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"Heavy Fluorous" Cyclopentadienes and Cyclopentadienyl Complexes with Three to Five Ponytails: Facile Syntheses from Polybromocyclopentadienyl Complexes, Phase Properties, and Electronic Effects

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Abstract: The reactions between $[(\eta^5\text{-}C_5H_{5-x}Br_x)M(CO)_3]$ (M = Re, Mn; x = 1, 3, 4, 5) and $[IZn\{(CH_2)_nR_{f8}\}]$ (n = 2, 3; $R_{f8} = (CF_2)_7CF_3$) in the presence of $[Cl_2PdL_2]$ catalysts give the title complexes $[\{\eta^5\text{-}C_5H_{5-x}[(CH_2)_nR_{f8}]_x\}M(CO)_3]$. In the case of $x = 5$, the major product is actually $[\{\eta^5\text{-}C_5H[(CH_2)_nR_{f8}]_4\}M(CO)_3]$, in which one of the bromides has been substituted by hydride. Minor amounts of multiple hydride substitution products are formed, all of them readily separable on fluorous silica gel. Irradiation of the manganese complexes in $CF_3C_6H_5$/MeOH/ether gives uncoordinated cyclopentadienes, which can be deprotonated and reattached to other metals. Partition coefficients have been measured ($CF_3C_6F_{11}$/toluene): complexes with three or more ponytails are highly fluorophilic, with values of $>99.8{:}<0.2$. The IR $\tilde{\nu}_{CO}$ bands have been used to probe the inductive effects of the ponytails at the metal centers.

Keywords: cyclopentadienyl ligands · fluorinated ligands · IR spectroscopy · partition coefficients · transition metals

Introduction

Cyclopentadienyl ligands are ubiquitous in transition-metal-based catalysts.[1] Unlike the phosphine moieties in many systems, cyclopentadienyl ligands normally remain bound for the entire catalytic cycle. Accordingly, many strategies for the recovery and reuse of cyclopentadienyl complexes have been developed:[2,3] they can, for example, be heterogenized by covalent tethers to polystyrene,[2a,3c] silica gel,[2b,d,3a,3b,3c] and various polysiloxane species.[2b–d] Dendrimer adducts have also been described.[2e] Outside of this last group, however, recoverable cyclopentadienyl complexes that can be employed under homogeneous conditions remain rare.

One recently developed method for catalyst recovery involves the introduction of fluorous "ponytails" or "phase labels" of formula $(CH_2)_m(CF_2)_{n-1}CF_3$ (abbreviated $(CH_2)_mR_{fn}$).[4,5] When molecules possess sufficient numbers of CF_2 groups, they exhibit high affinities for perfluoroalkanes and other fluorous phases. Reactions with fluorous catalysts can be conducted under a variety of single- or multiphase conditions.[6] Catalyst/product separation, as traditionally practiced, utilizes a perfluoroalkane/organic solvent mixture, which is commonly biphasic at room temperature. The organic products partition predominantly into the organic phase (>95%) and the catalyst into the fluorous phase. In newer fluorous solvent-free variants, the temperature-dependent solubilities of such catalysts in organic solvents are exploited.[6,7]

Some of the first fluorous metal complexes to be isolated were metallocenes or half-metallocenes.[8,9] As detailed in the Discussion section, however, these featured only one ponytail per cyclopentadienyl ring ($(CH_2)_2R_{fn}$, n = 6, 8, 10) and the fluorophilicities were generally modest. Similar observations with related complexes were subsequently reported.[10–12] More recently, Cermák and Kvícala have described routes to free cyclopentadienes with two ponytails ($(CH_2)_2R_{fn}$, n = 4, 6, 8), as well as iron and rhodium derivatives.[13,14] Certain ferrocenes gave $CF_3C_6F_{11}$/toluene partition coefficients as high as 98.6:1.4.

Surprisingly little attention has been given to the development of fluorous cyclopentadienyl complexes that exhibit very high fluorous-phase affinities (e.g., $>99{:}<1$ $CF_3C_6F_{11}$/toluene). We therefore sought routes to "heavy fluorous" species with three to five ponytails per ring, for which exceptional recycling efficiency and leaching resistance should be expected. Cyclopentadienyl complexes with four C_6F_5

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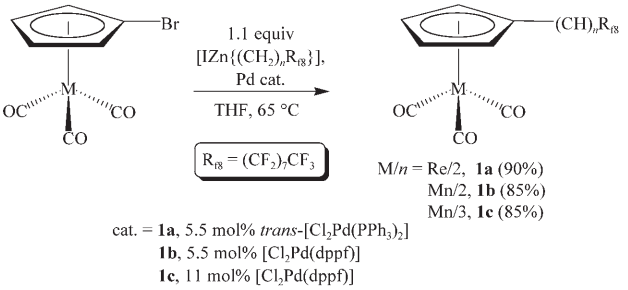
substituents are known,[15] but perfluoroaryl groups do not confer high fluorous-phase affinities.[5] A variety of cyclopentadienyl complexes with CF_3 groups have been prepared,[16] but these are not long enough for high fluorous-phase affinities.

Numerous polyhalocyclopentadienyl metal complexes are readily available.[17,18] In addition, substitutions of di- and tribromopyridines by the fluorous alkylzinc reagent $[IZn\{(CH_2)_2R_{f8}\}]$ are efficiently catalyzed by *trans*-$[Cl_2Pd(PPh_3)_2]$.[19] We therefore wondered whether such methodologies could be extended to polybromocyclopentadienyl ligands. In this paper we report the successful implementation of this strategy, as applied to the rhenium and manganese tricarbonyl complexes $[(\eta^5\text{-}C_5H_{5-x}Br_x)M(CO)_3]$ ($x = 5, 4, 3, 1$). The fluorous cyclopentadienyl ligands can furthermore be detached from the manganese complexes and transferred to other metals. The phase properties of all complexes have been carefully characterized, and the IR bands of the carbonyl ligands have been used to gauge the electronic influence of the ponytails[20] on the metal centers. A portion of this work has been communicated.[21]

Results

Reactions of monobromocyclopentadienyl complexes: As shown in Scheme 1, screening experiments were conducted with the rhenium and manganese monobromocyclopentadienyl complexes $[(\eta^5\text{-}C_5H_4Br)M(CO)_3]$.[22] Treatment with $[IZn\{(CH_2)_2R_{f8}\}]$ (1.1 equiv) at 65 °C in the presence of the catalysts *trans*-$[Cl_2Pd(PPh_3)_2]$ or $[Cl_2Pd(dppf)]$[23] (5.5 mol %) afforded the corresponding fluorous cyclopentadienyl complexes $[\{\eta^5\text{-}C_5H_4[(CH_2)_2R_{f8}]\}M(CO)_3]$ (**1**; M = Re (**a**), Mn (**b**)) in 90–85 % yields after workup. The latter catalyst gives slightly less hydride transfer in the manganese series,[24] a side reaction that becomes evident below. A similar reaction was conducted with $[(\eta^5\text{-}C_5H_4Br)Mn(CO)_3]$ and the alkylzinc reagent $[IZn\{(CH_2)_3R_{f8}\}]$, which has an additional methylene group. The corresponding complex $[\{\eta^5\text{-}C_5H_4[(CH_2)_3R_{f8}]\}Mn(CO)_3]$ (**1c**) was isolated in 85 % yield.



Scheme 1. Model reactions.

Complexes **1a–c**, as well as all homologues described below, were isolated as analytically pure, low-melting, air-stable solids. As summarized in Table 1, DSC measurements showed no phase transitions other than melting. Despite extensive efforts, in no case were crystals suitable for X-ray analysis obtained. Complexes **1a–c** were highly soluble in common organic solvents as well as in $CF_3C_6F_{11}$. The $CF_3C_6F_{11}$/toluene partition coefficients were determined by HPLC (Table 1). As expected, the complexes were not very fluorophilic, and were preferentially soluble in toluene.

Complexes **1a–c** were further characterized by IR and NMR (^1H, ^{13}C) spectroscopy and mass spectrometry, as summarized in the Experimental Section. The two IR $\tilde{\nu}_{CO}$ bands (Table 1) were at frequencies identical to or slightly higher than those of the parent compounds $[(\eta^5\text{-}C_5H_5)M(CO)_3]$. However, the IR trends and electronic effects of the ponytails are better analyzed in the multiply substituted complexes below, which afford greater resolution.

Table 1. IR and phase properties of new fluorous metal complexes.

	IR	M.p. [°C]		Partition	Solubilities									
	$\tilde{\nu}_{CO}$[a] [cm^{-1}]	capillary	DSC (T_e)	coefficient[b]	$CF_3C_6H_5$	$CF_3C_6F_{11}$	hexanes	THF	acetone	MeOH	CH_2Cl_2	$CHCl_3$	ether	CH_3CN
1a	2026/1930	42–45	48.7	26.1:73.9	high	high	high	high	high	high	high	high	high	high
3a	2026/1938	55–56	60.6	>99.8:<0.2	high	high	none	low	med	low	low	v. low	v. low	v. low
3′a	2026/1938	57–59	60.4	>99.8:<0.2	high	high	none	low	med	low	low	v. low	v. low	v. low
4a	2026/1939	56–57	61.3	>99.8:<0.2	high	high	none	low	low	none	v. low	none	none	none
5a	2030/1942	42–43	43.3	>99.8:<0.2	high	high	none	v. low	v. low	none	none	none	none	none
1b	2026/1938	55–58	60.1	44.4:55.6	high	high	high	high	high	high	high	high	high	high
2b	2026/1942	63–67	66.0	93.5:6.5	high	high	low	high	high	med	high	med	low	med
2′b	2026/1942	61–63	61.5	93.8:6.2	high	high	low	high	high	med	high	med	low	med
3b	2026/1943	57–58	63.6	>99.8:<0.2	high	high	none	low	med	low	low	v. low	v. low	v. low
3′b	2026/1943	52–53	53.2	>99.8:<0.2	high	high	none	low	med	low	low	v. low	v. low	v. low
4b	2026/1945	47–51	55.0	>99.8:<0.2	high	high	none[c]	low	low	none	v. low	none	none	none
5b	2026/1949	57–60	56.7	>99.8:<0.2	high	high	none	v. low	v. low	none	none	none	none	none
1c	2023/1938	51–55	57.3	44.1:55.9	high	high	high	high	high	high	high	high	high	high
3c	2020/1938	54–58	58.7	>99.8:<0.2	high	high	none	low	med	low	low	v. low	v. low	v. low
3′c	2020/1938	38–42	41.3	>99.8:<0.2	high	high	none	low	med	low	low	v. low	v. low	v. low
4c	2019/1938	54–55	53.9	>99.8:<0.2	high	high	none	low	low	none	v. low	none	none	none
3′e	2051/1986	–	–	>99.8:<0.2	high	high	none	low	med	low	low	v. low	v. low	v. low

[a] Recorded in $CF_3C_6H_5$. Data under identical conditions for reference compounds $[(\eta^5\text{-}C_5R_5)M(CO)_3]$: M/R = Re/H, 2026/1926; Re/CH_3, 2011/1911; Mn/H 2023/1922. [b] $CF_3C_6F_{11}$/toluene, 23 °C. [c] Soluble in heptane at 100 °C.

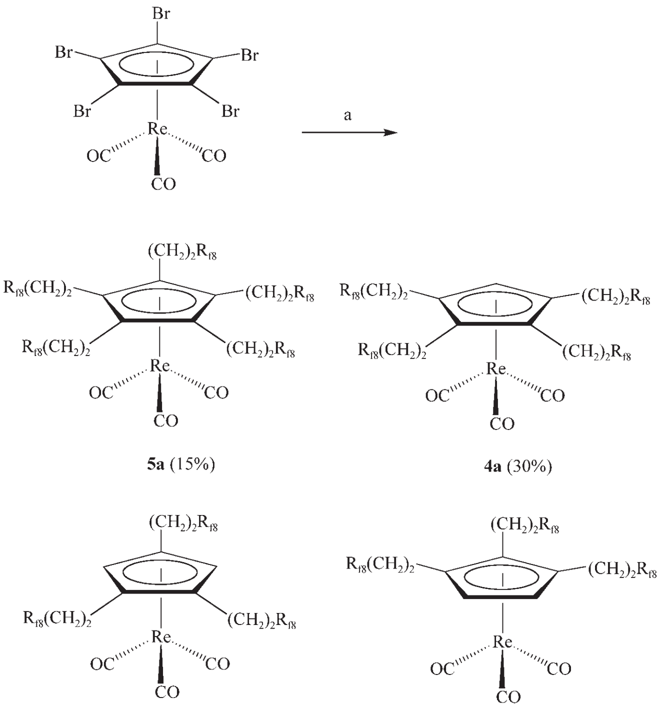
Reactions of polybromocyclopentadienyl rhenium complexes: A more challenging test of the above methodology was sought. A sample (0.500 g) of the rhenium pentabromocyclopentadienyl complex $[(\eta^5\text{-}C_5Br_5)Re(CO)_3]$[18] was thus similarly treated with $[IZn\{(CH_2)_2R_{f8}\}]$ (5.5 equiv) and *trans*-$[Cl_2Pd(PPh_3)_2]$ (11 mol% per carbon–bromine bond). Workup gave the product mixture shown in Scheme 2, which was separated by chromatography on fluorous silica gel.[25] As would be expected, the complexes eluted in inverse order of their fluorous content. The last fraction contained the target molecule with five ponytails, $[\{\eta^5\text{-}C_5[(CH_2)_2R_{f8}]_5\}Re(CO)_3]$ (**5a**), which was isolated in 15% yield (0.263 g) as a waxy white solid.

