π Complexes of Fluorous Alkynes, Cyclobutadienes, and Benzenes: Syntheses and Phase Properties of Cobalt and Chromium Tricarbonyl Adducts

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Reactions of $Cr(CO)_6$ and fluorous benzenes $C_6H_{6-x}((CH_2)_3R_{f8})_x$ ($x =$ **a**, 1; **b**, 2 (1,2); **c**, 2 (1,3); **d**, 2 (1,4); **e**, 3 (1,3,5); $R_{f8} = (CF_2)_7CF_3$; dibutyl ether, 140 °C) give the π complexes $(\eta^6\text{-}C_6H_{6-x}((CH_2)_3R_{f8})_x)$-$Cr(CO)_3$ (**1a−e**; 92−42%); $p\text{-}R_{f8}(CH_2)_3C_6H_4CH(S(CH_2)_3R_{f8})(CH_2)_2R_{f8}$ affords an analogous adduct (**1f**; 47%). The $CF_3C_6F_{11}$/toluene partition coefficients of **1a−f** increase with the number of ponytails (three, 99:1 to 97:3; two, 91:9; one, 49:51); the fluorophilicities are only slightly less than **a−f**. The IR ν_{CO} values show any residual inductive effect of the perfluoroalkyl groups at chromium to be slight. The reaction of $LiC\equiv CSi(CH_3)_3$ and $R_{f8}(CH_2)_3I$ gives the fluorous alkyne $R_{f8}(CH_2)_3C\equiv CSi(CH_3)_3$ (**2**; 63%). Addition of wet $n\text{-}Bu_4N^+$ F^- affords $R_{f8}(CH_2)_3C\equiv CH$ (71%), which upon treatment with t-BuLi and $R_{f8}(CH_2)_3I$ yields $R_{f8}(CH_2)_3C\equiv C(CH_2)_3R_{f8}$ (**4**; 58%). The reaction of **2** and $Co_2(CO)_8$ gives the alkyne complex $Co_2(CO)_6(\eta^2\text{-}\mu\text{-}R_{f8}(CH_2)_3CCSi(CH_3)_3)$ (88%). Reactions of **2** or **4** with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (2:1, decane, 150−160 °C) give the π cyclobutadiene complexes $(\eta^5\text{-}C_5H_5)Co\{\eta^4\text{-}C_4[Z]_2[(CH_2)_3R_{f8}]_2\}$ (Z = $Si(CH_3)_3$, **6**, 70%; $(CH_2)_3R_{f8}$, **7**, 32%). The $CF_3C_6F_{11}$/toluene partition coefficients show **6** and **7** to be more fluorophilic than their precursors **2** and **4**, despite the added $(\eta^5\text{-}C_5H_5)Co$ groups.

Introduction

Over the past decade, a variety of fluorous monofunctional organic compounds have been prepared for use as catalysts, reagents, and building blocks for more complex molecules.[1] Many of these, such as phosphines[2] and thioethers,[3] have been converted to isolable metal complexes. Complexes of multidentate or polyhapto fluorous ligands such as polyamines, salen, and cyclopentadienyl have also been characterized.[4,5] However, π complexes of fluorous alkynes, cyclobutadienes, and arenes—the "lower annulenes"—have remained unknown. These ligand types play significant roles in organometallic chemistry and catalysis.[6−8] Given the many unique properties and variety of applications associated with fluorous metal complexes, and the synthetic complications sometimes encountered due to phase properties or residual electronic effects of the perfluoroalkyl segments of the ponytails,[9] we sought to verify that such species could be accessed by standard methods.

We have reported efficient syntheses of fluorous benzenes featuring one, two, and three ponytails of the formula $(CH_2)_3$-$(CF_2)_7CF_3$ (abbreviated $(CH_2)_3R_{f8}$).[10] We have also studied their iodination and developed easily recyclable hypervalent iodide reagents.[11] However, we thought that certain transformations might be more tractable with the corresponding chromium tricarbonyl complexes. These syntheses constituted the starting point for the studies below. In a parallel effort, we set out to prepare simple fluorous alkynes,[12] an objective that has also been pursued in another group.[13] Among other applications, we sought to test the feasibility of cobalt complex formation, as well as cyclodimerizations to cobalt cyclobutadiene adducts. As described in the following narrative, all of the preceding objectives could be successfully realized.

Results

1. Fluorous Chromium Arene Complexes. Fluorous benzenes with one to three ponytails, $C_6H_{6-x}((CH_2)_3R_{f8})_x$ ($x =$ **a**,

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(5) Selected lead references: (a) Hughes, R. P.; Trujillo, H. A. *Organometallics* **1996**, *15*, 286. (b) Čermák, J.; Šťastná, L.; Sýkora, J.; Císařová, I.; Kvíčala, J. *Organometallics* **2004**, *23*, 2850, and earlier work cited therein. (c) Dinh, L. V.; Gladysz, J. A. *Chem. Commun.* **2004**, 998; *Chem. Eur. J.* **2005**, *12*, 7211.

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(9) (a) Gladysz, J. A. In *Handbook of Fluorous Chemistry*; Gladysz, J. A., Curran, D. P., Horváth, I. T., Eds.; Wiley/VCH: Weinheim, 2004; Chapter 5. (b) Jiao, H.; Le Stang, S.; Soós, T.; Meier, R.; Kowski, K.; Rademacher, P.; Jafarpour, L.; Hamard, J.-B.; Nolan, S. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 1516.

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Scheme 1. Syntheses of Fluorous Chromium Arene Complexes[a]
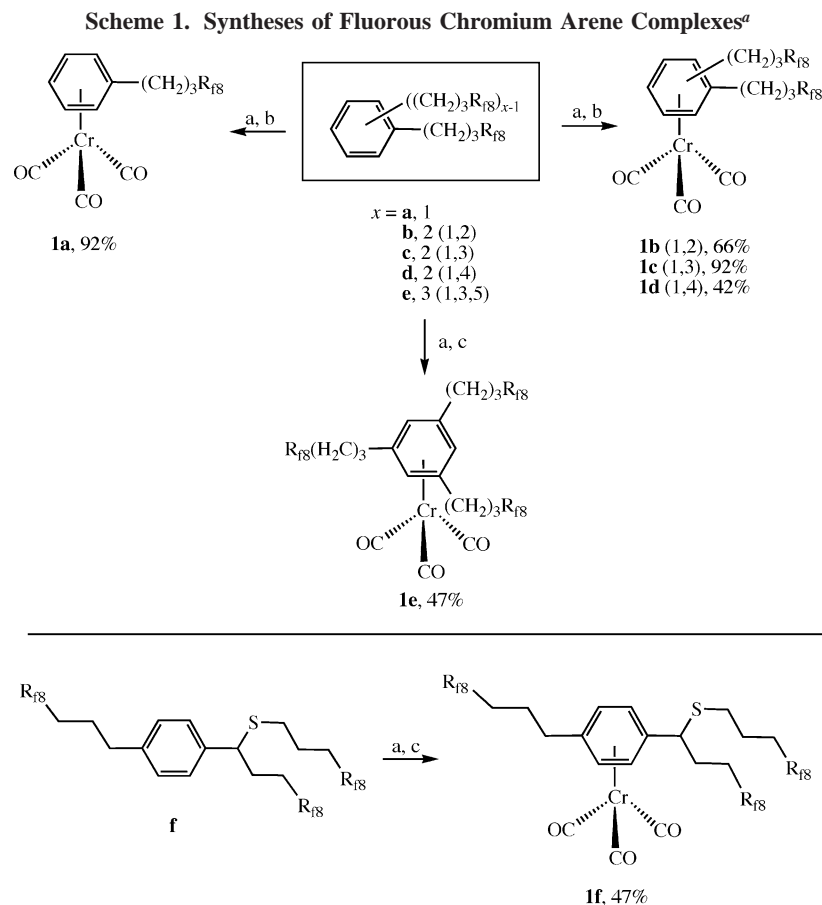
[a] (a) $Cr(CO)_6$, 140 °C, 18−24 h; (b) dibutyl ether/THF; (c) dibutyl ether/THF/$CF_3C_6H_5$.

1; **b**, 2 (1,2); **c**, 2 (1,3); **d**, 2 (1,4); **e**, 3 (1,3,5)),[10] were treated with $Cr(CO)_6$ under standard conditions for the formation of chromium arene tricarbonyl complexes (dibutyl ether, 140 °C).[14] As shown in Scheme 1 (top), workups gave the target complexes (η^6-C_6H_{6-x}((CH_2)$_3R_{f8}$)$_x$)$Cr(CO)_3$ (**1a−e**) as analytically pure light yellow crystals in 92−42% yields. As summarized in Table 1, the melting points were somewhat higher than normal for fluorous compounds (ca. 100 to 130 °C). DSC measurements showed no other phase transitions.

Complexes **1a−e** were characterized by mass spectrometry and IR and NMR (^{1}H, ^{13}C) spectroscopy, as summarized in the Experimental Section. The mass spectra showed intense peaks for the molecular ion and free arene. The NMR spectra exhibited chemical shifts typical of arenes coordinated to $Cr(CO)_3$. The IR ν_{CO} values (Table 1; 1972−1970 and 1899−1900 cm^{-1}) varied little from compound to compound, indicative of comparable chromium/CO back-bonding. They were close to those of the parent compound (η^6-C_6H_6)$Cr(CO)_3$ under identical conditions (1976 and 1897 cm^{-1}). Hence, the (CH_2)$_3$ spacers and five intervening σ bonds provide a high degree of insulation of the chromium from the electron-withdrawing perfluoroalkyl segments.

As summarized in Table 1, **1a−e** were very soluble in the fluorous solvent $CF_3C_6F_{11}$ (perfluoro(methylcyclohexane)) and the hybrid solvent $CF_3C_6H_5$ (α,α,α-trifluorotoluene). Complex **1a**, with a single ponytail, was highly to moderately soluble in common organic solvents. However, commensurate with other series of fluorous compounds,[5c] solubilities in organic solvents diminished as the numbers of ponytails increased. Complex **1e**,

with three ponytails, was insoluble or very sparingly soluble in hexanes, ether, and CHCl$_3$.

The $CF_3C_6F_{11}$/toluene partition coefficients were determined by HPLC as described in the Experimental Section. The values, summarized in Table 1, show that the fluorophilicities are only slightly lower than those of the free arenes.[10] In the case of **1e**, a small amount of complex can be detected in the nonfluorous phase, as opposed to none for the free arene **e**. Monoiodide derivatives of these arenes give distinctly less biased partition coefficients.[11] Hence, π $Cr(CO)_3$ substituents diminish fluorophilicities much less than other functional groups.

We sought to verify that functionalized fluorous arenes could be complexed as effectively as the model compounds **a−e**. Thus, as shown in Scheme 1 (bottom), the sulfur-containing arene p-R_{f8}(CH_2)$_3C_6H_4CH$(S(CH_2)$_3R_{f8}$)(CH_2)$_2R_{f8}$ (**f**)[15] and $Cr(CO)_6$ were reacted under similar conditions. The corresponding π complex **1f** was isolated in 47% yield. The fluorophilicity of **1f** was slightly less than that of **1e**, the molecular formulas of which differ by a sulfur atom, and slightly less than that of the free ligand **f** (Table 1).

2. Fluorous Alkyne and Cyclobutadiene Complexes. To access model fluorous alkynes, standard procedures for the deprotonation and alkylation of terminal alkynes were adapted.[16] As shown in Scheme 2, LiC≡CSi(CH_3)$_3$ (commercial or generated from HC≡CSi(CH_3)$_3$ and t-BuLi) and the fluorous alkyl iodide R_{f8}(CH_2)$_3$I[17] were combined in THF at −20 °C.

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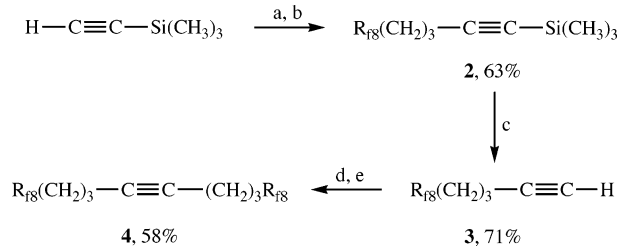
Table 1. IR and Phase Properties of Fluorous Arenes and Chromium Complexes

compound	IR ν_{CO} (cm^{-1})^a	melting point (°C) capillary	melting point (°C) DSC (T_e)	partition coefficient (CF$_3$C$_6$F$_{11}$/toluene, 23 °C)^b	solubilities^c CF$_3$C$_6$H$_5$	CF$_3$C$_6$F$_{11}$	hexanes	THF	acetone	MeOH	CH$_2$Cl$_2$	CHCl$_3$	ether	CH$_3$CN
1a	1972/1900	98–102	118.4	49.0:51.0	high	high	moderate	high	high	high	high	moderate	moderate	high
1b	1972/1899	96–97	106.9	91.0:9.0	high	high	low	high	high	high	high	moderate	moderate	high
1c	1972/1899	128–130	131.2	90.8:9.2	high	high	low	high	high	high	high	moderate	moderate	high
1d	1972/1899	103–107	120.1	90.5:9.5	high	high	low	high	high	high	high	moderate	moderate	high
1e	1970/1900	108–111	119.9	98.9:1.1	high	high	none	high	high	moderate	moderate	v. low	v. low	moderate
1f	1972/1903	89–94	95.0	97.5:2.5	high	high	none	high	high	moderate	moderate	v. low	v. low	moderate
a^d		oil		49.5:50.5	high	high	moderate	high	high	high	high	high	high	high
b^d				91.2:8.8	high	high	moderate	high	high	high	high	high	high	high
c^d		68		90.7:9.3	high	high	moderate	high	high	high	high	high	high	high
d^d		84–85		91.1:8.9	high	high	moderate	high	high	high	high	high	high	high
e^d		60–61		>99.7:<0.3	high	high	none	high	high	moderate	moderate	low	low	moderate
f^d		48	47.8	98.7:1.3	high	high	v. low	high	high	moderate	moderate	low	low	moderate

^{a} Recorded in CF$_3$C$_6$H$_5$. IR ν_{CF} bands are also observed (1243–1116 s br). Data under identical conditions for reference compound (η^6-C$_6$H$_6$)Cr(CO)$_3$: 1976/1897. ^{b} Determined by HPLC. ^{c} Based upon mass. ^{d} Melting points and partition coefficients for these compounds are taken from refs 10 and 15.

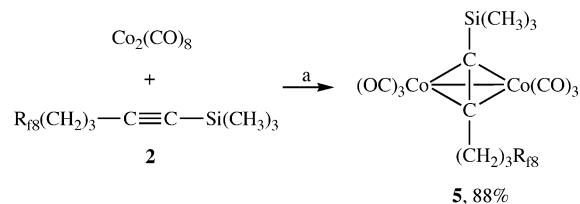## Scheme 2. Syntheses of Fluorous Alkynes^a

H—C≡C—Si(CH$_3$)$_3$ →(a, b)→ R$_{f8}$(CH$_2$)$_3$—C≡C—Si(CH$_3$)$_3$ **2**, 63%

↓ c

R$_{f8}$(CH$_2$)$_3$—C≡C—H **3**, 71%

→(d, e)→ R$_{f8}$(CH$_2$)$_3$—C≡C—(CH$_2$)$_3$R$_{f8}$ **4**, 58%

^{a} (a) *t*-BuLi, THF, −20 °C; (b) R$_{f8}$(CH$_2$)$_3$I, rt, 12 h; (c) *n*-Bu$_4$N$^+$F$^-$·3H$_2$O, THF, rt, 12 h; (d) *t*-BuLi, THF, −78 °C; (e) DMPU, R$_{f8}$(CH$_2$)$_3$I, reflux, 7 h.

Table 2. CF$_3$C$_6$F$_{11}$/Toluene Partition Coefficients of Fluorous Alkynes and Cobalt Cyclobutadiene Complexes (23 °C)

compound	value	method
2	57.4:42.6	^{19}F NMR
3	76.3:23.7	^{19}F NMR
4	95.4:4.6	^{19}F NMR
6a	82.4:17.6	^{19}F NMR
	82.9:17.1	HPLC
7	98.9:1.1	^{19}F NMR
	98.5:1.5	HPLC

Scheme 3. Synthesis of a Fluorous Cobalt Alkyne Complex^a

Co$_2$(CO)$_8$ + R$_{f8}$(CH$_2$)$_3$—C≡C—Si(CH$_3$)$_3$ (**2**) →(a)→ (OC)$_3$Co—[C(Si(CH$_3$)$_3$)=C((CH$_2$)$_3$R$_{f8}$)]—Co(CO)$_3$ **5**, 88%

^{a} (a) Hexane, −10 °C.

Distillation gave the analytically pure fluorous trimethylsilyl alkyne R$_{f8}$(CH$_2$)$_3$C≡CSi(CH$_3$)$_3$ (**2**) in 63% yield. The subsequent addition of wet *n*-Bu$_4$N$^+$F$^-$, followed by distillation, provided the fluorous terminal alkyne R$_{f8}$(CH$_2$)$_3$C≡CH (**3**) in 71% yield. Alkynes **2** and **3** were colorless oils and were characterized by IR and NMR (^{1}H, ^{13}C) spectroscopy (Experimental Section). All features were routine.

Next, **3** was sequentially treated with *t*-BuLi, DMPU,[16b,18] and R$_{f8}$(CH$_2$)$_3$I in THF at −78 °C (Scheme 2). The mixture was refluxed, and workup gave the analytically pure fluorous symmetrical alkyne R$_{f8}$(CH$_2$)$_3$C≡C(CH$_2$)$_3$R$_{f8}$ (**4**) in 58% yield. Compound **4** was a low-melting white solid and was characterized analogously to **2** and **3**. The CF$_3$C$_6$F$_{11}$/toluene partition coefficients of **2**–**4** were determined by ^{19}F NMR as described in the Experimental Section. As summarized in Table 2, the fluorophilicities progressively increased. However, the value for **3** was much lower than that of its trimer, the triply ponytailed arene **e** (76.3:23.7 vs >99.7:<0.3).

Complexes of the preceding compounds were sought. Alkynes are easily converted into dicobalt hexacarbonyl adducts. Following a standard procedure,[19] **2** and Co$_2$(CO)$_8$ (1:1.3) were combined in hexane (−10 °C). As shown in Scheme 3, chromatography gave the fluorous alkyne complex Co$_2$(CO)$_6$-(η^2-μ-R$_{f8}$(CH$_2$)$_3$CCSi(CH$_3$)$_3$) (**5**) in 88% yield, which was characterized analogously to the other new compounds above. The IR ν_{CO} values (2088, 2050, 2007 cm^{-1}) were very similar

(18) DMPU = 1,3-dimethyltetrahydro-2(1*H*)-pyrimidinone.
(19) Casagrande, O. L., Jr.; Gomes, E. L. S.; Dupont, J.; Burrow, R.; