effect is noted in the carbonyl stretching frequencies of $[Mn(CO)_3L]$, $[Re(CO)_3L]$, and $[Co(CO)_2L]$ derivatives ($L = \eta^5$-C_5H_4[2.10]), which are slightly to low energy of those in the corresponding parent cyclopentadienyl analogues. In contrast, the corresponding frequencies in $[Co(CO)_2L]$ derivatives ($L = \eta^5$-C_5H_4[0.10]; η^5-C_5H_4[0.12]) without the hydrocarbon spacer group are at higher energy than the parent compound.

Introduction

The unique solvent properties of saturated fluorocarbons have been recognized for almost a half-century. Indeed, as noted by Hildebrand, before the advent of perfluorocarbons, nonpolar liquids sufficiently unlike to form two-phase systems were rare;[1] hence, their preparation provided new opportunities for the investigation of liquid−liquid behavior. Pioneering studies of their low solubility in conventional nonfluorinated solvents by Scott and Hildebrand gave rise to the "solubility parameter", δ,[2] and the phase diagrams obtained by Hildebrand for mixtures of linear fluoroalkanes or perfluoro(methylcyclohexane) (PFMCH) with several common solvents show strong Raoult deviations, giving characteristic phase boundaries that rise steeply yet are flat at the consolute point.[1,3]

Solubilization of organic compounds in saturated fluorocarbons usually requires the presence of one or more perfluoroalkyl chains as substituent groups in the solute. This approach has been exploited, for example, in a series of fluorocarbon-compatible direct dyes containing perfluoroalkyl chains,[4] fluoroalkylated surfactants and antiwetting agents,[5] and crown ethers bearing both fluorocarbon and hydrocarbon alkyl tails, prepared as components for polymer/liquid crystal composite ion transport membranes.[6]

The unusual miscibility properties of fluorocarbon solvents have also been recognized recently as having potentially singular utility for synthesis and catalysis. Zhu, for example, has advocated the use of perfluorinated solvents in organic carbonyl condensations, noting that reactions are faster, products are cleaner and more easily isolated, and azeotropic distillations are more generally applicable than with many more common organic solvents.[7] A significant new concept in catalysis has been introduced by Horváth and Rabái, who have demonstrated that "fluorous biphasic systems" are a convenient means to recover catalysts and simplify product isolation.[8,9] The word "fluorous" to connote fluorocarbon media has been coined as an analogue of "aqueous".[8] The concept requires a catalyst that is *selectively* soluble in the fluorous phase, and products that are *selectively* soluble in a hydrocarbon phase, such as toluene. To confer fluorous solubility upon the transition metal complex selected as a hydroformylation catalyst, Horváth and Rabái designed and synthesized

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a phosphine, $P(C_2H_4C_6F_{13})_3$, in which three perfluoroalkyl "ponytails" afford fluorous solubility, while the intervening methylene groups serve as an insulating spacer group to isolate the strong electron-withdrawing effect of fluoroalkyl chains from the ligating phosphorus atom. Using $[RhH(CO)\{P(C_2H_4C_6F_{13})_3\}_3]$ as catalyst, they demonstrated that hydroformylation of 1-octene occurs in a homogeneous mixture of PFMCH/toluene at elevated temperatures. On cooling, a rapid phase separation afforded catalyst recovery in the fluorous phase and separation of the product in the hydrocarbon phase.[8]

Additional interest in enhancing the solubility of inorganic and organometallic compounds in saturated fluorocarbons stems from the similarity of the solvating properties of fluorous solvents and supercritical CO_2. There is considerable interest in performing chemical synthesis and catalysis in the latter medium, both for environmental reasons and for the simplification of reaction processing and workup. For example, recognition of the similar solvating properties of saturated fluorocarbons and supercritical CO_2 has led to new polymer processing methodology for fluorocarbon monomers in supercritical CO_2.[10] Thus, factors that enhance the solubility of transition metal complexes in fluorous solvents should also lead to significantly greater solubility in supercritical CO_2.

However, while many inorganic or organometallic complexes contain ligands bearing fluorine as a substituent,[11,12] those that are known to exhibit significant solubility in saturated fluorocarbons are rare. For example, while cyclopentadienyl is the most ubiquitous ligand in organometallic chemistry, only a few such ligands bearing fluorine or short fluoroalkyl substituents have been reported. (Trifluoromethyl)cyclopentadiene,[13] tetramethyl(trifluoromethyl)cyclopentadiene,[14] and various transition metal complexes of these ligands have been prepared to demonstrate "tuning" of the electronic properties of cyclopentadienyl ligands by the CF_3 group. Notably in these complexes, the electronic effect on the metal of the fluoroalkyl group directly bound to the ligated carbon is significant. The electron-withdrawing effects of perfluoroalkyl substituents on porphines have also been the subject of computational[15] and synthetic[16] study. Interestingly, tetrakis(perfluoropropyl)porphines form complexes soluble in aqueous methanol, a medium in which longer chain fluoroalkyl compounds are insoluble. Two tetrakis(trifluoromethyl)ruthenocenes as well as analogous rhodium and iridium half-sandwich complexes have been reported; these have been subjected to electrochemical study and also show a slight solubility in perfluorohexane.[17] Several partially fluorinated compounds in the recent literature have included $[(C_5F_5)(C_5R_4R')Ru]$ (R = Me; R′ = Me, Et),[18] (R = R′ = H),[19] and a tetrafluorinated cryptand, the fluorines of which provided an NMR probe to monitor ion coordination inside the moleclar host.[20] Clearly, ligands bearing longer fluoroalkyl chains are necessary to achieve significant solubility in fluorous media.

While there are many recent reports of transition metal complexes bearing ligands with long hydrocarbon tails, including acetylacetonates,[21−23] ferrocenes,[24] cobaltoximes,[25] and alkyliridium,[26] -manganese,[27] and -rhenium[28] carbonyl complexes, the paucity of analogous long-chain perfluoroalkyl complexes is notable. Only Horváth's rhodium ponytail−phosphine complex,[8] a fluoroalkylated cobalt phthalocyanine,[8] and a series of fluoroalkanoyl ferrocenes and the alcohols resulting from their reduction[29] appear to have been reported.

Given the prevalence of the cyclopentadienyl ligand in organometallic chemistry, we wished to extend Horváth's ponytail concept to cyclopentadienyl complexes, with two principal objectives: to assay the extent and selectivity of fluorous solubility conferred on complexes of cyclopentadienyl ligands by fluorocarbon ponytails of differing lengths and to confirm the insulating power of the intervening methylene spacer groups against the inductive effects of the fluoroalkyl ponytail. Here we report on the results of a preliminary study that suggests some design features that will be required to effect the enhanced and, where necessary, the selective solubility of organometallic compounds in saturated fluorocarbons and, by extension, in supercritical CO_2.

Results and Discussion

Synthesis of Ponytail Cyclopentadienes. Our chosen target ligand precursors were (fluoroalkyl)-cyclopentadienes of general form C_5H_5R, which could either be used directly to form metal complexes or be deprotonated to give the corresponding cyclopentadienyl anion prior to complexation. To facilitate discussion, and minimize space, the prefix [*n.m*] for the substituent chain, $R = (CH_2)_n(CF_2)_mF$, will be used: e.g., for the ponytail having two CH_2 groups and six CF_2 groups, the

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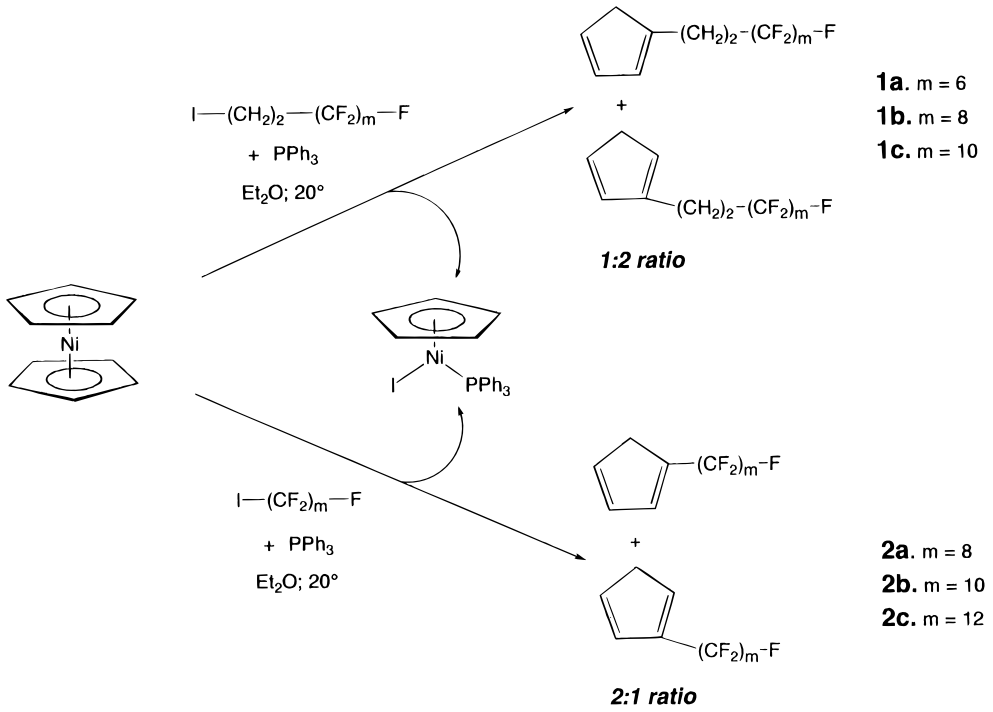
Scheme 1



abbreviation [2.6] instead of 1H,1H,2H,2H-perfluorooctyl is used to define the ponytail; the corresponding perfluorooctyl ponytail is abbreviated as [0.8].

The method of choice for preparation of these cyclopentadienes is by the reaction of nickelocene with an appropriate [*n*.*m*] iodide (Scheme 1), according to a method developed by Månsson.[30] Both the [0.*m*] and [2.*m*] iodides ($m = 6, 8, 10$) are commercially available, and the [2.*m*] analogues are also readily prepared by radical addition of the [0.*m*] iodides to ethylene.[31] In this manner, cyclopentadienes **1a** (71%), **1b** (88%), and **1c** (92%), bearing [2.6], [2.8], and [2.10] ponytails, respectively, were conveniently prepared in high yields and easily separated from the [NiCpI(PPh_3)] also produced in this reaction. Analogous methodology afforded the [0.8], [0.10], and [0.12] cyclopentadienes **2a** (70%), **2b** (94%), and **2c** (91%), which lack the C_2H_4 spacer. Moberg,[32] Månsson,[30] and Lemenovskii[33] have observed that similar alkylation of cyclopentadienyl ligands of nickelocene occurs in the absence of triphenylphosphine, although more slowly than in its presence;[32] this would be attractive, as both rings of the nickelocene would be utilized and the NiI_2 side product could be recycled to nickelocene. Unfortunately, in the present case, the ponytail iodides fail to react with nickelocene until the phosphine is added: after stirring 3 days at room temperature followed by overnight reflux in THF, only starting materials were detected by NMR when the phosphine was omitted. The mechanism of this reaction is unclear, but it works very well!

The more direct route to the desired cyclopentadienes via coupling of sodium cyclopentadienide and [*n*.*m*] alkyl iodides proceeded in poor yields in refluxing THF, affording the [2.6], [2.8], and [2.10] cyclopentadienes in only 33% (**1a**), 28% (**1b**), and 55% (**1c**) yields, respectively. Phase transfer methodology was explored briefly as a means of increasing the yield of **1a**.[34] Due to the exceedingly low polarity and highly hydrophobic nature of the [2.6] iodide, the addition of benzene as a cosolvent was found to increase the yield in this latter procedure, and the yield of the [2.6] cyclopentadiene was increased to 92% Although convenient, this phase transfer has drawbacks: it is necessary to use a 2.5-fold excess of iodide, the more expensive of the principal reagents, to obtain a good yield, and consequently, the product always contains some dialkylated cyclopentadiene. The nickelocene route appears to be the most cost-effective and cleanest method.

Both the [2.*m*] and [0.*m*] series of cyclopentadienes **1** and **2** are formed as a mixture of double-bond isomers. In the case of the [2.*m*] compounds **1**, the 2-isomer predominates over the 1-isomer in a roughly 2:1 ratio. The identity of the two isomers was clearly shown by their proton NMR spectra: the methylene group of the ring of the 1-isomer is split into a six-line multiplet by the remaining three ring protons and the two α-protons of the adjacent ponytail, whereas the ring CH_2 of the 2-isomer is only split by the three other protons in the ring, giving a pseudoquartet. In contrast, the major isomer of the [0.*m*] series **2** is the 1-isomer. Proton NMR shows that the isomers are in a 2:1 ratio, but the broad peaks for the ring methylenes are otherwise uninterpretable. In the carbon spectrum of the mixture, however, a 2 Hz coupling between the ring methylene and the α-fluorines in the major isomer demonstrates it to be the 1-alkylated isomer; the coupling is absent in the minor, 2-alkylated isomer. In neither series was the symmetric 5-alkylated isomer observed.

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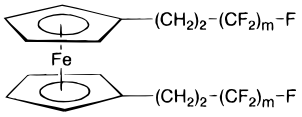
As well as differing in the predominant isomer, the [0.*m*] and [2.*m*] series of dienes have notably different stabilities: whereas an NMR sample of [2.6] diene **1a** was stable for several days at room temperature, samples of all the [0.*m*] compounds **2** began dimerizing with hours at room temperature. This contrasts with the lack of dimerization tendencies noted by Olsson for (trifluoromethyl)cyclopentadiene.[35] Likewise, the anions of the [0.*m*] and [2.*m*] cyclopentadienes show differing degrees of thermal instability. In the [2.*m*] series **1**, the cyclopentadienes can be deprotonated with butyllithium at low temperatures but decompose on warming to room temperature or attempted isolation. The cold solutions, however, may be warmed in the presence of metal halides, leading to the corresponding cyclopentadienyl complexes **3**, **4**, and **5**. In the [0.*m*] series **2**, on the other hand, attempts at deprotonation using either butyllithium or thallium ethoxide caused decomposition,[13] precluding the synthetic use of the anions. This behavior is similar to that noted by Gassman for tetramethyl(trifluoromethyl)cyclopentadiene,[14] and limited the organometallic derivatives of the [0.*m*] compounds to those which could be prepared without deprotonation.

Ponytail Ferrocenes. The ferrocene derivatives of [2.*m*] cyclopentadienes **1** were prepared by reaction of $FeCl_2$·2THF with the deprotonated dienes. Conveniently, the low solubility of $FeCl_2$·2THF in diethyl ether allowed the iron halide to be present in situ in the mixture as the ligand was deprotonated with butyllithium at −78 °C; reaction with the iron then occurred as the mixture was warmed to room temperature. In this manner, 1,1′-bis[2.6]-, 1,1′-bis[2.8]-, and 1,1′-bis[2.10]ferrocenes **3a**−**c** were prepared in good yields. The



3a. m = 6
3b. m = 8
3c. m = 10

purification of these compounds proved difficult due to their low solubilities in common organic solvents. Shorter chain **3a** was conveniently purified by chromatography, but the low solubilities of the longer chain homologues caused extensive tailing, and the chromatographic separation of the desired complexes from fluorine-containing impurities and unreacted cyclopentadiene was poor. Likewise, just as the solubility of fluorous solvents in protic solvents shows a marked temperature dependence, so do the solubilities of the longer chain ferrocenes, which typically have a threshold (∼40 °C) above which their solubility increases greatly. Thus, during attempts to recrystallize these complexes, a combination of fluorinated materials often coprecipitated as the temperature was lowered. Consequently, Soxhlet extraction with hexanes proved to be the most viable purification method for **3b** and **3c**, allowing the major compound to slowly saturate a hot solution and to avoid sizable losses due to precipitation during standard hot filtration. As numerous attempts to grow diffractable crystals of the ferrocenes invariably gave unusable lamellae or fluffy microcrystals, the perfluoroalkyl tails most likely impede the crystal packing of these molecules. Interestingly, the ^{19}F NMR spectra of [2.6] compound **3a** shows complex but sharp multiplets for the various fluorines, yet those of the [2.8] and [2.10] homologues **3b** and **3c** retain the sharp triplet of triplets for the terminal $CF_3(\omega)$, while the other resonances are broad. This phenomenon is also evident in other derivatives discussed below.

The solubilities of these 1,1′-bis[*n*.*m*]ferrocenes are strongly dependent on the length of the tail. 1,1′-Bis-[2.6]ferrocene **3a** dissolves readily in common nonpolar solvents, as well as in perfluoroheptane and PFMCH. It also dissolves slightly in acetonitrile, methanol, and ethanol at room temperature, although not in DMSO. The 1,1′-bis[2.8]ferrocene complex **3b** is less soluble but still dissolves in common solvents other than acetonitrile or alcohols. In contrast, 1,1′-bis[2.10]ferrocene **3c** dissolves easily in diethyl ether, moderately in hexanes, and sparingly in chloroform, acetone, and toluene at room temperature, although it dissolves easily in these solvents hot. It is completely insoluble in alcohols, acetonitrile, pyridine, and DMSO. Due to their slight room-temperature solubility in chloroform, it was necessary to obtain NMR spectra of the longer chain compounds at 40−50 °C, above the solubility threshold temperature. The 1,1′-bis[2.10]ferrocene **3c** easily forms supersaturated solutions in toluene, perfluoroheptane, or PFMCH when warm solutions are cooled to room temperature; these solutions slowly precipitate copious quantities of the ferrocene. For example, a 0.1 M solution of **3c** in PFMCH may be prepared at 40 °C, although its solubility is only 0.003 M at room temperature. The solubility increases greatly as the chain length shortens: the molar solubility of **3b** in PFMCH is 0.06 M and that of **3a** is >0.09 M.

On mixing equal volumes of toluene and a saturated perfluoroheptane solution of **3c**, a partition constant of $C_{C_7F_{16}}/C_{tol} = 20$ was determined gravimetrically from the evaporation residue of each layer. A similar tendency to partition into the fluorous layer was observed when solutions of the other [2.*m*] ferrocenes in PFMCH were mixed with toluene, although the partitioning showed a strong dependence on the chain length: with the 1,1′-bis[2.10]ferrocene **3c**, no color was visible in the toluene layer, the 1,1′-bis[2.8]ferrocene **3b** remained primarily in the fluorous layer while the toluene layer acquired a hint of color, and with the 1,1′-bis[2.6]ferrocene **3a**, the orange color was equally distributed between the two layers. Not surprisingly, unsubstituted ferrocene remained entirely in the toluene phase. The addition of each additional C_2F_4 segment to the chain length thus results in a significant increase in the partitioning into the fluorous solvent, but also decreases the molar solubility in the fluorinated solvent.

The oxidation potentials of ferrocenes **3a** and **3c** are given in Table 1. Both compounds showed Nernstian behavior under the experimental conditions. Both have oxidation potentials very close to that of unsubstituted ferrocene; hence the C_2H_4 spacer effectively insulates the metal from the perfluoroalkyl chain. This behavior contrasts with the large positive potential of [$(C_5H_4CF_3)_2$Fe],[13] which lacks the ethylene spacer. Interestingly, the electron-withdrawing effect of the perfluoro-

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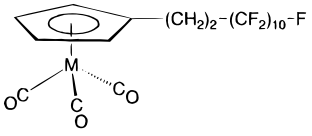
Table 1. Electrochemical Data[a] for Ferrocenes

		rel diffusion	
	E/mV[b]	coeff	ref
Cp^*_2Fe	−449	1.00	
Cp'_2Fe	−65 (MeCN)		45
Cp_2Fe	0.00		
([2.6]-Cp)$_2$Fe (**3a**)	+34 ± 2	0.83	*c*
([2.10]-Cp)$_2$Fe (**3c**)	+38 ± 2	0.16	*c*
([0.1]-Cp)$_2$Fe	+640 (CH_2Cl_2)		13

[a] 25 °C, 0.20 M Bu_4NPF_6 in THF, Pt disk and Ag/AgCl electrodes. Cp, C_5H_5: Cp*, C_5Me_5. Cp′, C_5H_4Me. [*n.m*]-Cp, $C_5H_4[(CH_2)_n(CF_2)_mF]$. [b] referenced to internal $(C_5Me_5)_2Fe$ and reported as mV vs Cp_2Fe. [c] This work.

alkyl tail is slightly greater than the donating effect of the spacer in these complexes, shifting the potentials to values slightly positive of ferrocene. The data obtained also permitted the calculation of diffusion coefficients for these compounds; while the value for 1,1′-bis[2.6]ferrocene **3a** is relatively close to that of decamethylferrocene, that of 1,1′-bis[2.10]ferrocene **3c** is only one-sixth of the decamethylferrocene value, indicating that the longer chain compound migrates much more sluggishly in solution, as expected. The [2.*m*] ponytail groups thus profoundly influence the solubility and mobility of these ferrocenes yet only negligibly perturb the redox properties of the metal center.

Ponytail Manganese and Rhenium Carbonyl Complexes. The manganese and rhenium derivatives of [2.10]cyclopentadiene **1c** were prepared by reaction of the anion, prepared in situ, with the appropriate metal pentacarbonyl bromide.[36,37] Again, the inaccessibility of the [0.*n*] cyclopentadienyl anions precluded the preparation of the series lacking the ethylene spacer. Both compounds **4a** and **4b** are air-stable solids and are

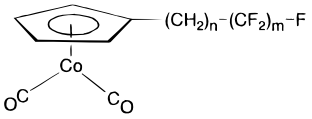


4a. M = Mn
4b. M = Re

relatively soluble in diethyl ether but less so in hexanes. A partition experiment in which the relative concentrations of **4a** in PFMCH and toluene phases was observed by IR spectroscopy gave a C_{PFMCH}/C_{tol} value of 1.8. The difference between this value and that of 20 obtained for the partitioning of [2.10]ferrocene **3c** between perfluoroheptane and toluene illustrates the substantial effect of the second ponytail in enticing the ferrocene into the fluorous phase.

The IR carbonyl stretches of these Mn and Re compounds show them to be similar to their C_5H_4Me homologues (Table 2). In the manganese compounds, the two carbonyl stretches of the parent compound [$MnCp(CO)_3$] are lowered by 8 and 5 cm^{-1} on introduction of one [2.10] ponytail to form **4a**, an effect almost identical to that of introduction of a methyl group. In the rhenium tricarbonyl family, introduction of a methyl group or one [2.10] ponytail results in only a very slight shift to low energy of the carbonyl stretching frequencies in cyclohexane or in CS_2. In view of their enhanced fluorous solubility, the infrared spectra of compounds **4a** and **4b** were also obtained in perfluoroheptane. In the fluorous solvent, the carbonyl stretching frequencies move to higher energy from the values observed in cyclohexane (Mn: +6, +8 cm^{-1}. Re: +6, +11 cm^{-1}), but no changes in the peak width or shape were observed.

Ponytail Cobalt Carbonyl Complexes. While ferrocenes are indeed available from cyclopentadienes having an inaccessible anion, the 4% overall yield with which Gassman prepared [$(C_5Me_4CF_3)CpFe$] (Cp = η^5-C_5H_5) via the [$(C_5Me_5CF_3)(CO)_2Fe]_2$ dimer[14] led us to choose an alternative system for comparing cyclopentadienes **1** and **2**. The differential effects of ponytails with an without hydrocarbon spacer groups were investigated through the corresponding cobalt carbonyl complexes, which may be prepared from the cyclopentadienes without passing through the anions. The methodology involves direct reaction of the cyclopentadiene with [$Co_2(CO)_8$], using 1,3-cyclohexadiene as a hydrogen acceptor.[38] Even so, while the [2.10] cobalt complex **5a** was prepared in 70% yield using this meth-



5a. n = 2; m = 10
5b. n = 0; m = 10
5c. n = 0; m = 12

odology, the analogous [0.10] and [0.12] complexes, **5b** and **5c**, lacking C_2H_4 spacer groups, were formed in under 30% yield. Similar low yields were obtained by Gassman in the preparation of the $C_5Me_5CF_3$ complex.[14]

In contrast to the [2.10] compound **5a**, a moderately air-sensitive red solid, the [0.10] and [0.12] complexes, an orange oil **5b** and solid **5c**, respectively, are somewhat more sensitive. All three show broad ^{19}F NMR resonances, as noted in ferrocenes **3b** and **3c**, although the fluorines α to the cyclopentadiene ring in **5b** and **5c** are split into clean triplets by the β-fluorines. Bearing only one ponytail, [2.10] cobalt complex **5a** shows a significantly greater solubility in $CDCl_3$ than does 1,1′-bis[2.10]ferrocene **3c**, allowing its NMR spectrum to be obtained at room temperature. When the tail is completely fluorinated, however, the solubility decreases such that the NMR spectra of [0.12] compound **5c** necessitated elevated temperatures.

The carbonyl stretching frequencies of these compounds, listed in Table 2, show that [2.10] complex **5a** is electronically similar to [$Co(C_5H_4Me)(CO)_2$].[39,40] With carbonyl stretches 5 and 8 cm^{-1} less energetic in CH_2Cl_2 than those of the unsubstituted complex [$CoCp(CO)_2$], the [2.10] tail is a slightly electron-donating substituent in these compounds, just as it is in the Mn and Re analogues **4**. On the other hand, **5b** and **5c**, lacking the hydrocarbon spacer groups, have carbonyl stretches shifted 11 cm^{-1} to higher energy than those

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Table 2. Infrared Data[a] for Cyclopentadienyl Metal Carbonyl Compounds

	hexane	c′hex	CH_2Cl_2	other	ref.
Cp*Co(CO)$_2$		2011, 1949			46
Cp′Co(CO)$_2$	2020, 1970			2021, 1956 ($CHCl_3$)	39, 40
($C_5Me_5CF_3$)Co(CO)$_2$	2026, 1969				14
[2.10]-CpCo(CO)$_2$ (**5a**)		2029, 1970	2023, 1959		*b*
CpCo(CO)$_2$			2028, 1967		47
[0.10]-CpCo(CO)$_2$ (**5b**)		2044, 1987	2039, 1978		*b*
[0.12]-CpCo(CO)$_2$ (**5c**)	2045, 1988	2044, 1987	2039, 1978		*b*
Cp*Mn(CO)$_3$	2017, 1928	2000, 1915			48, 49
[2,10]-CpMn(CO)$_3$ (**4a**)		2027, 1948		2033, 1956 (C_7F_{16})	*b*
Cp′Mn(CO)$_3$		2030, 1946		2016, 1923 (KBr)	37
CpMn(CO)$_3$		2035, 1953		2018, 1919 (KBr)	37
[0.1]-CpMn(CO)$_3$				2030, 2010 sh, 1942 (neat, KBr)	13
Cp*Re(CO)$_3$	2015, 1925	2017, 1925			46, 49
Cp′Re(CO)$_3$	2030, 1935	2028, 1937			50, 51
[2.10]-CpRe(CO)$_3$ (**4b**)		2030, 1941		2036, 1952 (C_7F_{16}), 2025, 1933 (CS_2)	*b*
CpRe(CO)$_3$		2034, 1941, 2030, 1939		2026, 1931 (CS_2)	46, 52, 53

[a] ν_{CO} in cm^{-1}. Cp, C_5H_5. Cp*, C_5Me_5. Cp′, C_5H_4Me. [*n.m*]-Cp, $C_5H_4[(CH_2)_n(CF_2)_mF]$. c′hex, cyclohexane. [b] This work.

of the unsubstituted compound, again demonstrating the insulating role of the ethylene spacer between the ring and the perfluoroalkyl tail. In Gassman's analogous complex, [($C_5Me_4CF_3$)Co(CO)$_2$], this electron-withdrawing effect is mitigated by the four methyl groups on the cyclopentadienyl ring, resulting in ν_{CO} values approaching those of **5a**.

Conclusions

In summary, a series of cyclopentadienes bearing fluorinated ponytails have been prepared both with and without an ethylene spacer between the cyclopentadiene ring and the perfluoroalkyl chain. Electrochemical studies of ferrocenes and IR data for several cyclopentadienylmetal carbonyl complexes illustrate that the hydrocarbon spacer group is necessary to effectively insulate the cyclopentadienyl ring from the electron-withdrawing effects of the perfluoroalkyl chain. These ponytails enhance the fluorocarbon solubility of some simple organometallic complexes. The solubilities of these compounds in both fluorocarbons and "normal" solvents are strongly temperature-dependent and often show an approximate threshold temperature above which the solubility increases markedly. The solubilities and partitioning of these complexes also change dramatically with the length of the perfluoroalkyl tail, a strong selectivity for fluorous solvents not appearing until the compound bears two $C_{10}F_{21}$ tails. It would seem that in order to achieve *selective* fluorous solubility for organometallic compounds bearing only one cyclopentadienyl ligand, more than one ponytail will be required. Attempts to synthesize such ligands are underway, as are more quantitative studies of the solubility properties of these compounds in fluorocarbons and in supercritical CO_2.

Experimental Procedures

General Procedures. All reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen which had been deoxygenated over BASF catalyst and dried over molecular sieves. Ethers and hydrocarbon solvents other than hexanes were distilled under nitrogen from Na, K, or Na/K alloy, hexanes, and chlorinated solvents, from CaH_2, and acetone, from activated molecular sieves. ^{1}H (300 MHz), ^{19}F (282 MHz), and ^{13}C{^{1}H} (74.5 MHz) NMR spectra were recorded on a Varian Unity-300 Spectrometer at 25 °C unless otherwise noted. Chemical shifts are reported as ppm downfield of either TMS (^{1}H and ^{13}C NMR, referenced to the solvent) or external $CFCl_3$ (^{19}F NMR). Coupling constants are reported in hertz. IR spectra were recorded on a Perkin-Elmer 1600 Fourier transform infrared spectrophotometer. Melting points were obtained using an electrically heated Thiel tube and are uncorrected. Elemental analyses were performed by Schwarzkopf (Woodside, NY).

Adogen 464, *n*-BuLi (titrated before use), and 1,3-cyclohexadiene were obtained from Aldrich, $AgBF_4$ from ATOChem, PPh_3 from Lancaster, $Co_2(CO)_8$ from Johnson Matthey, and perfluoroheptane from 3M (product PF-5070). Perfluoro(methylcyclohexane), [0.*m*] and [2.*m*] alkyl iodides were obtained from PCR. Nickelocene was prepared as described by Brauer.[41] $Mn(CO)_5Br$[42] [and, analogously $Re(CO)_5Br$], anhydrous $NiBr_2$,[41] and CpNa[43] were prepared as described in the literature. [$FeCl_2$·2THF],[44a] and [$NiBr_2(py)_4$][44b] were prepared by Soxhlet extraction of the anhydrous metal salts.

[2.6] Cyclopentadiene Isomers 1a. (a) Through Cp$_2$Ni.[30] Nickelocene (2.29 g, 12.1 mmol), triphenylphosphine (3.17 g, 12.1 mmol), and 1-iodo-1H,1H,2H,2H-perfluorooctane (3.0 mL, 12.1 mmol) were dissolved under nitrogen in diethyl ether (50 mL). After stirring 2 days at room temperature, the purple mixture was concentrated and then hexanes were added. The mixture was further concentrated and the [CpNiI(PPh_3)] which precipitated was removed and washed with hexanes. The filtrate and washings were passed through a short column of silica to give ponytail cyclopentadiene **1a** as a pale lavender oil, which was distilled to give a colorless oil: 3.56 g, 71%. bp 38 °C (0.02 mmHg). Anal. Calcd for $C_{13}H_9F_{13}$: C, 37.88; H, 2.02. Found: C, 38.41; H, 2.26. ^{1}H NMR ($CDCl_3$) δ 6.4−6.2 (m, olefinic, 3H), 2.97 (sext, $J_{HH} = 1.7$,

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ring CH_2, 1-isomer), 2.90 (q, J_{HH} = 1.5, ring CH_2, 2-isomer), 2.68 (m, 2H, H_α), 2.31 (m, 2H, H_β). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 176.71 (C_ω); 149.94, 144.22 (C_{ipso}); 134.85, 134.00, 132.49 (J_{CH} = 170), 131.62 (J_{CH} = 176), 127.74 (J_{CH} = 170), 127.12 (J_{CH} = 168); Cp olefinic carbons; 107−123 (m, CF_2), 43.42, 41.63 (J_{CH} = 155, Cp CH_2); 31.15, 30.62 (t, J_{CF} = 22, J_{CH} = 129, C_β); 21.16 (J_{CH} = 129), 20.73 (J_{CH} = 126, C_α). ^{19}F NMR ($CDCl_3$) δ −81.42 (tt, J_{FF} = 2.7, 10.0, 3F, F_ω); −115.26 (br pent, J = 16.5, 2F, F_γ); −122.44 (br pent, J = 12.3, 2F, F_δ); −123.41 (m, 2F, F_η); −124.08 (br t, J = 14, 2F, F_ξ); −126.72 (m, 2F, F_ϵ). IR (neat, cm^{-1}) 1364 m, 1318 m, 1239 s, 1205 s,br; 1145 s, 1121 m.

(b) By Direct Addition. Cyclopentadienyl sodium (1.20 g, 13.6 mmol, 2.6 equiv) was dissolved in THF (50 mL). 1-Iodo-1H,1H,2H,2H-perfluorooctane (1.25 mL, 5.10 mmol) was added, and the mixture was refluxed overnight. On cooling, a white precipitate appeared. The reaction was quenched with aqueous ammonium chloride (20%, 20 mL) and extracted with diethyl ether (3 × 40 mL). The combined extracts were washed with water (4 × 30 mL) and dried over brine and $MgSO_4$. The resulting amber solution was passed through a column of silica (2 × 30 cm) with petroleum ether (200 mL). Trap-to-trap distillation gave 686 mg (33%) of the alkylated cyclopentadiene isomers **1a** as a colorless oil.

(c) By Phase Transfer.[34] Adogen 464 ($C_{10-12}Me_3NCl$, 1 drop) and potassium hydroxide (2.7 g) in water (2.5 mL) were added to a solution of 1-iodo-1H,1H,2H,2H-perfluorooctane (1.0 mL, 4.1 mmol, 2.7 equiv) and cyclopentadiene (0.12 mL, 1.5 mmol) in benzene (2.5 mL). The mixture was heated under nitrogen at 60 °C for 1 h with vigorous stirring, and at reflux for an additional hour. The cooled mixture was diluted with diethyl ether (10 mL) and filtered through Celite. The aqueous layer was extracted with diethyl ether (10 mL), and the organic layers were washed with water (2 × 5 mL) and then with brine and finally dried over $MgSO_4$. The extracts were filtered through a short column of silica, evaporated, and trap-to-trap distilled to given monoalkylated cyclopentadiene isomers **1a** (570 mg, 92%) containing small amounts of dialkylated products.

[2.8] Cyclopentadiene Isomers 1b. (a) Through Cp_2Ni.[30] Nickelocene (2.29 g, 12.1 mmol), triphenylphosphine (3.17 g, 12.1 mmol), and 1-iodo-1H,1H,2H,2H-perfluorodecane (6.95 g, 12.1 mmol) were dissolved under nitrogen in diethyl ether (50 mL). After stirring 2 days at room temperature, the purple mixture was concentrated and hexanes were added. The mixture was further concentrated, and the [CpNiI(PPh_3)] that precipitated was removed and washed with hexanes. The filtrate and washings were passed through a short column of silica to give the ponytail cyclopentadiene **1b** as a pale lavender oil: 5.44 g, 88%. bp 80 °C (0.02 mmHg). Anal. Calcd for $C_{15}H_9F_{17}$: C, 35.17; H, 1.77. Found: C, 35.00; H, 1.81. ^1H NMR ($CDCl_3$) δ 6.05−6.50 (m, 3H, Cp), 2.96 (sext, J_{HH} = 1.5, 1-isomer), 2.90 (q, J_{HH} = 1.5, 2-isomer); 2H, ring CH_2; 2.70 (m, 2H, H_α), 2.30 (m, 2H, H_β). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (a) 2-isomer, δ 146.05 (C_{ipso}); 134.87 (J_{CH} = 177), 131.64 (J_{CH} = 174), 127.80 (J_{CH} = 156): Cp; 102−107 (br m, CF_2), 43.44 (J_{CH} = 130, Cp CH_2), 31.25 (t, J_{CF} = 22, J_{CH} = 130, C_β), 21.51 (t, J_{CF} = 5, J_{CH} = 129, C_α). (b) 1-isomer, δ 144.39 (C_{ipso}); 134.06 (J_{CH} = 171), 132.55 (J_{CH} = 169), 127.11 (J_{CH} = 171): Cp; 102−107 (br m, CF_2), 41.65 (J_{CH} = 126, Cp CH_2), 30.73 (t, J_{CF} = 20, J_{CH} = 130, C_β), 20.80 (t, J_{CF} = 4, J_{CH} = 128, C_α). ^{19}F NMR ($CDCl_3$) δ −81.81 (t, 3F, J_{FF} = 10.2, F_ω), −115.61 (pent, J_{FF} = 15.8, 2F, F_γ), −122.47, −122.70 (br, 6F, $F_{\delta,\theta,\tau,}$); −123.52 (br, 2F, F_η), −124.25 (br, 2F, F_ξ), −127.00 (br, 2F, F_ϵ). IR (neat, cm^{-1}): 1617 w, 1154 s, 1380 s, 765 w, 732 m.

(b) Through Direct Addition. Cyclopentadienylsodium (1.95 g, 22.1 mmol, 1.9 equiv) and 1H,1H,2H,2H-iodoperfluorodecane (6.52 g, 11.4 mmol) were brought to reflux in THF (50 mL). The initially colorless mixture became a cloudy dark blue overnight. The mixture was then cooled, quenched with aqueous NH_4Cl (20 mL, 20%), and diluted with hexanes (50 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 × 50 mL). The combined organic layers were washed with water (4 × 50 mL) and then with brine and finally dired over $MgSO_4$. The resulting oil was passed through a column of silica (5 × 30 cm) with petroleum ether (750 mL) to give the alkylated cyclopentadiene isomers **1b** (1.63 g, 28%) on evaporation. An analytical sample was prepared by distillation.

[2.10] Cyclopentadiene Isomers 1c. (a) Through Cp_2Ni.[30] Nickelocene (1.89 g, 10 mmol) and triphenylphosphine (2.64 g, 10 mmol) were dissolved under nitrogen in diethyl ether (60 mL). 1-Iodo-1H,1H,2H,2H-perfluorododecane (6.74 g, 10 mmol) dissolved in diethyl ether (30 mL) was added dropwise over 30 min, causing the deep green solution to become an intense burgundy. After stirring 2 days at room temperature, the mixture was evaporated and extracted from the [CpNiI(PPh_3)] side product with hexanes (50 mL). The extracts were passed through a short column of silica to give the ponytail cyclopentadiene **1c** as a white solid with a very pale green cast (5.62 g, 92%), which could be further purified by recrystallization from hexanes: mp 45−47 °C, bp 50 °C (0.02 mmHg). Anal. Calcd for $C_{17}H_9F_{21}$: C, 33.35; H, 1.48. Found: C, 32.41; H, 1.55. ^1H NMR ($CDCl_3$, 40 °C) δ 6.05−6.50 (m, 3H, H_{ring}), 2.96 (sext, J_{HH} = 1.5, ring CH_2, 1-isomer), 2.90 (q, J_{HH} = 1.4, ring CH_2, 2-isomer), 2.68 (m, 2H, H_α), 2.31 (m, 2H, H_β). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 40 °C) δ 146.0, 144.4 (C_{ipso}); 134.8 (J_{CH} = 170), 134.0 (J_{CH} = 172), 132.5 (J_{CH} = 167), 131.6 (J_{CH} = 180), 127.9 (J_{CH} = 170), 127.2 (J_{CH} = 166), Cp; 118.6, 115.6, 111.6, 107.6 (br, CF_2); 43.4 (J_{CH} = 128), 41.7 (J_{CH} = 125), Cp CH_2; 31.5 (t, J_{CF} = 20, J_{CH} = 133), 30.9 (t, J_{CF} = 22, J_{CH} = 133), C_β; 21.6 (J_{CH} = 124), 20.9 (J_{CH} = 131), C_α. The remaining CF_2 resonances could not be unambiguously located. ^{19}F NMR ($CDCl_3$, 40 °C) δ −81.18 (tt, 3F, J_{FF} = 6.3, 9.6, F_ω), −114.89 (br, 2F, F_γ), −122.01 (br, 10F, $F_{\delta,\theta,\tau,\kappa,\lambda}$), −123.00 (br, 2F, F_η), −123.80 (br, 2F, F_ξ), −126.34 (br, 2F, F_ϵ). IR (neat, cm^{-1}): 1616 w, 1453 m, 1240 s, 1210 s, 1151 s, 1109 m.

(b) By Direct Addition. Cyclopentadienylsodium (1.37 g, 15.5 mmol, 2.1 equiv) and 1-iodo-1H,1H,2H,2H-perfluorododecane (5.04 g, 7.47 mmol) were dissolved in THF (30 mL) and brought to reflux. After heating for 2 h, the resulting dark blue suspension was quenched with aqueous ammonium chloride (15 mL, 20%). Diethyl ether (50 mL) was added, and the layers were separated. The aqueous layer of the filtrate was extracted with diethyl ether (3 × 25 mL) and hexanes (2 × 25 mL). The combined organic layers were passed through Celite, washed with water (6 × 25 mL) and then with brine, and finally dried over $MgSO_4$. Silica (10 mL) was added to the solution, and the suspension evaporated to give a yellow powder. The product **1c** was eluted from the solid and through a column of silica (5 × 30 cm) with hexanes (1 L): 2.5 g, 55%. An analytical sample was purified by distillation [50 °C (0.02 mmHg)].

[0.8] Cyclopentadiene Isomers (2a). Perfluorooctyl iodide (1.35 mL, 2.71 g, 5 mmol) was added dropwise to a solution of nickelocene (0.936 g, 5 mmol) and triphenylphosphine (1.30 g, 5 mmol) in diethyl ether (30 mL) under nitrogen. The resulting deep purple solution was stirred 24 h at room temperature, evaporated, and extracted from the [CpNiI(PPh_3)] side product with hexanes. The extracts were passed through a short column of silica with hexanes. The yellow eluate was evaporated, and the residue trap-to-trap distilled [~40 °C (0.02 mmHg)] to give ponytail cyclopentadiene **2a** as a pale yellow oil: 1.68 g, 70%. ^1H NMR ($CDCl_3$, 50 °C) δ 6.4−7.1 (m, 3H, Cp), 3.22*, 3.16 (br, 2H, Cp) (*, major isomer). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 138.23,* 137.75 (t, J_{CF} = 7, C_{ipso}), 138.09,* 137.75, 135.53,* 135.18, 131.58,* 129.22 (Cp); 106−121 (m, CF_2), 42.40 (CH_2, 2-isomer), 41.03* (t, J_{CF} = 2.4, CH_2, 1-isomer). ^{19}F NMR ($CDCl_3$) δ −81.61 (tt, J_{FF} = 9.9, 2.2, 3F, F_ω), −106.76,* −110.75 (t, J_{FF} = 13.8, 2F, F_α); −122.15 (br, 2F), −122.65 (br, 6F), −123.40 (br, 2F), −126.86 (br, 2F). IR (neat, cm^{-1}): 1365 m, 1318 m, 1240 s, 1210 s, 1152 s, 1116 m, 1080 m.

[0.10] Cyclopentadiene Isomers 2b. Nickelocene (1.13 g, 6 mmol), triphenylphosphine (1.58 g, 6 mmol), and perfluo-

rodecyl iodide (3.91 g, 6 mmol) were dissolved in diethyl ether (40 mL) under nitrogen. The resulting deep purple solution was stirred 2 days at room temperature, then evaporated, and extracted from the [CpNiI(PPh_3)] side product with hexanes. The extracts were passed through a short column of silica with hexanes to give the ponytail cyclopentadiene as a pale yellow oily solid: 3.27 g, 94%. ^{1}H NMR ($CDCl_3$) δ 6.5−7.1 (m, 3H, Cp), 3.22*, 3.16 (br, 2H, Cp) (*, major isomer). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 138.13,* 137.65 (t, J_{CF} = 8, C_{ipso}); 138.00,* 135.42,* 135.20, 131.49,* 129.14: Cp; 106−120 (m, CF_2), 42.32 (CH_2, 2-isomer), 40.94* (t, J_{CF} = 2, CH_2, 1-isomer. ^{19}F NMR ($CDCl_3$) δ −81.61 (t, J_{FF} = 10, 3F, F_ω), −106.80,* −110.80 (t, J_{FF} = 13.4, 2F, F_α); −122.20 (br, 2F), −122.51 (br, 6F), −122.67 (br, 4F), −123.44 (br, 2F), −126.91 (br, 2F). IR (neat, cm^{-1}): 1678 w, 1609 w, 1524 m, 1366 s, 1319 s, 1182 br vs, 1082 s, 901 s. This compound was also characterized as its cobalt carbonyl complex.

[0.12] Cyclopentadiene Isomers 2c. Nickelocene (1.14 g, 6 mmol), triphenylphosphine (1.58 g, 6 mmol), and perfluorododecyl iodide (4.47 g, 6 mmol) were dissolved in diethyl ether (40 mL) under nitrogen. The resulting deep purple solution was stirred 24 h at room temperature, evaporated, and extracted from the [CpNiI(PPh_3)] side product with hexanes. The extracts were passed through a short column of silica with hexanes to give ponytail cyclopentadiene **2c** as a pale yellow solid: 3.73 g, 91%. mp 63−65 °C. ^{1}H NMR ($CDCl_3$, 50 °C): δ 6.5−7.2 (m, 3H, Cp), 3.22*, 3.16 (br, 2H, Cp) (*, major isomer). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 °C) δ 138.26* (t, J_{CF} = 7, C_{ipso}), 138.08,* 137.87, 135.54,* 133.95, 131.63,* 129.32: Cp; 106−120 (m, CF_2), 42.49, 41.12* (CH_2). ^{19}F NMR ($CDCl_3$, 50 °C) δ −81.26 (t, J_{FF} = 10.2, 3F, F_ω), −106.27,* −110.26 (t, J_{FF} = 12.1, 2F, F_α); −121.95 (br, 16F), −122.93 (br, 2F), −126.39 (br, 2F). IR (neat, cm^{-1}): 1355 w, 1322 w, 1245 s sh, 1214 s, 1154 s. The diene was analyzed as its cobalt carbonyl complex.

1,1′-Bis[2.6]ferrocene (3a). [2.6] cyclopentadiene **1a** (205 mg, 0.497 mmol, 1.3 equiv) and $FeCl_2$·2THF (100 mg, 0.370 mmol) were suspended in diethyl ether (15 mL). The mixture was cooled to −78 °C and then *n*-BuLi (200 μL, 2.5 M in hexanes, 0.50 mmol, 1.3 equiv) was added. The mixture was allowed to warm to room temperature while stirring overnight, after which time a greenish yellow suspension was obtained. The reaction mixture was passed through Celite. Neutral alumina (1 g) was added to the liquor, and the mixture was evaporated to give a yellow powder. Elution of the compound from the powder and through a 1 × 10 cm column of alumina with hexanes gave 189 mg (87%) of ferrocene **3a** as an orange solid on evaporation. An analytical sample was recrystallized from methanol/diethyl ether to give yellow flakes: mp 47−48 °C. Anal. Calcd for $C_{26}H_{16}F_{26}Fe$: C, 35.56; H, 1.84. Found: C, 35.38; H, 1.81. ^{1}H NMR (C_6D_6) δ 3.80 (t, 4H, J_{HH} = 1.8, Cp), 3.66 (t, 4H, J_{HH} = 1.8, Cp), 2.40 (m, 4H, H_α), 2.08 (m, 4H, H_β). ^{13}C NMR ($CDCl_3$) δ 107−123 (CF_2), 86.67 (quint, J_{CH} = 6, C_{ipso}), 68.74, 68.72 (d, J_{CH} = 175, Cp); 32.89 (t, J_{CF} = 22, C_β), 20.40 (tt, J_{CH} = 127, J_{CF} = 4, C_α). ^{19}F NMR ($CDCl_3$) δ −79.15 (tt, 3F, J_{FF} = 10.1, 2.6, F_ω), −114.91 (m, 2F, F_γ), −122.36 (br t, 2F, J_{FF} = 10.4, F_δ), −123.34 (m, 2F, F_η), −123.78 (br t, 2F, J_{FF} = 12.2, F_ξ), −126.61 (m, 2F, F_ϵ). IR (neat, cm^{-1}) 1239 s br, 1201 s br, 1144 s, 1120 m, 845 w, 828 m, 807 m.

1,1′-Bis[2.8]ferrocene (3b). A −78 °C suspension of [2.8] cyclopentadiene **1b** (961 mg, 1.85 mmol, 2.0 equiv) and $FeCl_2$·2THF (270 mg, 0.996 mmol, 1.1 equiv) in diethyl ether (40 mL) was treated with *n*-BuLi (3.24 mmol, 2.40 M in hexanes, 2.2 equiv). The mixture was slowly warmed to room temperature and then stirred overnight. The resulting dark mixture was evaporated, and the residue was extracted with hexanes in a small Soxhlet extractor to give **3b** as orange flakes: 736 mg, 74%. mp 86−87 °C. Anal. Calcd for $C_{30}H_{16}F_{34}Fe$: C, 33.42; H, 1.49. Found: C, 33.07; H, 1.41. ^{1}H NMR ($CDCl_3$, 50 °C) δ 4.05 (d, 4H, J_{HH} = 1.7, Cp), 4.03 (s, 4H, Cp), 2.61 (m, 4H, H_α), 2.29 (m, 4H, H_β). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 °C) δ 114.60 (br t, J_{CF} = 273, CF_2), 86.48 (C_{ipso}), 68.78, 68.73 (J_{CH} = 176.1, Cp): 33.07 (t, J_{CF} = 22.0, J_{CH} = 130.1, C_β), 20.51 (t, J_{CF} = 4.5, J_{CH} = 127.2, C_α). ^{19}F NMR ($CDCl_3$, 50 °C) δ −81.31 (tt, 6F, J_{FF} = 11.1, 4.4, F_ω), −114.58 (br, 4F, F_γ), −121.97, −121.98 (br, 12F, $F_{\delta,\theta,\tau}$); −123.02 (br, 4F, F_η), −123.78 (br, 4F, F_ξ) −126.42 (br, 4F, F_ϵ). IR (KBr, cm^{-1}) 1370 m, 1332 m, 1246 vs, 1220 vs, 1200 vs, 1147 vs. 1116 m, 1201 m, 658 s.

1,1′-Bis[2.10]ferrocene (3c). A −78 °C suspension of **1c** (2.00 g, 3.26 mmol, 2.2 equiv) in diethyl ether (35 mL) was treated with *n*-BuLi (1.35 mL, 2.40 M in hexanes, 3.24 mmol, 2.2 equiv). The mixture was warmed to −10 °C and combined with a suspension of $FeCl_2$·2THF (399 mg, 1.47 mmol) in THF (15 mL). After stirring overnight at room temperature, the dark mixture was evaporated. The residue was extracted with hexanes in a small Soxhlet extractor to give ferrocene **3c** as a maize yellow solid (1.87 g, 84%). An analytical sample was recrystallized from $CHCl_3$: mp 101−102 °C. Anal. Calcd for $C_{34}H_{16}F_{42}Fe$: C, 31.95; H, 1.26. Found: C, 31.57; H, 1.34. ^{1}H NMR ($CDCl_3$, 50 °C) δ 4.06 (t, 4H, J_{HH} = 2.0, Cp), 4.02 (t, 4H, J_{HH} = 2.0, Cp), 2.62 (m, 4H, H_α), 2.29 (m, 4H, H_β). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50°): δ 104−120 (m, CF_2), 86.82 (C_{ipso}), 68.76, 68.68 (Cp); 33.04 (t, J_{CF} = 22.5, C_β), 20.47 (t, J_{CF} = 4.6, C_α). ^{19}F NMR ($CDCl_3$, 50 °C) δ −81.12 (tt, 6F, J_{FF} = 10.1, 2.2, F_ω), −114.49 (br, 4F, F_γ), −121.94 (br, 20F, $F_{\delta,\theta,\tau,\kappa,\lambda}$), −122.95 (br, 4F, F_η), −123.73 (br, 4F, F_ξ), −126.35 (br, 4F, F_ϵ). IR (Nujol, cm^{-1}) 1344 w, 1260 m, 1214 m, 1150 m, 1105 m, 1078 w, 1021 w, 810 w, 803 w, 661 w.

[([2.10]-Cp)Mn(CO)$_3$] (4a). *n*-Butyllithium (1.01 mmol, hexanes solution, 1.0 equiv) was added to a −78 °C suspension of [2.10] cyclopentadiene **1c** (0.614 g, 1.0 mmol, 1.0 equiv) in THF (10 mL) under nitrogen. The mixture was stirred for 10 min, warmed to −10 °C, and then cooled again. A THF (3 mL) solution of $Mn(CO)_5Br$ (0.274 g, 1.0 mmol, 1.0 equiv) was added dropwise to give an intense red-orange solution, which was stirred for 1 h at room temperature and then evaporated. The solid was thoroughly extracted with hexanes. The extracts were evaporated, and volatile impurities were removed by sublimation under vacuum at 70 °C. The residue was extracted with warm hexanes, filtered through Celite, and evaporated to give a butter-yellow solid (314 mg, 42%). An analytical sample was purified by recrystallization from hexanes: mp 57−69 °C. Anal. Calcd for $C_{20}H_8O_3F_{21}Mn$: C, 32.02; H, 1.07. Found: C, 31.66; H, 1.09. ^{1}H NMR ($CDCl_3$) δ 4.66 (br, 4H, Cp), 2.54 (m, 2H, H_α), 2.28 (br m, 2H, H_β). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 224.82 (CO), 107−118 (m, CF_2), 103.50 (C_{ipso}), 81.41, 82.28 (J_{CH} = 179.5, Cp), 32.41 (t, J_{CF} = 22.3, J_{CH} = 128.7, C_β), 19.50 (t, J_{CF} = 4.7, J_{CH} = 130.5, C_α). ^{19}F NMR ($CDCl_3$) δ −81.10 (t, J_{FF} = 9.6, 3F, F_ω), −114.66 (br, 2F, F_γ), −122.09 (br, 10F, $F_{\delta,\tau,\theta,\kappa,\lambda}$), −123.03 (br, 2F, F_η), −123.75 (br, 2F, F_ξ), −126.47 (br, 2F, F_ϵ). IR (cyclohexane, cm^{-1}) 2027 vs, 1948 vs, 1242 s, 1222 s, 1157 m, 668 m, 636 w.

[([2.10]-Cp)Re(CO)$_3$] (4b). *n*-Butyllithium (1.32 mmol, hexanes solution, 1.0 equiv) was added to a −78 °C suspension of [2.10] cyclopentadiene **1c** (0.812, 1.0 mmol, 1.0 equiv) in THF (30 mL). The mixture was stirred for 10 min, warmed to −10 °C, and cooled again. The cold suspension was transferred onto solid [$Re(CO)_5Br$] to give a dark mixture which was stirred 1 h at room temperature, brought to reflux for 3 h, and then evaporated. Soxhlet extraction of the residue under nitrogen with hexanes (25 mL) gave **4b** as a pale orange solid (669 mg, 57%). An analytical sample was prepared by precipitation from hot hexanes: mp 76−78 °C. Anal. Calcd for $C_{20}H_8O_3F_{21}Re$: C, 27.25; H, 0.91. Found: C, 27.40, H, 1.03. ^{1}H NMR ($CDCl_3$) δ 5.28 (m, 4H, Cp), 2.75 (m, 2H, H_α), 2.28 (m, 2H, H_β). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 193.96 (CO), 111.5 (br t, J_{HF} = 275, CF_2), 107.62 (C_{ipso}), 84.22 (J_{CH} = 180.6 [d], 5.8 [q], Cp), 83.43 (J_{CH} = 181.7, Cp), 33.34 (t, J_{CF} = 22.3, J_{CH} = 131.0, C_β), 19.57 (t, J_{CF} = 5.25, J_{CH} = 131.0). ^{19}F NMR ($CDCl_3$) δ −81.15 (tt, J_{FF} = 10.0, 0.9, 3F, F_ω), −114.56 (br, 2F, F_γ), −122.13 (br, 10F, $F_{\delta,\tau,\theta,\kappa,\lambda}$), −123.90 (br, 2F, F_η), −123.76 (br, 2F, F_ξ), −126.51 (br, 2F, F_ϵ). IR (cyclohexane, cm^{-1}): 2030 s, 1941 vs, 1240 m, 1220 m, 1156 w, 737 m.

[([2.10]-Cp)Co(CO)$_2$] (5a). Dicobaltoctacarbonyl (488 mg, 2.85 mmol of Co), **1c** (2.00 g, 3.26 mmol, 1.1 equiv), and 1,3-cyclohexadiene (0.13 mL, 1.4 mmol, 0.5 equiv) were refluxed in CH_2Cl_2 (5 mL) for 5 h. The deep orange mixture was concentrated, hexanes were added, and the mixture was evaporated. Soxhlet extraction of the residue with hexanes (25 mL) gave a solid which was further purified by chromatography through alumina with hexanes under nitrogen to give **5a** as orange flakes: 1.45 g, 70%. mp 49−51 °C dec. Anal. Calcd for $C_{19}H_8O_2F_{21}Co$: C, 31.43; H, 1.11. Found: C, 31.06; H, 1.03. ^{1}H NMR (C_6D_6) δ 4.26 (s, 2H, Cp), 4.22 (s, 2H, Cp), 1.97 (m, 4H, $H_{\alpha,\beta}$). $^{13}C\{^1H\}$ NMR (C_6D_6) δ 111.8 (br t, J_{CF} = 274, CF_2), 104.51 (C_{ipso}), 84.87, 83.73 (Cp); 32.73 (t, J_{CF} = 22.3, C_β), 19.40 (t, J_{CF} = 4.2, C_α). The CO resonance could not be located. ^{19}F NMR (C_6D_6) δ −81.56 (t, J_{FF} = 10, 3F, F_ω), −111.68 (br, 2F, F_γ), −112.28 (br, 10F, $F_{\delta,\theta,\tau,\kappa,\lambda}$), −123.33 (br, 2F, F_η), −126.42 (br, 2F, F_ϵ). IR (cyclohexane, cm^{-1}) 2029 vs, 1970 vs, 1240 s, 1220 s, 1156 m; (CH_2Cl_2, cm^{-1}) 2023 vs, 1959 vs, 1219 s, 1154 m, 812 w.

[([0.10]-Cp)Co(CO)$_2$] (5b). Dicobaltoctacarbonyl (245 mg, 1.43 mmol of Co), **2b** (451 mg, 0.77 mmol, 0.55 equiv); and 1,3-cyclohexadiene (0.13 mL, 1.4 mmol) were refluxed in CH_2Cl_2 (5 mL) for 1 h. A second portion of **2b** (450 mg, 0.77 mmol, 0.55 equiv) dissolved in CH_2Cl_2 (2 mL) was added, and reflux was continued for an additional 3 h. The deep orange mixture was concentrated, hexanes (5 mL), Al_2O_3 (4 mL) and Celite (4 mL) were added, and the mixture was evaporated. The resulting dark powder was placed atop a column of Al_2O_3 (1.5 × 30 cm). Elution with hexanes under nitrogen gave a yellow band followed by an orange band; evaporation of the orange band left **5b** as an oily orange solid: 275 mg, 28%. Anal. Calcd for $C_{17}H_4O_2F_{21}Co$: C, 28.25; H, 0.58. Found: C, 31.06; H, 0.51. ^{1}H NMR (C_6D_6) δ 4.50 (br, 2H, Cp), 4.26 (br, 2H, Cp). $^{13}C\{^1H\}$ NMR (C_6D_6) δ 86.56, 83.70 (br, Cp). The remaining resonances could not be located. ^{19}F NMR (C_6D_6) δ −81.45 (t, J_{FF} = 10, 3F, F_ω), −103.33 (t, J_{FF} = 14, 2F, F_α), −121.52 (br, 2F, F_β), −122.10, −122.30 (br, 10 F, $F_{\gamma,\delta,\epsilon,\xi,\eta}$), −123.17 (br, 2F, F_τ), −126.65 (br, 2F, F_θ). IR (cyclohexane, cm^{-1}) 2044 vs, 1987 vs, 1240 s, 1220 s, 1155 m.

[([0.12]-Cp)Co(CO)$_2$] (5c). Dicobaltoctacarbonyl (245 mg, 1.43 mmol of Co), [0.12] cyclopentadiene isomers **2c** (536 mg, 0.78 mmol, 0.55 equiv), and 1,3-cyclohexadiene (0.13 mL, 1.4 mmol) were refluxed in CH_2Cl_2 (5 mL) for 1 h. A second portion of **2c** (526 mg, 0.77 mmol, 0.55 equiv) dissolved in CH_2Cl_2 (2 mL) was added, and reflux was continued for an additional 4 h. The deep orange mixture was concentrated, hexanes (5 mL) and Al_2O_3 (5 mL) were added, and the mixture was evaporated. The resulting dark powder was placed atop a column of Al_2O_3 (1.5 × 30 cm). Elution with hexanes under nitrogen gave a yellow band followed by an orange band. Evaporation of the orange band left **5c** as an orange solid: 316 mg, 28%. mp 72−74 °C, sealed capillary. Anal. Calcd for $C_{19}H_4O_2F_{25}Co$: C, 28.59; H, 0.51. Found: C, 28.46; H, 1.01. ^{1}H NMR (C_6D_6, 60 °C) δ 4.61 (br, 2H, Cp), 4.36 (br, 2H, Cp). $^{13}C\{^1H\}$ NMR (C_6D_6, 60 °C) δ 107−121 (m, CF_2), 86.37, 83.71 (Cp). The remaining resonances could not be located. ^{19}F NMR (C_6D_6, 60 °C) δ −81.43 (t, J_{FF} = 10.3, 3F, F_ω), −102.89 (t, J_{FF} = 14.5, 2F, F_α), −121.19 (br, 2F, F_β), −121.70, −121.95 (br, 14 F, $F_{\gamma,\delta,\epsilon,\zeta,\eta,\theta,\tau}$), −122.88 (br, 2F, F_κ), −126.34 (br, 2F, F_λ). IR (cyclohexane, cm^{-1}) 2044 vs, 1987 vs, 1241 s, 1222 s, 1156 m, 745 m.

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