The penultimate fraction contained the major product, $[\{\eta^5\text{-}C_5H[(CH_2)_2R_{f8}]_4\}Re(CO)_3]$ (**4a**), in which one of the bromine atoms had been replaced by hydrogen and the other four by ponytails (30%, 0.435 g).[24] Two more rapidly eluting fractions contained analogous species with three ponytails (1,2,4-isomer **3′a**, 2%, 0.023 g; 1,2,3-isomer **3a**, 5%, 0.057 g). The substitution pattern makes **3a** slightly more polar than **3′a**. Accordingly, **3a** eluted first, as confirmed by an independent synthesis (below). Complexes with two ponytails were not isolated, but trace amounts were detected in the crude product by mass spectrometry. There was no evidence for any **1a**.

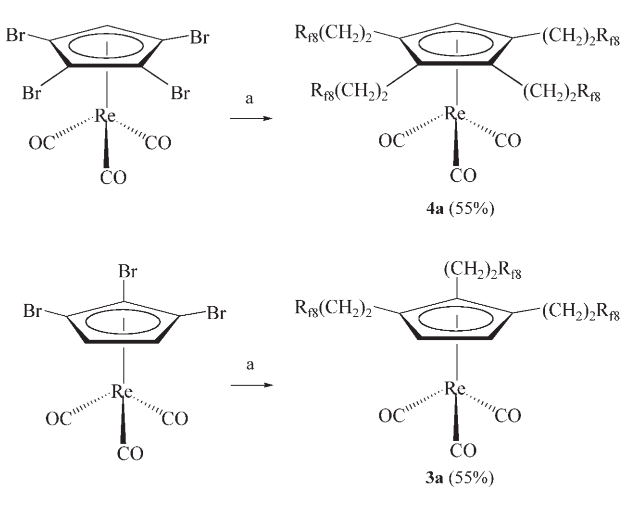
The complexes in Scheme 2 were characterized analogously to those in Scheme 1. They could be stored indefinitely at −4 °C, and TGA measurements showed no mass loss below 200 °C. As summarized in Table 1, all complexes were soluble in $CF_3C_6F_{11}$ and $CF_3C_6H_5$. Solubilities in organic solvents decreased markedly in the order **3′a**/**3a** > **4a** > **5a**. Only THF and acetone could dissolve trace amounts of **5a** at room temperature. Importantly, the $CF_3C_6F_{11}$/toluene partition coefficients were so biased that no detectable amount of complex remained in the toluene phase. The IR $\tilde{\nu}_{CO}$ values increased steadily with the number of ponytails, consistently with diminishing rhenium/CO backbonding. This trend was more pronounced in the lower-frequency band. The NMR properties were unexceptional,[26] sharing many features of the corresponding polybromocyclopentadienyl complexes.[18]

Because of the high formula weights of the ponytails, the combined isolated mass of **5a** and **4a** was much greater than that of the starting material, ameliorating the modest yields. The tetra- and trisubstituted complexes presumably arise through hydride transfer from the organozinc reagent, as is well documented for related cross-coupling reactions.[24] Although more selective reactions are often sought, Scheme 2 can be viewed as a facile one-pot synthesis of an easily separable library of compounds, all of which were desired at the outset of this study. Nonetheless, higher-yielding routes to complexes with three and four ponytails were sought, so reactions of other polybromocyclopentadienyl complexes were investigated.

As shown in Scheme 3 (top), the tetrabromocyclopentadienyl complex $[(\eta^5\text{-}C_5HBr_4)Re(CO)_3]$[18] (0.500 g) was treated with $[IZn\{(CH_2)_2R_{f8}\}]$ and *trans*-$[Cl_2Pd(PPh_3)_2]$. The conditions were analogous to those given in Scheme 2, but with the stoichiometry adjusted to the number of carbon–bromine bonds. Workup gave the expected product **4a** in 55% yield (0.896 g) after chromatography on fluorous silica gel. Small quantities of **3′a** and **3a** were also produced. The tribromocyclopentadienyl complex $[(\eta^5\text{-}1,2,3\text{-}C_5H_2Br_3)Re(CO)_3]$[18] was treated similarly. As shown in Scheme 3 (bottom), workup gave **3a** in 55% yield. No other



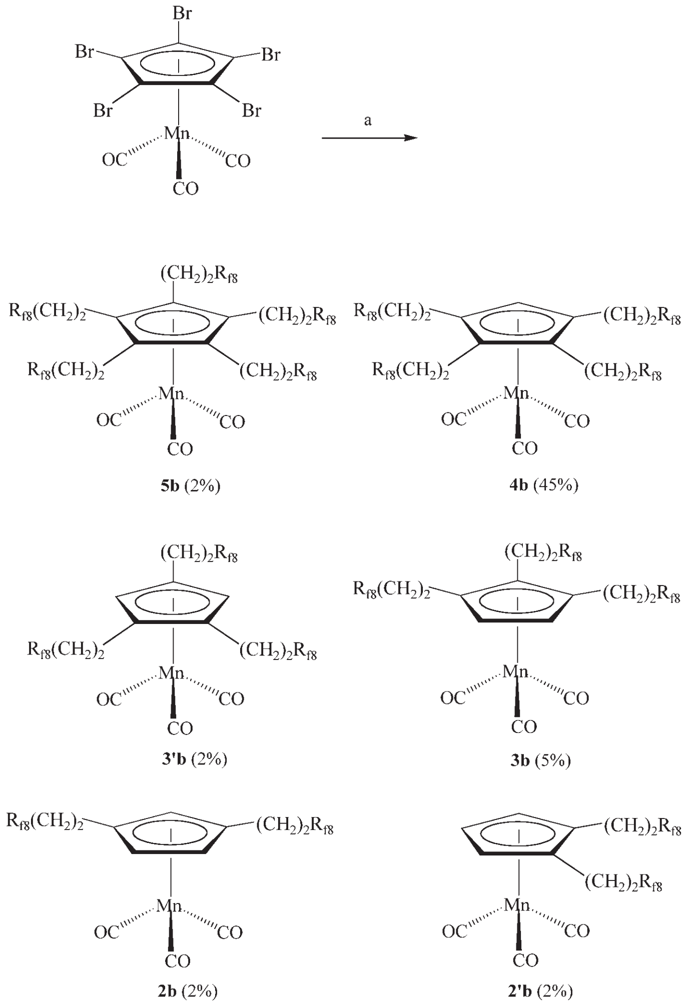
Scheme 2. Reaction of the pentabromocyclopentadienyl rhenium complex: a) $[IZn\{(CH_2)_2R_{f8}\}]$/*trans*-$[Cl_2Pd(PPh_3)_2]$ (1.1 equiv/11 mol% per C–Br bond), THF, 65 °C.



Scheme 3. Reactions of tetra- and tribromocyclopentadienyl rhenium complexes: a) $[IZn\{(CH_2)_2R_{f8}\}]$/*trans*-$[Cl_2Pd(PPh_3)_2]$ (1.1 equiv/11 mol% per C–Br bond), THF, 65 °C.

products were detected, so purification on fluorous silica gel was unnecessary.

Reactions of polybromocyclopentadienyl manganese complexes: A reaction similar to that shown in Scheme 2 was carried out with [(η^5-C_5Br_5)Mn(CO)$_3$] (1.002 g)[27] and the catalyst [Cl_2Pd(dppf)]. Chromatography on fluorous silica gel gave the products summarized in Scheme 4, which are depicted in inverse order of elution. The complex with five ponytails, [{η^5-C_5[(CH$_2$)$_2$R$_{f8}$]$_5$}Mn(CO)$_3$] (**5b**), was obtained in only 2 % yield (0.081 g), much lower than that obtained for the rhenium analogue. The major product, [{η^5-C_5H-[(CH$_2$)$_2$R$_{f8}$]$_4$}Mn(CO)$_3$] (**4b**), was isolated in 45 % yield (1.495 g). The two isomeric complexes with three ponytails were obtained in 2–5 % yields (**3b**, **3′b**; 0.178 g total). In contrast with the results given in Scheme 2, the two isomeric complexes with two ponytails (**2b**, **2′b**) were formed in sufficient amounts to be isolated (2 % each; 0.073 g total).



Scheme 4. Reaction of the pentabromocyclopentadienyl manganese complex: a) [IZn{(CH$_2$)$_2$R$_{f8}$}]/*trans*-[Cl_2Pd(dppf)] (1.1 equiv/11 mol % per C–Br bond), THF, 65 °C.

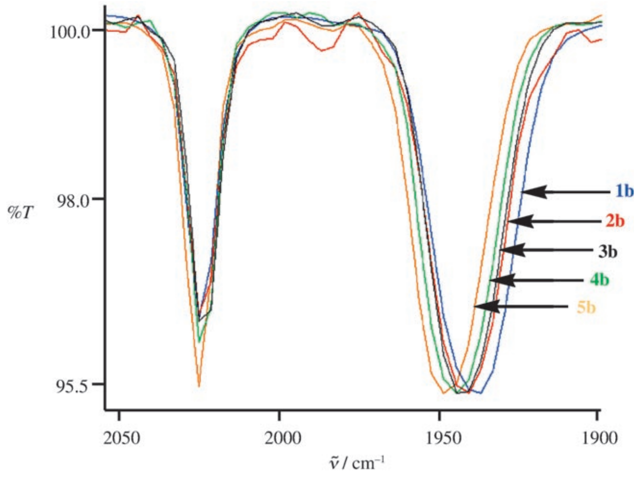
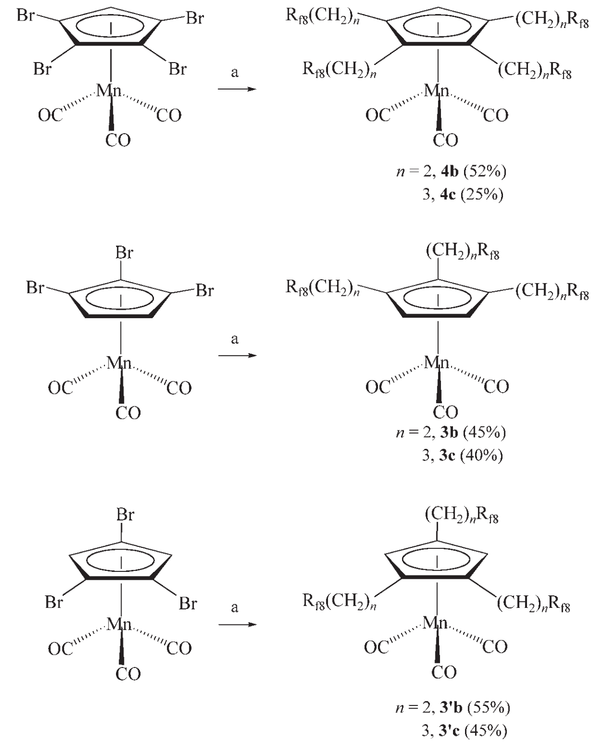


Figure 1. Representative IR spectra: $\tilde{\nu}_{CO}$ region for the manganese complexes shown in Scheme 4 (% *T* is the transmission percentage).

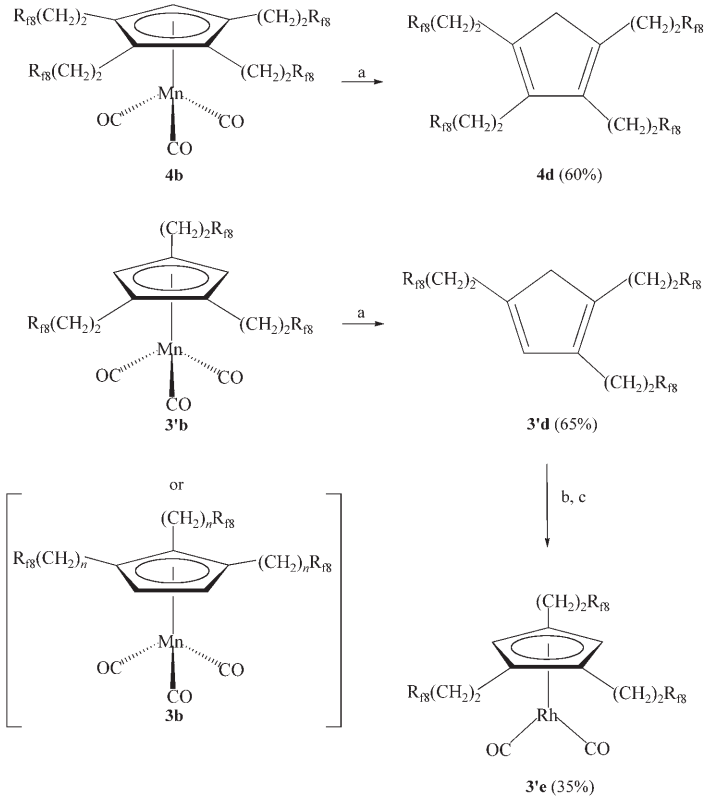
The manganese complexes shown in Scheme 4 were yellow solids, and were characterized analogously to the rhenium homologues (Table 1 and Experimental Section).[26] Their solubilities and TGA properties were comparable, but they turned brown upon extended exposure to light (> 10 h), and mass spectra showed somewhat more fragmentation. The IR $\tilde{\nu}_{CO}$ values exhibited analogous trends to the rhenium complexes, as illustrated by the spectra shown in Figure 1. Structures were assigned to **2b** and **2′b** from their ^{1}H NMR spectra. The cyclopentadienyl signals were coupled in the latter (t, 1 H; d, 2 H), consistent with vicinal ponytails, but uncoupled in the former. Complex **2′b**, which should be more polar than **2b**, accordingly eluted more rapidly on fluorous silica gel.

In order to access several of the complexes shown in Scheme 4 more efficiently, reactions of other polybromocyclopentadienyl complexes were investigated. As shown in Scheme 5 (top), the tetrabromocyclopentadienyl complex [(η^5-C_5HBr_4)Mn(CO)$_3$] (1.003 g)[18] was similarly treated with [IZn{(CH$_2$)$_2$R$_{f8}$}] and [Cl_2Pd(dppf)]. Chromatography on fluorous silica gel gave **4b** in 52 % yield (1.987 g). Small quantities of **3′b** and **3b** were also detected. As also shown in Scheme 5 (middle and bottom), the tribromocyclopentadienyl complexes [(η^5-1,2,3-$C_5H_2Br_3$)Mn(CO)$_3$][18] and [(η^5-1,2,4-$C_5H_2Br_3$)Mn(CO)$_3$][18] were treated similarly. Chromatography on non-fluorous silica gel gave **3b** and **3′b** in 45 % and 55 % yields, respectively.

We sought to investigate the effect of the length of the methylene spacer on various properties, so three analogous reactions were conducted with the homologous alkylzinc reagent [IZn{(CH$_2$)$_3$R$_{f8}$}], as also shown in Scheme 5. Workup gave [{η^5-C_5H[(CH$_2$)$_3$R$_{f8}$]$_4$}Mn(CO)$_3$] (**4c**), [{η^5-1,2,3-C_5H_2-[(CH$_2$)$_3$R$_{f8}$]$_3$}Mn(CO)$_3$] (**3c**), and [{η^5-1,2,4-C_5H_2-[(CH$_2$)$_3$R$_{f8}$]$_3$}Mn(CO)$_3$] (**3′c**) in 25 %, 40 %, and 45 % yields, respectively. The diminished yields might be due in part to incomplete generation of [IZn{(CH$_2$)$_3$R$_{f8}$}] from the precursor I(CH$_2$)$_3$R$_{f8}$, some of which was recovered after the reaction. This zinc reagent is new to this study, and does not appear to form as readily as the lower homologue. Complexes **4c**, **3c**, and **3′c** gave IR $\tilde{\nu}_{CO}$ values 7–5 cm^{-1} lower



Scheme 5. Reactions of tetra- and tribromocyclopentadienyl manganese complexes: a) $[IZn\{(CH_2)_nR_{f8}\}]$/*trans*-$[Cl_2Pd(dppf)]$ (1.1 equiv/11 mol% per C−Br bond), THF, 65 °C.



Scheme 6. Detachment and recomplexation of fluorous cyclopentadienyl ligands: a) *hν*, MeOH, ether, $CF_3C_6H_5$; b) *n*BuLi/THF, −78 °C; c) $[Rh(CO)_2Cl]_2$, $CF_3C_6H_5$, −78 °C to RT.

than those for **4b**, **3b**, and **3b′** (Table 1).[26] This trend is analyzed below.

Fluorous cyclopentadienyl ligands; other experiments: A number of techniques for detaching cyclopentadienyl ligands from transition metals have been developed. One of the most reliable involves the photolysis of manganese tricarbonyl adducts.[28] Thus, $CF_3C_6H_5$/MeOH/ether solutions of **4b** and **3′b** were irradiated with a high-pressure mercury lamp. As shown in Scheme 6, chromatographic workup gave the free fluorous cyclopentadienes **4d** and **3′d**, with four and three ponytails in 60 % and 65 % yields, respectively.

Compounds **4d** and **3′d** were air-stable, waxy, white solids that could be stored for several months at −4 °C. They were characterized analogously to the metal complexes. The $CF_3C_6F_{11}$/toluene partition coefficients were $>99.7{:}<0.3$, as assayed by GC (Table 2). The NMR spectra indicated tautomeric purities of $>95\%$, with the dominant isomers as depicted in Scheme 6.[26] The ^1H NMR spectrum of **4d** showed a diagnostic singlet for the ring CH_2 group at $\delta = 2.50$ ppm. That of **3′d** showed an analogous signal, together with a singlet for one vinylic proton ($\delta = 2.81$, 5.95 ppm).

Interestingly, the isomeric 1,2,3-substituted complex **3b** also gave the 1,2,4-substituted cyclopentadiene **3′d** under analogous conditions. We are not aware of any literature data on the relative stabilities of 1,2,3- and 1,2,4-substituted cyclopentadienes.[29] The required sigmatropic shifts might be promoted by the photochemical conditions or metal-containing byproducts.

Although syntheses of substituted cyclopentadienyl complexes from free cyclopentadienes are routine, a specific example was desired. Reactions of $[Rh(CO)_2Cl]_2$ and cyclopentadienide anions are known to give cyclopentadienyl rhodium dicarbonyl complexes.[9,13b,30] Accordingly, **3′d** was treated first with *n*BuLi in THF and then with $[Rh(CO)_2Cl]_2$ in $CF_3C_6H_5$ at −78 °C as shown in Scheme 6. Workup afforded the fluorous rhodium complex $[\{\eta^5\text{-}1,2,4\text{-}C_5H_2\text{-}[(CH_2)_2R_{f8}]_3\}Rh(CO)_2]$ (**3′e**) as an air-sensitive, orange oil in 35 % yield. It was characterized analogously to the other new compounds (Table 1 and Experimental Section).

In recent work, certain fluorous complexes have been found to coat Teflon tape efficiently,[31] so preliminary investigations with the preceding compounds were undertaken.

Table 2. Partition coefficients for fluorous cyclopentadienes.

Compound	Partition coefficient ($CF_3C_6F_{11}$/toluene)[a]
3′d, 1,2,4-$C_5H_3[(CH_2)_2R_{f8}]_3$	$>99.7{:}<0.3$[a]
4d, 1,2,3,4-$C_5H_2[(CH_2)_2R_{f8}]_4$	$>99.7{:}<0.3$[a]
$C_5H_4[(CH_2)_2R_{f4}]_2$[b]	60:40[c]
$C_5H_4[(CH_2)_2R_{f6}]_2$[b]	83:17[c]
$C_5H_4[(CH_2)_2R_{f8}]_2$[b]	90:10[c]
$C_5H_4[(CH_2)_2R_{f4}][(CH_2)_2R_{f6}]$[b]	75:25[c]
$C_5H_4[(CH_2)_2R_{f4}][(CH_2)_2R_{f8}]$[b]	82:18[c]
$C_5H_4[(CH_2)_2R_{f6}][(CH_2)_2R_{f8}]$[b]	86:14[c]

[a] 23 °C. [b] Mixture of isomers. [c] 25 °C, from ref. [13b].

In a representative experiment, **4b** (0.015 g, 0.008 mmol)—insoluble in hydrocarbons at room temperature—was dissolved in heptane at 100 °C. Two 50 × 12 × 0.0075 mm strips of tape were added, and the sample was cooled. An appreciable amount of **4b** precipitated onto the tape, but not uniformly. Some **4b** also precipitated onto the walls of the flask. Hence, although some coating is possible, the maximum loading appears to be lower than for other complexes.

Discussion

Fluorous cyclopentadienyl complexes—scope and syntheses: As noted in the Introduction, a number of fluorous cyclopentadienyl complexes, all depicted in Figure 2, have been reported previously. These "light fluorous" and "medium fluorous" species include ferrocenes with both one (**I**) and two (**IX**) ponytails per ring, homologues of **1a** and **1b** with longer perfluoroalkyl groups (**II**), cobalt and rhodium dicarbonyl complexes with both one (**III**, **IV**) and two (**X**) ponytails per ring, and zirconium(IV) and titanium(IV) species with an average of one ponytail per ring (**V**, **VI**, **XI**, **XII**). Our new compounds with three to five ponytails per ring (Schemes 2–6) represent the first "heavy fluorous" cyclopentadienyl complexes. To the best of our knowledge, **5a** and **5b** contain the first examples of "totally ponytailed" or "perfluorous" π ligands.

In contrast to the fluorous cyclopentadienyl complexes in Schemes 1–5, those in Figure 2 were prepared by standard methods from free fluorous cyclopentadienes. As shown in Scheme 7 (top), Hughes found that cyclopentadienes with one ponytail could be conveniently prepared by addition of fluorous alkyl iodides to nickelocenes.[8] As depicted in Scheme 7 (middle), Cermák and Kvícala demonstrated that

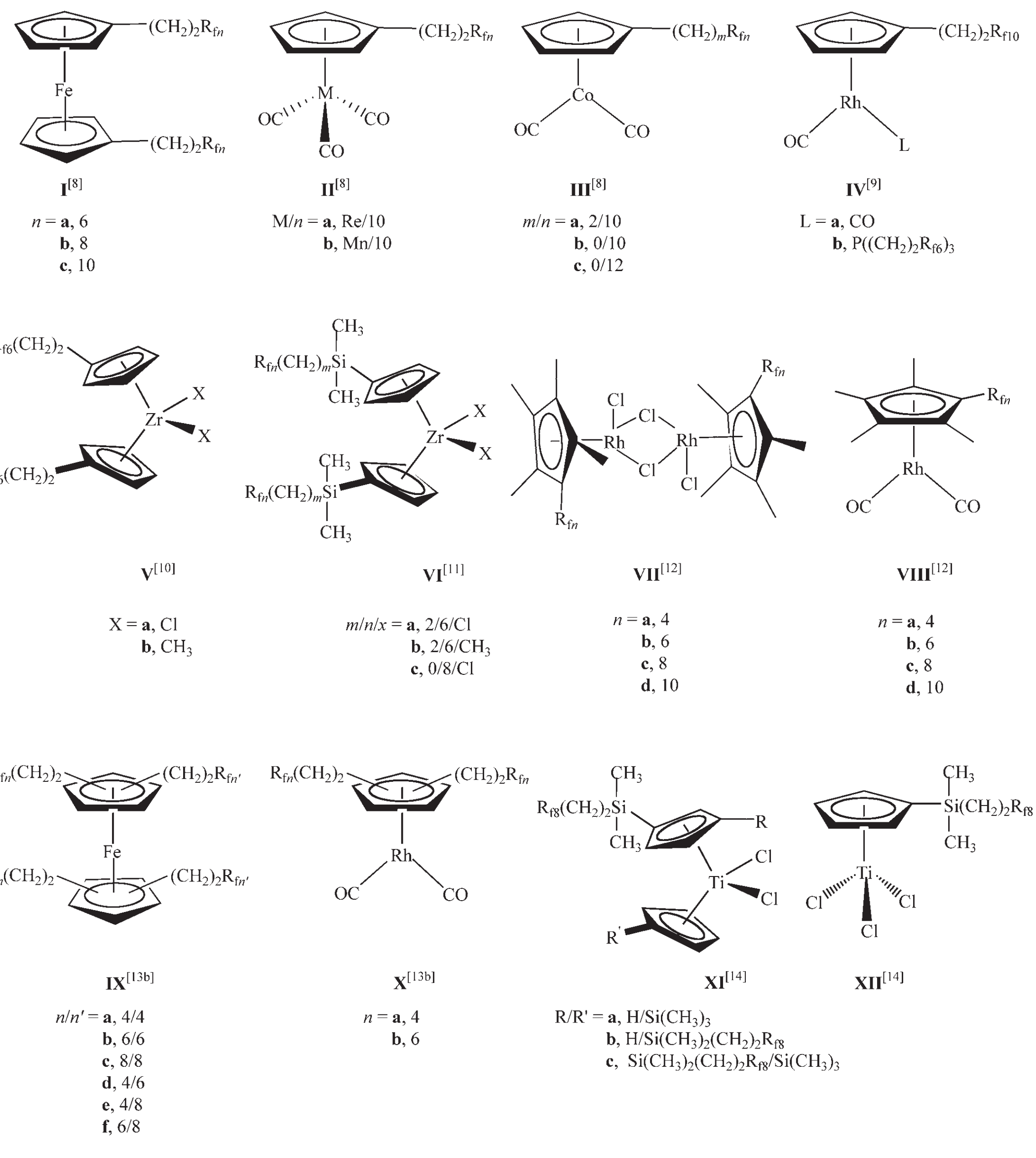
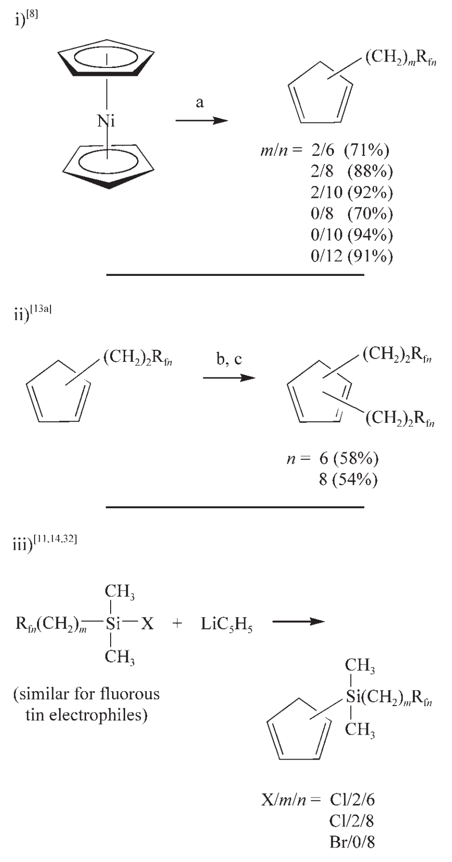


Figure 2. Previously reported fluorous cyclopentadienyl complexes.

the these could be deprotonated and alkylated to give cyclopentadienes with two ponytails as mixtures of 1,2- and 1,3-isomers.[13a] Cyclopentadienes with one or two fluorous silyl or stannyl substituents have been synthesized by similar routes, as illustrated for singly substituted silyl species in Scheme 7 (bottom).[11,14,32]

We have investigated various approaches to cyclopentadienes with four and five ponytails modeled after established routes to pentamethylcyclopentadiene and related species. However, the results have not been very encouraging, as detailed elsewhere.[33] In contrast, the photochemical syntheses of **4d** and **3′d** shown in Scheme 6 are very easy to conduct, and involve about the same number of steps from commercially available materials. The only restriction appears to involve 1,2,3-trisubstituted systems, which—at least in the case of **3b**—afford 1,2,4-trisubstituted cyclopentadienes.

The bromocyclopentadienyl starting materials in Schemes 1–5 are easily accessible from the corresponding bromodiazocyclopentadienes and bromide complexes $[(CO)_5MBr]$.[18,22,27] The major drawback of our methodology is the hydride-transfer side reaction, which precludes isolation of the pentasubstituted complexes **5a** and **5b** in high yields. Fortunately, this well-precedented process[24] is not a significant problem in reactions of the tetra- and tribromocyclopentadienyl complexes. For some reason, the manganese complexes are more prone to hydride transfer. Presumably there is a steric or electronic factor that slows the rate of cyclopentadienyl/$(CH_2)_nR_{f8}$ reductive elimination relative to β-hydride elimination, or that accelerates a step in the β-hydride elimination.



Scheme 7. Previous syntheses of fluorous cyclopentadienes (i–iii): a) $I(CH_2)_mR_{fn}$, PPh_3, Et_2O; b) *n*BuLi, dimethoxyethane, −80 to −10°C; c) $R_{fn}(CH_2)_2OSO_2CF_3$, reflux.

Fluorophilicities: The $CF_3C_6F_{11}$/toluene partition coefficients given in Table 1 show that the new fluorous cyclopentadienyl complexes with three to five ponytails are highly fluorophilic, with no detectable quantities remaining in the non-fluorous phase. As would be expected, the values become progressively more biased upon going from the manganese complex with one ponytail (**1b**: 44.4:55.6) to those with two (**2b**, **2′b**: 93.5–93.8:6.5–6.2) and then three (**3b**, **3′b**: $>99.8:<0.2$). The complexes with four and five ponytails should be still more fluorophilic, with partition coefficients that may be orders of magnitude greater.

The partition coefficients for **1b**, **2b**, **2′b**, **3b**, and **3′b** are uncannily similar to those of simple benzenes and pyridines bearing one, two, and three ponytails of the type $(CH_2)_mR_{f8}$ ($m=2$, 3).[19,34,35] In each series of compounds, the substitution pattern seems to have little influence upon the fluorophilicity. To the best of our knowledge, compounds with four or more ponytails per arene ring are unknown. Compounds **4a**, **4b**, **4c**, **4d**, **5a**, and **5b** should hence represent new benchmarks in terms of recycling efficiency and leaching resistance.

Partition coefficients have been determined for selected compounds in Figure 2, as summarized in Table 3. The manganese complex **IIb**, which has an R_{f10} segment, is, as would be expected, slightly more fluorophilic than the R_{f8} homologue **1b** (64:36 vs 44.4:55.6). In the same vein, **1c**, which has a longer $(CH_2)_m$ segment than **1b**, is slightly less fluorophilic (44.1:55.9). The rhenium complex **1a**, which is larger and more polarizable than **1b**, is much less fluorophilic (26.1:73.9). The partition coefficient of **Ic** shows that a ferrocene with one $(CH_2)_2R_{10}$ ponytail per ring has a fluorophi-

Table 3. Partition coefficients of previously reported fluorous cyclopentadienyl complexes.[a]

	Complex	Partition coefficient ($CF_3C_6F_{11}$/toluene)
IIb	$[\{\eta^5\text{-}C_5H_4[(CH_2)_2R_{f10}]\}Mn(CO)_3]$	64:36
IVa	$[\{\eta^5\text{-}C_5H_4[(CH_2)_2R_{f10}]\}Rh(CO)_2]$	44:56
IVb	$[\{\eta^5\text{-}C_5H_4[(CH_2)_2R_{f10}]\}Rh(CO)\text{-}\{P[(CH_2)_2R_{f6}]_3\}]$	96.7:3.3
Ic	$[\{\eta^5\text{-}C_5H_4[(CH_2)_2R_{f10}]_2\}Fe]$	95.2:4.8[b]
IXb	$[\{\eta^5\text{-}C_5H_3[(CH_2)_2R_{f6}]_2\}_2Fe]$[c]	98.6:1.4
IXa	$[\{\eta^5\text{-}C_5H_3[(CH_2)_2R_{f4}]_2\}_2Fe]$[c]	90.9:9.1
IXd	$[\{C_5H_3[(CH_2)_2R_{f4}][(CH_2)_2R_{f6}]\}_2Fe]$[c]	94.4:5.6
IXe	$[\{C_5H_3[(CH_2)_2R_{f4}][(CH_2)_2R_{f8}]\}_2Fe]$[c]	95.7:4.3
IXf	$[\{C_5H_3[(CH_2)_2R_{f6}][(CH_2)_2R_{f8}]\}_2Fe]$[c]	95.7:4.3
VIa	$[\{\eta^5\text{-}C_5H_4\{SiMe_2[(CH_2)_2R_{f6}]\}_2\}ZrCl_2]$	19:81
VIc	$[\{\eta^5\text{-}C_5H_4(SiMe_2R_{f8})\}_2ZrCl_2]$	44:56
Va	$[\{\eta^5\text{-}C_5H_4[(CH_2)_2R_{f6}]\}_2ZrCl_2]$	95.4:4.6
Vb	$[\{\eta^5\text{-}C_5H_4[(CH_2)_2R_{f6}]\}_2ZrMe_2]$	87.5:12.5

[a] Data are from the references given in Figure 2. [b] C_7F_{16}/toluene. [c] Mixture of isomers.

licity comparable to the half-metallocenes **2b** and **2′b**, with two $(CH_2)_2R_8$ ponytails per ring (95.2:4:8 vs 93.5–93.8:6.5–6.2). That of **IXb** (98.6:1.4) shows that ferrocenes with two $(CH_2)_2R_{f6}$ ponytails per ring are even more fluorophilic, and with longer R_{fn} segments may approach the range of **3a**, **3b**, **3′a**, and **3′b**. However, the partition coefficient of **IXf**, which features one $(CH_2)_2R_{f6}$ and one $(CH_2)_2R_{f8}$ ponytail per ring, actually tends in the opposite direction (95.7:4.3). Such phenomena are rare, but not without precedent.[35]

As summarized in Table 2, the fluorous cyclopentadienes **4d** and **3′d** also give highly biased $CF_3C_6F_{11}$/toluene partition coefficients (>99.7:<0.3). Because of their higher fluorine weight percentages, the exact values should be even greater than those of the metal tricarbonyl complexes. The other fluorous cyclopentadienes in Table 2, which have only two ponytails, give lower partition coefficients. The most relevant value is that for $C_5H_4[(CH_2)_2R_{f8}]_2$ (90:10), which is the lower homologue of **3′d**. Interestingly, the ferrocenes in Table 3 exhibit much higher partition coefficients than the corresponding cyclopentadienes in Table 2.

Electronic properties: The electronic influence of ponytails and their perfluoroalkyl segments upon the reactive centers of catalysts and reagents has been of interest since the beginning of fluorous chemistry.[4,20] This is easiest to analyze in series of compounds in which the numbers of ponytails are varied, such that cumulative effects can be defined. The IR $\tilde{\nu}_{CO}$ values of the title compounds offer sensitive probes for metal/CO backbonding and the electronic properties of the metal center. A referee has remarked that quantitative data are best extracted from the higher-frequency symmetric stretches.[15] Other approaches have also been taken.[36a]

Among the trends noted above, the most important are as follows. Firstly, for the complexes with $(CH_2)_2$ spacers, the $\tilde{\nu}_{CO}$ values steadily increase with the number of ponytails, consistently with reduced backbonding. With the rhenium complexes **1a**–**5a**, the shifts are 4 cm^{-1} (higher-frequency band) and 12 cm^{-1} (lower-frequency band). With the manganese complexes **1b**–**5b** (Figure 1), the shifts are less than 1 and 11 cm^{-1}, respectively. Although these trends are modest, we believe they indicate that the ponytails are slightly more electron-withdrawing than the hydrogen atoms they replace. In other words, the $(CH_2)_2$ spacers do not completely insulate the metal from the electron-withdrawing R_{f8} segments, despite the four intervening σ bonds. This is further supported by Hughes' electrochemical data for the ferrocenes **Ia** and **Ib** (Figure 2).[8,36b]

Accordingly, the $\tilde{\nu}_{CO}$ values *decrease* in the manganese complexes with $(CH_2)_3$ spacers (**1c**, **3c**, **3′c**, **4c**), where there are five intervening σ bonds (e.g., 2026/1945 vs 2019/1938 cm^{-1} for **4b** vs **4c**). This indicates improved insulation of the metal from the R_{f8} groups. Furthermore, there is little change with successive substitution. Upon going from **1c** to **4c**, the $\tilde{\nu}_{CO}$ value of the lower-frequency band remains constant, while that of the higher-frequency band *decreases* by 4 cm^{-1}. This suggests that the ponytails are electronically very similar to hydrogen atoms—or possibly slightly more electron-releasing. Other studies have shown that the inductive effects of R_{fn} groups can be transmitted through far greater numbers of σ bonds.[20] Perhaps the geometric constraints of the $M{-}C_{Cp}{-}CH_2$- segment, or other attributes of cyclopentadienyl ligands, result in less-efficient electronic transmission.

Conclusions

A simple and scalable route to "heavy fluorous" cyclopentadienyl complexes and cyclopentadienes bearing three to five $(CH_2)_mR_{f8}$ ponytails has been developed. The methodology utilizes readily available polybromocyclopentadienyl complexes that undergo efficient palladium-catalyzed cross-couplings with fluorous alkylzinc reagents. When pentabromocyclopentadienyl complexes are employed, the dominant products contain four ponytails, with the remaining bromide replaced by hydride. The fluorous cyclopentadienyl ligands are easily detached from manganese tricarbonyl adducts and transferred to other metals. Thus, families of cyclopentadienyl complexes with gradated fluorophilicities, absolute solubilities, and electronic properties, including the first cases with highly biased partition coefficients suitable for application in "heavy fluorous" chemistry, are now accessible.

Experimental Section

General: All reactions were conducted under N_2 unless noted. Chemicals were used as follows: THF was distilled from Na/benzophenone, $CF_3C_6F_{11}$ and $CF_3C_6H_5$ (Fluorochem or ABCR) were distilled from CaH, and *n*BuLi (1.6 M in hexanes, Fluka) was standardized.[37] $CDCl_3$, $[D_8]THF$, C_6D_6, $I(CH_2)_2R_{f8}$, 1,2-dibromoethane, $(CH_3)_3SiCl$, $[Rh(CO)_2Cl]_2$, eicosane (all Aldrich) and $[Cl_2Pd(dppf)]$,[23] and *trans*-$[Cl_2Pd(PPh_3)_2]$ (both Strem) were used as received, whilst $I(CH_2)_3R_{f8}$ was synthesized by a published method.[38] Fluorous silica gel was obtained from Fluorous Technologies.

NMR spectra were recorded on standard 400 MHz FT spectrometers and referenced to the solvent signals of $CDCl_3$, $[D_8]THF$, or C_6D_6 (^{13}C, $\delta = 77.0, 25.37, 128.0$ ppm; ^1H (residual protons), $\delta = 7.27, 3.58, 7.15$ ppm). IR and mass spectra were recorded on ASI React-IR 1000 and Micromass Zabspec instruments, respectively. DSC and TGA data were recorded with a Mettler–Toledo DSC821 instrument and were treated by standard methods.[39] Microanalyses were conducted with a Carlo Erba EA1110 instrument (in-house).

$[IZn\{(CH_2)_nR_{f8}\}]$:[19,40] A Schlenk flask was charged with zinc grains (0.435 g, 6.65 mmol), THF (3.0 mL), and 1,2-dibromoethane (0.091 mL, 1.06 mmol). The mixture was gently refluxed (heat gun) with stirring and allowed to cool to room temperature (4×). $(CH_3)_3SiCl$ (0.037 mL, 0.29 mmol) was then added. After 10 min, a solution of $I(CH_2)_nR_{f8}$ ($n = 2$, 0.761 g, 1.33 mmol; $n = 3$, 0.782 g, 1.33 mmol) in THF (2 mL) was slowly added by cannula. The mixture was stirred ($n = 2$, 1 h, ambient temperature; $n = 3$, 14 h, 40 °C). The resulting solutions of $[IZn\{(CH_2)_nR_{f8}\}]$ were used as described below.

$[\{\eta^5\text{-}C_5H_4[(CH_2)_2R_{f8}]\}Re(CO)_3]$ (1a): A Schlenk flask was charged with $[(\eta^5\text{-}C_5H_4Br)Re(CO)_3]$[22a] (0.503 g, 1.21 mmol), *trans*-$[Cl_2Pd(PPh_3)_2]$ (0.047 g, 0.066 mmol),[41] and THF (20.0 mL). A solution of $[IZn\{(CH_2)_2R_{f8}\}]$ (1.33 mmol; above) was slowly added by cannula with stirring. The mixture was kept at 65 °C for 5 h, the solvent was removed by rotary evaporation, the residue was filtered through silica gel with hexanes, and the hexanes were removed by rotary evaporation. The yellow residue was chromatographed on non-fluorous silica gel with hexanes as eluent. Solvent was removed from the product fractions by oil pump vacuum to give **1a** as a clear oil, which became a cloudy, waxy solid upon cooling (0.848 g, 1.085 mmol, 90 %). M.p. and IR data: Table 1; elemental analysis calcd (%) for $C_{18}H_8F_{17}O_3Re$: C 27.67, H 1.03; found: C 27.98, H 1.05; TGA: onset of mass loss 130 °C (T_e).

^{1}H NMR ($C_6D_6/CF_3C_6F_5$, 1:1 v/v): $\delta = 1.60$–1.81 (m; CH$_2$C*H*$_2$CF$_2$), 2.00–2.10 (m; C*H*$_2$CH$_2$CF$_2$), 4.20 (t, *J*(H,H) = 2.1 Hz; 2 × C*H*), 4.29 ppm (t, *J*(H,H) = 2.1 Hz; 2 × C*H*); ^{13}C{^{1}H}: $\delta = 19.1$ (s; *C*H$_2$CH$_2$CF$_2$), 33.0 (t, ^2J(C,F) = 22 Hz; CH$_2$*C*H$_2$CF$_2$), 82.9 (s; 2 × *C*H), 83.7 (s; 2 × *C*H) 107.3 (s; *C*CH$_2$CH$_2$CF$_2$), 194.3 ppm (s; CO).

[{η^5-1,2,3-C$_5$H$_2$[(CH$_2$)$_2$R$_{f8}$]$_3$}Re(CO)$_3$] (3a): The complex [(η^5-1,2,3-C$_5$H$_2$Br$_3$)Re(CO)$_3$][18] (0.502 g, 0.874 mmol), *trans*-[Cl$_2$Pd(PPh$_3$)$_2$] (0.202 g, 0.288 mmol),[41] THF (20.0 mL), and a solution of [IZn{(CH$_2$)$_2$R$_{f8}$}] (2.88 mmol; see above) were combined in a procedure analogous to that used for **1a**. A workup analogous to that used for the reaction of [(η^5-C$_5$Br$_5$)Re(CO)$_3$] (below) gave **3a** as a cloudy oil, which became a waxy, white solid when cooled to −20 °C (0.805 g, 0.481 mmol, 55 %). M.p. and IR data: Table 1; MS (FAB$^+$): *m*/*z*: 1674 [*M*]$^+$ (100 %); elemental analysis calcd (%) for $C_{38}H_{14}F_{51}O_3Re$: C 27.26, H 0.84; found: C 27.46, H 0.84; TGA: onset of mass loss 202 °C (T_e).

^{1}H NMR ($C_6D_6/CF_3C_6F_5$, 1:1 v/v): $\delta = 1.96$–2.14 (m; 3 × CH$_2$C*H*$_2$CF$_2$), 2.43–2.56 (m; 3 × C*H*$_2$CH$_2$CF$_2$), 4.44 ppm (s; 2 × C*H*); ^{13}C{^{1}H}: $\delta = 15.6$ (s; 1 × *C*H$_2$CH$_2$CF$_2$), 17.5 (s; 2 × *C*H$_2$CH$_2$CF$_2$), 32.1–33.5 (apparent m; 3 × CH$_2$*C*H$_2$CF$_2$), 81.1 (s; 2 × *C*H), 101.9 (s; 1 × *C*CH$_2$CH$_2$CF$_2$), 105.2 (s; 2 × *C*CH$_2$CH$_2$CF$_2$), 194.3 ppm (s; CO).

[{η^5-C$_5$H[(CH$_2$)$_2$R$_{f8}$]$_4$}Re(CO)$_3$] (4a): The complex [(η^5-C$_5$HBr$_4$)Re(CO)$_3$][18] (0.500 g, 0.768 mmol), *trans*-[Cl$_2$Pd(PPh$_3$)$_2$] (0.237 g, 0.338 mmol),[41] THF (20.0 mL), and a solution of [IZn{(CH$_2$)$_2$R$_{f8}$}] (3.379 mmol; above) were combined in a procedure analogous to that used for **1a**. A workup analogous to that used for the reaction of [(η^5-C$_5$Br$_5$)Re(CO)$_3$] gave **4a** as a cloudy oil, which became a waxy, white solid when cooled to −20 °C (0.896 g, 0.422 mmol, 55 %). M.p. and IR data: Table 1; MS (FAB$^+$): *m*/*z*: 2120 [*M*]$^+$ (100 %); elemental analysis calcd (%) for $C_{48}H_{17}F_{68}O_3Re$: C 27.20, H 0.81; found: C 27.29, H 0.99; TGA: onset of mass loss 225 °C (T_e).

^{1}H NMR ($C_6D_6/CF_3C_6F_5$, 1:1 v/v): $\delta = 2.11$–2.38 (m; 4 × CH$_2$C*H*$_2$CF$_2$), 2.55–2.70 (m; 4 × C*H*$_2$CH$_2$CF$_2$), 4.57 ppm (s; C*H*); ^{13}C{^{1}H}: $\delta = 16.9$ (s; 2 × *C*H$_2$CH$_2$CF$_2$), 18.1 (s; 2 × *C*H$_2$CH$_2$CF$_2$), 33.4 (t, ^2J(C,F) = 22 Hz; 2 × CH$_2$*C*H$_2$CF$_2$), 34.2 (t, ^2J(C,F) = 22 Hz; 2 × *C*H$_2$CH$_2$CF$_2$), 80.8 (s; *C*H), 102.9 (s; 2 × *C*CH$_2$CH$_2$CF$_2$), 105.9 (s; 2 × *C*CH$_2$CH$_2$CF$_2$), 194.3 ppm (s; CO).

Reaction of [(η^5-C$_5$Br$_5$)Re(CO)$_3$] and [IZn{(CH$_2$)$_2$R$_{f8}$}]: [{η^5-C$_5$-[(CH$_2$)$_2$R$_{f8}$]$_5$}Re(CO)$_3$] (5a), 4a, 3a, [{η^5-1,2,4-C$_5$H$_2$[(CH$_2$)$_2$R$_{f8}$]$_3$}Re(CO)$_3$] (3′a): A Schlenk flask was charged with [(η^5-C$_5$Br$_5$)Re(CO)$_3$][18] (0.501 g, 0.684 mmol), *trans*-[Cl$_2$Pd(PPh$_3$)$_2$] (0.265 g, 0.377 mmol),[41] and THF (20.0 mL). A solution of [IZn{(CH$_2$)$_2$R$_{f8}$}] (3.763 mmol; see above) was slowly added by cannula with stirring. The mixture was kept at 65 °C for 10 h, the solvent was removed by rotary evaporation, the residue was filtered through non-fluorous silica gel with hexanes/CF$_3$C$_6$H$_5$ (6:1 v/v) as eluent, and the solvents were removed by rotary evaporation and oil pump vacuum. The yellow residue was chromatographed on fluorous silica gel, first with hexanes and then with 6:1 v/v hexanes/CF$_3$C$_6$H$_5$. The first product-containing fractions gave **3a** (0.057 g, 0.034 mmol, 5 %; data above). The next product-containing fractions gave **3′a** as a cloudy oil, which became a waxy, white solid when cooled to −20 °C (0.023 g, 0.014 mmol, 2 %). M.p. and IR data: Table 1; MS (FAB$^+$): *m*/*z*: 1673 [*M*]$^+$ (100 %); elemental analysis calcd (%) for $C_{38}H_{14}F_{51}O_3Re$: C 27.26, H 0.84; found: C 27.05, H 1.11; TGA: onset of mass loss 206 °C (T_e).

^{1}H NMR ($C_6D_6/CF_3C_6F_5$, 1:1 v/v): $\delta = 1.91$–2.14 (m; 3 × CH$_2$C*H*$_2$CF$_2$), 2.39–2.46 (m; 3 × C*H*$_2$CH$_2$CF$_2$), 4.42 ppm (s; 2 × C*H*); ^{13}C{^{1}H}: $\delta = 17.9$ (s; 2 × *C*H$_2$CH$_2$CF$_2$), 19.7 (s; 1 × *C*H$_2$CH$_2$CF$_2$), 33.1 (apparent m; 3 × CH$_2$*C*H$_2$CF$_2$), 81.9 (s; 2 × *C*H), 103.9 (s; 3 × *C*CH$_2$CH$_2$CF$_2$), 194.4 ppm (s; CO).

The next product-containing fractions gave **4a** (0.435 g, 0.205 mmol, 30 %; data above) and then **5a** as a cloudy oil, which became a waxy, white solid when cooled to −20 °C (0.263 g, 0.103 mmol, 15 %). M.p. and IR data: Table 1; MS (FAB$^+$): *m*/*z*: 2565 [*M*]$^+$ (100 %); elemental analysis calcd (%) for $C_{58}H_{20}F_{85}O_3Re$: C 27.15, H 0.79; found: C 27.18, H 1.00; TGA: onset of mass loss 215 °C (T_e).

^{1}H NMR ($C_6D_6/CF_3C_6F_5$, 1:1 v/v): $\delta = 2.29$–2.44 (m; 5 × CH$_2$C*H*$_2$CF$_2$), 2.73–2.76 ppm (m; 5 × C*H*$_2$CH$_2$CF$_2$); ^{13}C{^{1}H}: $\delta = 17.0$ (s; *C*H$_2$CH$_2$CF$_2$), 34.6 (t, ^2J(C,F) = 22 Hz; CH$_2$*C*H$_2$CF$_2$), 102.0 (s; *C*CH$_2$CH$_2$CF$_2$), 193.9 ppm (s; CO).

[{η^5-C$_5$H$_4$[(CH$_2$)$_2$R$_{f8}$]}Mn(CO)$_3$] (1b): The complex [(η^5-C$_5$H$_4$Br)Mn(CO)$_3$][22b] (0.504 g, 1.78 mmol), *trans*-[Cl$_2$Pd(PPh$_3$)$_2$] (0.068 g, 0.097 mmol),[41] THF (20.0 mL), and a solution of [IZn{(CH$_2$)$_2$R$_{f8}$}] (1.943 mmol; see above) were combined in a procedure analogous to that used for **1a**. A similar workup gave **1b** as a light yellow, waxy solid (0.976 g, 1.502 mmol, 85 %). M.p. and IR data: Table 1.

^{1}H NMR ($C_6D_6/CF_3C_6F_5$, 1:1 v/v): $\delta = 1.81$–1.87 (m; CH$_2$C*H*$_2$CF$_2$–), 2.06–2.09 (m; C*H*$_2$CH$_2$CF$_2$), 3.76 (t, *J*(H,H) = 2.1 Hz; 2 × C*H*), 3.88 ppm (t, *J*(H,H) = 2.1 Hz; 2 × C*H*); ^{13}C{^{1}H}: $\delta = 19.2$ (s; *C*H$_2$CH$_2$CF$_2$), 32.1 (t, ^2J(C,F) = 22 Hz; CH$_2$*C*H$_2$CF$_2$), 82.0 (s; 4 × *C*H), 103.4 (s; *C*CH$_2$CH$_2$CF$_2$), 225.1 ppm (s; CO).

[{η^5-1,2,3-C$_5$H$_2$[(CH$_2$)$_2$R$_{f8}$]$_3$}Mn(CO)$_3$] (3b): A Schlenk flask was charged with [(η^5-1,2,3-C$_5$H$_2$Br$_3$)Mn(CO)$_3$][18] (1.002 g, 2.270 mmol), [Cl$_2$Pd(dppf)] (0.549 g, 0.750 mmol),[41] and THF (20.0 mL). A solution of [IZn{(CH$_2$)$_2$R$_{f8}$}] (7.49 mmol; see above) was slowly added by cannula with stirring. The mixture was kept at 65 °C for 10 h, the solvent was removed by rotary evaporation, the residue was filtered through non-fluorous silica gel with hexanes/CF$_3$C$_6$H$_5$ (6:1 v/v) as eluent, the solvents were removed by rotary evaporation, and the yellow residue was chromatographed on fluorous silica gel with hexanes and then with hexanes/CF$_3$C$_6$H$_5$ (6:1 v/v) to give **3b** as a waxy yellow solid (1.576 g, 1.020 mmol, 45 %). M.p. and IR data: Table 1; MS (FAB$^+$): *m*/*z*: 1543 [*M*]$^+$ (20 %), 1458 [*M*−3 CO]$^+$ (100 %); elemental analysis calcd (%) for $C_{38}H_{14}F_{51}O_3Mn$: C 29.59, H 0.91; found: C 29.46, H 1.12; TGA: onset of mass loss 197 °C (T_e).

^{1}H NMR ($C_6D_6/CF_3C_6F_5$, 1:1 v/v): $\delta = 2.17$–2.30 (m; 3 × CH$_2$C*H*$_2$CF$_2$), 2.51–2.63 (m; 3 × C*H*$_2$CH$_2$CF$_2$), 4.22 ppm (s; 2 × C*H*); ^{13}C{^{1}H}: $\delta = 16.6$ (s; 1 × *C*H$_2$CH$_2$CF$_2$), 18.1 (s; 2 × *C*H$_2$CH$_2$CF$_2$), 32.1–32.6 (apparent m; 3 × CH$_2$*C*H$_2$CF$_2$), 79.6 (s; 2 × *C*H), 99.1 (s; 1 × *C*CH$_2$CH$_2$CF$_2$), 106.1 (s; 2 × *C*CH$_2$CH$_2$CF$_2$), 224.8 ppm (s; CO).

[{η^5-1,2,4-C$_5$H$_2$[(CH$_2$)$_2$R$_{f8}$]$_3$}Mn(CO)$_3$] (3′b): The complex [(η^5-1,2,4-C$_5$H$_2$Br$_3$)Mn(CO)$_3$][18] (1.002 g, 2.270 mmol), [Cl$_2$Pd(dppf)] (0.549 g, 0.750 mmol),[41] THF (20.0 mL), and a solution of [IZn{(CH$_2$)$_2$R$_{f8}$}] (7.490 mmol; see above) were combined in a procedure analogous to that used for **3b**. A similar workup gave **3′b** as a waxy, yellow solid (1.930 g, 1.250 mmol, 55 %). M.p. and IR data: Table 1; MS (FAB$^+$): *m*/*z*: 1543 [*M*]$^+$ (20 %), 1458 [*M*−3 CO]$^+$ (100 %); elemental analysis calcd (%) for $C_{38}H_{14}F_{51}O_3Mn$: C 29.59, H 0.91; found: C 29.73, H 1.14; TGA: onset of mass loss 202 °C (T_e).

^{1}H NMR ($C_6D_6/CF_3C_6F_5$, 1:1 v/v): $\delta = 2.24$–2.28 (m; 3 × CH$_2$C*H*$_2$CF$_2$), 2.46–2.55 (m; 3 × C*H*$_2$CH$_2$CF$_2$), 4.24 ppm (s; 2 × C*H*); ^{13}C{^{1}H}: $\delta = 17.9$ (s; 2 × *C*H$_2$CH$_2$CF$_2$), 19.8 (s; 1 × *C*H$_2$CH$_2$CF$_2$), 32.2–32.6 (apparent m; 3 × CH$_2$*C*H$_2$CF$_2$), 82.4 (s; 2 × *C*H), 100.5 (s; 1 × *C*CH$_2$CH$_2$CF$_2$), 100.8 (s; 2 × *C*CH$_2$CH$_2$CF$_2$) 225.0 ppm (s; 3 × CO).

[{η^5-C$_5$H[(CH$_2$)$_2$R$_{f8}$]$_4$}Mn(CO)$_3$] (4b): The complex [(η^5-C$_5$HBr$_4$)Mn(CO)$_3$][18] (1.003 g, 1.923 mmol), [Cl$_2$Pd(dppf)] (0.621 g, 0.850 mmol),[41] THF (20.0 mL), and a solution of [IZn{(CH$_2$)$_2$R$_{f8}$}] (8.46 mmol; see above) were combined in a procedure analogous to that used for **3b**. The solvent was removed by rotary evaporation, the residue was filtered through non-fluorous silica gel with hexanes/CF$_3$C$_6$H$_5$ (6:1 v/v) as eluent, the solvents were removed by rotary evaporation, and the yellow residue was flash chromatographed on fluorous silica gel with hexanes to remove the disubstituted and trisubstituted byproducts. Further elution with hexanes/CF$_3$C$_6$H$_5$ (6:1 v/v) gave **4b** as a yellow, waxy solid (1.987 g, 0.999 mmol, 52 %). M.p. and IR data: Table 1; MS (FAB$^+$): *m*/*z*: 1987 [*M*]$^+$ (18 %), 1903 [*M*−3 CO]$^+$ (100 %); elemental analysis calcd (%) for $C_{48}H_{17}F_{68}O_3Mn$: C 28.99, H 0.86; found: C 29.25, H 0.95; TGA: onset of mass loss 229 °C (T_e).

^{1}H NMR ($\mathrm{C_6D_6/CF_3C_6F_5}$, 1:1 v/v): $\delta=2.26$–2.43 (m; 4× $\mathrm{CH_2\mathit{CH}_2CF_2}$), 2.51–2.74 (m; 4× $\mathrm{\mathit{CH}_2CH_2CF_2}$), 4.34 ppm (s; CH); ^{13}C{^{1}H}: $\delta=16.4$ (s; 2× $\mathrm{\mathit{C}H_2CH_2CF_2}$), 18.1 (s; 2× $\mathrm{\mathit{C}H_2CH_2CF_2}$), 32.1–33.5 (apparent m; 4× $\mathrm{CH_2\mathit{C}H_2CF_2}$), 80.2 (s; CH), 99.0 (s; 2× $\mathrm{\mathit{C}CH_2CH_2CF_2}$), 99.3 (s; 2× $\mathrm{\mathit{C}CH_2CH_2CF_2}$), 224.1 ppm (s; CO).

Reaction of $[(\eta^5\text{-}\mathrm{C_5Br_5})\mathrm{Mn(CO)_3}]$ and $[\mathrm{IZn\{(CH_2)_2R_{f8}\}}]$: $[\{\eta^5\text{-}\mathrm{C_5}\text{-}[\mathrm{(CH_2)_2R_{f8}}]_5\}\mathrm{Mn(CO)_3}]$ (5b), 4b, 3b, 3′b, $[\{\eta^5\text{-}1{,}3\text{-}\mathrm{C_5H_3}\text{-}[\mathrm{(CH_2)_2R_{f8}}]_2\}\mathrm{Mn(CO)_3}]$ (2b), and $[\{\eta^5\text{-}1{,}2\text{-}\mathrm{C_5H_3}[\mathrm{(CH_2)_2R_{f8}}]_2\}\mathrm{Mn(CO)_3}]$ (2′b): The complex $[(\eta^5\text{-}\mathrm{C_5Br_5})\mathrm{Mn(CO)_3}]$[27] (1.002 g, 1.670 mmol), $[\mathrm{Cl_2Pd(dppf)}]$[23] (0.674 g, 0.920 mmol),[41] THF (20.0 mL), and a solution of $[\mathrm{IZn\{(CH_2)_2R_{f8}\}}]$ (9.200 mmol; see above) were combined in a procedure analogous to that used for **3b**. The solvent was removed by rotary evaporation, the residue was filtered through non-fluorous silica gel with hexanes/$\mathrm{CF_3C_6H_5}$ (6:1 v/v) as eluent, the solvents were removed by rotary evaporation, and the yellow residue was chromatographed on fluorous silica gel, first with hexane (flash elution to separate the di- and trisubstituted products) and then with hexanes/$\mathrm{CF_3C_6H_5}$ (6:1 v/v) (standard elution). The first hexanes/$\mathrm{CF_3C_6H_5}$ fractions gave **4b** (1.495 g, 0.7520 mmol, 45 %; data above). The next product-containing fractions gave **5b** as a yellow oil, which became a waxy, yellow solid when cooled to −20 °C (0.081 g, 0.033 mmol, 2 %). M.p. and IR data: Table 1; MS (FAB$^+$): m/z: 2433 $[M]^+$ (24 %), 2349 $[M{-}3\,\mathrm{CO}]^+$ (100 %); elemental analysis calcd (%) for $\mathrm{C_{58}H_{20}F_{85}O_3Mn}$: C 28.61, H 0.83; found: C 29.15, H 1.02; TGA: onset of mass loss 202 °C (T_e).

^{1}H NMR ($\mathrm{C_6D_6/CF_3C_6F_5}$, 1:1 v/v): $\delta=2.29$–2.44 (m; 5× $\mathrm{CH_2\mathit{CH}_2CF_2}$), 2.73–2.76 ppm (m; 5× $\mathrm{\mathit{CH}_2CH_2CF_2}$); ^{13}C{^{1}H}: $\delta=17.0$ (s; $\mathrm{\mathit{C}H_2CH_2CF_2}$), 33.6 (t, $^2J(\mathrm{C,F})=22$ Hz; $\mathrm{CH_2\mathit{C}H_2CF_2}$), 98.9 (s; $\mathrm{\mathit{C}CH_2CH_2CF_2}$), 224.1 ppm (s; CO).

The hexane washings from the flash chromatography step were taken to dryness and chromatographed on fluorous silica gel, first with hexanes and then with 8:1 v/v hexanes/$\mathrm{CF_3C_6H_5}$. The first product-containing fractions gave **2′b** as a yellow oil, which became a waxy yellow solid when cooled to −20 °C (0.037 g, 0.0330 mmol, 2 %). M.p. and IR data: Table 1; MS (FAB$^+$): m/z: 1096 $[M]^+$ (20 %), 1012 $[M{-}3\,\mathrm{CO}]^+$ (100 %); elemental analysis calcd (%) for $\mathrm{C_{28}H_{11}F_{34}O_3Mn}$: C 30.68, H 1.01; found: C 30.65, H 1.10.

^{1}H NMR ([D$_8$]THF): $\delta=2.41$–2.51 (m; 2× $\mathrm{CH_2\mathit{CH}_2CF_2}$), 2.59–2.77 (m; 2× $\mathrm{\mathit{CH}_2CH_2CF_2}$), 4.75 (t, $^3J(\mathrm{H,H'})=2.5$ Hz; CH), 4.99 ppm (d, $^3J(\mathrm{H',H})=2.8$ Hz; 2× CH); ^{13}C{^{1}H}: $\delta=17.7$ (s; 2× $\mathrm{\mathit{C}H_2CH_2CF_2}$), 32.2 (t, $^2J(\mathrm{C,F})=22$ Hz; 2× $\mathrm{CH_2\mathit{C}H_2CF_2}$), 79.4 (s; 1× CH), 82.4 (s; 2× CH), 101.3 (s; 2× $\mathrm{\mathit{C}CH_2CH_2CF_2}$), 225.0 ppm (s; CO).

The next product-containing fractions gave **2b** as a yellow oil, which became a waxy, yellow solid when cooled to −20 °C (0.037 g, 0.033 mmol, 2 %). M.p. and IR data: Table 1; MS (FAB$^+$): m/z: 1096 $[M]^+$ (20 %), $[M{-}3\,\mathrm{CO}]^+$ (100 %); elemental analysis calcd (%) for $\mathrm{C_{28}H_{11}F_{34}O_3Mn}$: C 30.68, H 1.01; found: C 30.75, H 1.10.

^{1}H NMR ([D$_8$]THF): $\delta=2.43$–2.52 (m; 2× $\mathrm{CH_2\mathit{CH}_2CF_2}$), 2.57–2.78 (m; 2× $\mathrm{\mathit{CH}_2CH_2CF_2}$), 4.73 (s; CH), 5.02 ppm (s; 2× CH); ^{13}C{^{1}H}: $\delta=19.7$ (s; 2× $\mathrm{\mathit{C}H_2CH_2CF_2}$), 32.7 (t, $^2J(\mathrm{C,F})=22$ Hz; 2× $\mathrm{CH_2\mathit{C}H_2CF_2}$), 81.2 (s; 2× CH), 82.3 (s; 1× CH), 103.2 (s; 2× $\mathrm{\mathit{C}CH_2CH_2CF_2}$), 225.0 ppm (s; CO).

The next product-containing fractions gave **3b** (0.127 g, 0.083 mmol, 5 %; data above) and then **3′b** (0.051 g, 0.033 mmol, 2 %; data above).

$[\{\eta^5\text{-}\mathrm{C_5H_4}[\mathrm{(CH_2)_3R_{f8}}]\}\mathrm{Mn(CO)_3}]$ (1c): The complex $[(\eta^5\text{-}\mathrm{C_5H_4Br})\mathrm{Mn(CO)_3}]$[22b] (0.250 g, 0.886 mmol), $[\mathrm{Cl_2Pd(dppf)}]$ (0.071 g, 0.098 mmol),[41] THF (10.0 mL), and a solution of $[\mathrm{IZn\{(CH_2)_3R_{f8}\}}]$ (1.064 mmol; see above) were combined in a procedure analogous to that used for **3b**. The solvent was removed by rotary evaporation, the residue was filtered through silica gel with hexanes/$\mathrm{CF_3C_6H_5}$ (6:1 v/v) as eluent, and the solvent was removed by rotary evaporation to give **1c** as a yellowish oil, which became a waxy solid when cooled to −20 °C (0.499 g, 0.753 mmol, 85 %). M.p. and IR data: Table 1; MS (FAB$^+$): m/z: 664 $[M]^+$ (45 %), 580 $[M{-}3\,\mathrm{CO}]^+$ (100 %); elemental analysis calcd (%) for $\mathrm{C_{19}H_{10}F_{17}O_3Mn}$: C 34.36, H 1.52; found: C 34.53, H 1.75; TGA: onset of mass loss 126 °C (T_e).

^{1}H NMR ($\mathrm{C_6D_6/CF_3C_6F_5}$, 1:1 v/v): $\delta=1.41$–1.52 (m; $\mathrm{CH_2CH_2\mathit{CH}_2CF_2}$), 1.71–1.92 (m; $\mathrm{\mathit{CH}_2\mathit{CH}_2CH_2CF_2}$), 4.05 (t, $J(\mathrm{H,H})=2.1$ Hz; 2× CH), 4.13 ppm (t, $J(\mathrm{H,H})=2.1$ Hz; 2× CH); ^{13}C{^{1}H}: $\delta=21.9$ (s; $\mathrm{\mathit{C}H_2CH_2CH_2CF_2}$), 27.6 (s; $\mathrm{CH_2\mathit{C}H_2CH_2CF_2}$), 30.5 (t, $^2J(\mathrm{C,F})=22$ Hz; $\mathrm{CH_2CH_2\mathit{C}H_2CF_2}$), 81.87 (s; 2× CH), 81.90 (s; 2× CH), 103.4 (s; $\mathrm{\mathit{C}CH_2CH_2CH_2CF_2}$), 225.3 ppm (s; CO).

$[\{\eta^5\text{-}1{,}2{,}3\text{-}\mathrm{C_5H_2}[\mathrm{(CH_2)_3R_{f8}}]_3\}\mathrm{Mn(CO)_3}]$ (3c): The complex $[(\eta^5\text{-}1{,}2{,}3\text{-}\mathrm{C_5H_2Br_3})\mathrm{Mn(CO)_3}]$[18] (0.500 g, 1.135 mmol), $[\mathrm{Cl_2Pd(dppf)}]$ (0.274 g, 0.375 mmol),[41] THF (20.0 mL), and a solution of $[\mathrm{IZn\{(CH_2)_3R_{f8}\}}]$ (3.741 mmol; see above) were combined in a procedure analogous to that used for **3b**. The solvent was removed by rotary evaporation, the residue was filtered through non-fluorous silica gel with hexanes/$\mathrm{CF_3C_6H_5}$ (6:1 v/v) as eluent, the solvents were removed by rotary evaporation, the residue was chromatographed on fluorous silica gel with hexanes, and solvent was removed from the product fractions by oil pump vacuum to give **3c** as a yellow oil, which became a waxy solid when cooled to −20 °C (0.720 g, 0.454 mmol, 40 %). M.p. and IR data: Table 1; MS (FAB$^+$): m/z: 1584 $[M]^+$ (37 %), 1500 $[M{-}3\,\mathrm{CO}]^+$ (100 %); elemental analysis calcd (%) for $\mathrm{C_{41}H_{20}F_{51}O_3Mn}$: C 31.08, H 1.27; found: C 31.51, H 1.33; TGA: onset of mass loss 202 °C (T_e).

^{1}H NMR ($\mathrm{C_6D_6/CF_3C_6F_5}$, 1:1 v/v): $\delta=1.50$–1.56 (m; 3× $\mathrm{CH_2CH_2\mathit{CH}_2CF_2}$), 1.81–1.98 (m; 3× $\mathrm{\mathit{CH}_2\mathit{CH}_2CH_2CF_2}$), 3.99 ppm (s; 2× CH); ^{13}C{^{1}H}: $\delta=22.0$ (s; 2× $\mathrm{\mathit{C}H_2CH_2CH_2CF_2}$), 22.8 (s; 1× $\mathrm{\mathit{C}H_2CH_2CH_2CF_2}$), 25.9 (s; 1× $\mathrm{CH_2\mathit{C}H_2CH_2CF_2}$), 26.5 (s; 2× $\mathrm{CH_2\mathit{C}H_2CH_2CF_2}$), 31.0–31.4 (apparent m; 3× $\mathrm{CH_2CH_2\mathit{C}H_2CF_2}$), 79.4 (s; 2× CH), 100.1 (s; 1× $\mathrm{\mathit{C}CH_2CH_2CH_2CF_2}$), 103.8 (s; 2× $\mathrm{\mathit{C}CH_2CH_2CH_2CF_2}$), 225.7 ppm (s; CO).

$[\{\eta^5\text{-}1{,}2{,}4\text{-}\mathrm{C_5H_2}[\mathrm{(CH_2)_3R_{f8}}]_3\}\mathrm{Mn(CO)_3}]$ (3′c): The complex $[(\eta^5\text{-}1{,}2{,}4\text{-}\mathrm{C_5H_2Br_3})\mathrm{Mn(CO)_3}]$[18] (0.500 g, 1.135 mmol), $[\mathrm{Cl_2Pd(dppf)}]$ (0.274 g, 0.375 mmol),[41] THF (20.0 mL), and a solution of $[\mathrm{IZn\{(CH_2)_3R_{f8}\}}]$ (3.746 mmol; see above) were combined in a procedure analogous to that used for **3c**. An identical workup gave **3′c** as a yellow oil, which became a waxy solid when cooled to −20 °C (0.810 g, 0.509 mmol, 45 %). M.p. and IR data: Table 1; MS (FAB$^+$): m/z: 1584 $[M]^+$ (27 %), 1500 $[M{-}3\,\mathrm{CO}]^+$ (100 %); elemental analysis calcd (%) for $\mathrm{C_{41}H_{20}F_{51}O_3Mn}$: C 31.08, H 1.27; found: C 31.34, H 1.21; TGA: onset of mass loss 212 °C (T_e).

^{1}H NMR ($\mathrm{C_6D_6/CF_3C_6F_5}$, 1:1 v/v): $\delta=1.62$–1.65 (m; 3× $\mathrm{CH_2CH_2\mathit{CH}_2CF_2}$), 1.90–2.08 (m; 3× $\mathrm{\mathit{CH}_2\mathit{CH}_2CH_2CF_2}$), 4.09 ppm (s; 2× CH); ^{13}C{^{1}H}: $\delta=21.9$ (s; 2× $\mathrm{\mathit{C}H_2CH_2CH_2CF_2}$), 22.4 (s; 1× $\mathrm{\mathit{C}H_2CH_2CH_2CF_2}$), 26.1 (s; 2× $\mathrm{CH_2\mathit{C}H_2CH_2CF_2}$), 26.4 (s; 1× $\mathrm{CH_2\mathit{C}H_2CH_2CF_2}$), 30.5–31.3 (m; 3× $\mathrm{CH_2CH_2\mathit{C}H_2CF_2}$), 82.0 (s; 2× CH), 101.8 (s; 2× $\mathrm{\mathit{C}CH_2CH_2CH_2CF_2}$), 101.9 (s; 1× $\mathrm{\mathit{C}CH_2CH_2CH_2CF_2}$), 225.7 ppm (s; CO).

$[\{\eta^5\text{-}\mathrm{C_5H}[\mathrm{(CH_2)_3R_{f8}}]_4\}\mathrm{Mn(CO)_3}]$ (4c): The complex $[(\eta^5\text{-}\mathrm{C_5HBr_4})\mathrm{Mn(CO)_3}]$[18] (1.002 g, 1.927 mmol), $[\mathrm{Cl_2Pd(dppf)}]$ (0.621 g, 0.850 mmol),[41] THF (20.0 mL), and a solution of $[\mathrm{IZn\{(CH_2)_3R_{f8}\}}]$ (8.470 mmol; see above) were combined in a procedure analogous to that used for **3c**. A similar workup (chromatography on fluorous silica gel first with hexanes to remove the di- and trisubstituted byproducts, and then with hexanes/$\mathrm{CF_3C_6H_5}$ (6:1 v/v) to elute the product) gave **4c** as a yellow oil, which became a waxy solid when cooled to −20 °C (0.983 g, 0.482 mmol, 25 %). M.p. and IR data: Table 1; MS (FAB$^+$): m/z: 2044 $[M]^+$ (24 %), 1960 $[M{-}3\,\mathrm{CO}]^+$ (100 %); elemental analysis calcd (%) for $\mathrm{C_{52}H_{25}F_{68}O_3Mn}$: C 30.55, H 1.23; found: C 30.96, H 1.10; TGA: onset of mass loss 224 °C (T_e).

^{1}H NMR ($\mathrm{C_6D_6/CF_3C_6F_5}$, 1:1 v/v): $\delta=1.75$–1.78 (m; 4× $\mathrm{CH_2CH_2\mathit{CH}_2CF_2}$), 2.03–2.09 (m; 4× $\mathrm{\mathit{CH}_2\mathit{CH}_2CH_2CF_2}$), 4.30 ppm (s; CH); ^{13}C{^{1}H}: $\delta=22.4$ (s; 2× $\mathrm{\mathit{C}H_2CH_2CH_2CF_2}$), 23.4 (s; 2× $\mathrm{\mathit{C}H_2CH_2CH_2CF_2}$), 25.8 (s; 2× $\mathrm{CH_2\mathit{C}H_2CH_2CF_2}$), 26.6 (s; 2× $\mathrm{CH_2\mathit{C}H_2CH_2CF_2}$), 31.2–31.8 (apparent m; 4× $\mathrm{CH_2CH_2\mathit{C}H_2CF_2}$), 80.7 (s; CH), 100.9 (s; 2× $\mathrm{\mathit{C}CH_2CH_2CH_2CF_2}$), 101.0 (s; 2× $\mathrm{\mathit{C}CH_2CH_2CH_2CF_2}$), 225.9 ppm (s; CO).

$\overline{\mathrm{C[(CH_2)_2R_{f8}]{=}C[(CH_2)_2R_{f8}]CH{=}C[(CH_2)_2R_{f8}]C}}\mathrm{H_2}$ (3′d): A quartz-well photochemical immersion reactor was charged with **3′b** (0.502 g, 0.324 mmol), $\mathrm{CF_3C_6H_5}$ (10 mL; to dissolve **3′b**), MeOH (5 mL), and diethyl ether (10 mL). The solution was irradiated with a Heraeus TQ150 high-pressure mercury lamp (20 min). The solvent was removed by rotary evaporation. The brown residue was chromatographed (silica gel column, 8:1 v/v hexanes/$\mathrm{CF_3C_6H_5}$) to give **3′d** as a white oil that solidified under oil pump vacuum (0.296 g, 0.211 mmol, 65 %). M.p. 47–49 °C (capillary), 52.3 °C (DSC, T_e); MS (FAB$^+$): m/z: 1404 $[M]^+$ (100 %), 971 $[M{-}(\mathrm{CH_2(CF_2)_7CF_3})]^+$ (45 %); elemental analysis calcd (%) for $\mathrm{C_{35}H_{15}F_{51}}$: C 29.93, H 1.08; found: C 29.55, H 1.15.

^{1}H NMR ($\mathrm{C_6D_6/CF_3C_6F_5}$, 1:1 v/v): $\delta = 1.95$–2.09 (m; 2 × $\mathrm{CH_2C}\mathit{H}_2\mathrm{CF_2}$), 2.15–2.30 (m; $\mathrm{CH_2C}\mathit{H}_2\mathrm{CF_2}$), 2.56–2.58 (m; $\mathrm{C}\mathit{H}_2\mathrm{CH_2CF_2}$), 2.35–2.47 (m; 2 × $\mathrm{C}\mathit{H}_2\mathrm{CH_2CF_2}$), 2.81 (s, $=\mathrm{CC}\mathit{H}_2\mathrm{C}=$), 5.95 ppm (s; $\mathrm{C}\mathit{H}=$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$: $\delta = 15.7$ (s; 1 × $\mathit{C}\mathrm{H_2CH_2CF_2}$), 18.5 (s; 1 × $\mathit{C}\mathrm{H_2CH_2CF_2}$), 18.6 (s; 1 × $\mathit{C}\mathrm{H_2CH_2CF_2}$), 30.3 (t, $^2J(\mathrm{C,F}) = 22$ Hz; 1 × $\mathrm{CH_2}\mathit{C}\mathrm{H_2CF_2}$), 31.1–31.7 (apparent m; 2 × $\mathrm{CH_2}\mathit{C}\mathrm{H_2CF_2}$), 40.7 (s, $=\mathrm{C}\mathit{C}\mathrm{H_2C}=$), 124.7 (s; 1 $\mathit{C}\mathrm{H}=$), 138.2 (s; 1 × $\mathit{C}\mathrm{CH_2CH_2CF_2}$), 140.3, (s; 1 × $\mathit{C}\mathrm{CH_2CH_2CF_2}$), 145.0 ppm (s; 1 × $\mathit{C}\mathrm{CH_2CH_2CF_2}$).

$\overline{\mathbf{C[(CH_2)_2R_{f8}]{=}C[(CH_2)_2R_{f8}]C[(CH_2)_2R_{f8}]{=}C[(CH_2)_2R_{f8}]C}}\mathrm{H_2}$ (4d): Complex **4b** (0.501 g, 0.251 mmol), $\mathrm{CF_3C_6H_5}$ (20 mL; to dissolve **4b**), MeOH (10 mL), and diethyl ether (10 mL) were combined in a procedure analogous to that used for **3′d**. An identical workup gave **4d** as a white oil that became a waxy white solid under oil pump vacuum (0.279 g, 0.151 mmol, 60%). M.p. 65–69 °C (capillary). MS (FAB$^+$): *m*/*z*: 1850 $[M]^+$ (100%), 1417 $[M-(\mathrm{CH_2(CF_2)_7CF_3})]^+$ (65%), 969 $([1417-((\mathrm{CH_2})_2(\mathrm{CF_2})_7\mathrm{CF_3})]^+$ (70%).

^{1}H NMR ($\mathrm{C_6D_6/CF_3C_6F_5}$, 1:1 v/v): $\delta = 2.10$–2.22 (m; 4 × $\mathrm{CH_2C}\mathit{H}_2\mathrm{CF_2}$), 2.50 (s; $=\mathrm{CC}\mathit{H}_2\mathrm{C}=$), 2.56–2.63 ppm (m; 4 × $\mathrm{C}\mathit{H}_2\mathrm{CH_2CF_2}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$: $\delta = 16.7$ (s; 2 × $\mathit{C}\mathrm{H_2CH_2CF_2}$), 19.3 (s; 2 × $\mathit{C}\mathrm{H_2CH_2CF_2}$), 31.6–32.1 (apparent m; 4 × $\mathrm{CH_2}\mathit{C}\mathrm{H_2CF_2}$), 43.4 (s,$=\mathrm{C}\mathit{C}\mathrm{H_2C}=$), 138.5, (s; 2 × $\mathit{C}\mathrm{CH_2CH_2CF_2}$), 138.6 ppm (s; 2 × $\mathit{C}\mathrm{CH_2CH_2CF_2}$).

$[\{\eta^5\text{-1,2,4-}\mathbf{C_5H_2[(CH_2)_2R_{f8}]_3}\}\mathbf{Rh(CO)_2}]$ (3′e): A Schlenk flask was charged with **3′d** (0.151 g, 0.107 mmol) and THF (10.0 mL), and cooled to −78 °C. *n*BuLi (1.6 M in hexanes; 0.074 mL, 0.118 mmol) was then added with stirring. A solution of $[\mathrm{Rh(CO)_2Cl}]_2$ (0.042 g, 0.107 mmol) in THF (2.0 mL) and $\mathrm{CF_3C_6H_5}$ (2.0 mL) was then added by cannula. The solution was allowed to warm slowly to room temperature. After 10 h, solvents were removed by oil pump vacuum, the dark residue was chromatographed on a short alumina column with $\mathrm{CF_3C_6F_{11}}$ under $\mathrm{N_2}$, and solvent was removed from the product fractions by oil pump vacuum to give **3′e** as an air-sensitive, orange oil (0.059 g, 0.038 mmol, 35%). IR data: Table 1; MS (FAB$^+$): *m*/*z*: 1506 $[M-2\mathrm{CO}]^+$ (100%); elemental analysis calcd (%) for $\mathrm{C_{37}H_{14}F_{51}O_2Rh}$: C 28.44, H 0.90; found: C 28.33, H 1.09.

^{1}H NMR ($\mathrm{CDCl_3/CF_3C_6F_5}$, 1:1 v/v): $\delta = 2.25$–2.28 (m; 3 × $\mathrm{CH_2C}\mathit{H}_2\mathrm{CF_2}$), 2.46–2.55 (m; 3 × $\mathrm{C}\mathit{H}_2\mathrm{CH_2CF_2}$), 5.34 ppm (s; 2 × $\mathrm{C}\mathit{H}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$: $\delta = 17.9$ (s; 2 × $\mathit{C}\mathrm{H_2CH_2CF_2}$), 19.8 (s; 1 × $\mathit{C}\mathrm{H_2CH_2CF_2}$), 32.2–32.5 (apparent m; 3 × $\mathrm{CH_2}\mathit{C}\mathrm{H_2CF_2}$), 82.4 (d, $^1J(\mathrm{C,Rh}) = 4.3$ Hz; 2 × $\mathit{C}\mathrm{H}$), 100.5 (d, $^1J(\mathrm{C,Rh}) = 4.5$ Hz; 1 × $\mathit{C}\mathrm{CH_2CH_2CF_2}$), 100.8 (d, $^1J(\mathrm{C,Rh}) = 4.5$ Hz; 2 × $\mathit{C}\mathrm{CH_2CH_2CF_2}$) 192.0 ppm (d, $^1J(\mathrm{C,Rh}) = 84.5$ Hz; CO).

Partition coefficients: The following are representative.

A) A 10 mL vial was charged with **3b** (0.0502 g, 0.0324 mmol), $\mathrm{CF_3C_6F_{11}}$ (2.000 mL), and toluene (2.000 mL), fitted with a mininert valve, and gently heated until **3b** dissolved. The vial was vigorously shaken (2 min) to ensure good phase mixing, and was kept for 12–24 h at room temperature (23 °C). An aliquot (0.500 mL) was removed from each layer and taken to dryness (oil pump vacuum). $\mathrm{CF_3C_6F_{11}}$ (1.000 mL) was then added to each residue, and the solutions were analyzed by HPLC (average of five 10 µL autoinjections, 200 × 4 mm Nucleosil 100–5 column, UV/visible detector). No **3b** could be detected in the toluene phase. To establish a detection limit, a 10 mL volumetric flask was charged with **3b** (0.0050 g, 0.0032 mmol) and $\mathrm{CF_3C_6F_{11}}$ (10 mL). An aliquot (1.000 mL) was diluted to 4.000 mL, giving a concentration of $1.25 \times 10^{-4}\,\mathrm{g\,mL^{-1}}$. When this solution was analyzed by HPLC, **3b** was easily detected. Another aliquot (1.000 mL) was diluted to 2.000 mL, giving a concentration of $6.25 \times 10^{-5}\,\mathrm{g\,mL^{-1}}$. The **3b** was still detectable. The 0.500 mL toluene aliquot therefore contained less than 3.12×10^{-5} g of **3b**, and the 2.000 mL toluene phase less than 1.25×10^{-4} g of **3b**. This corresponds to a $\mathrm{CF_3C_6F_{11}}$/toluene partition coefficient of $>99.8:<0.2$.

B) Compound **3′d** (0.0502 g, 0.0360 mmol), $\mathrm{CF_3C_6F_{11}}$ (2.000 mL), and toluene (2.000 mL) were combined as in Procedure A. An aliquot (0.500 mL) was removed from each layer and taken to dryness (oil pump vacuum). A stock solution of eicosane in $\mathrm{CF_3C_6H_5}$ (2.000 mL, 0.00449 M) was added to both aliquots. GLC analysis showed 0.00897 mmol of **3′d** in the $\mathrm{CF_3C_6F_{11}}$ aliquot (average of five injections). The toluene phase gave no signal for **3′d**, indicating a partition coefficient of $>99.7:<0.3$.

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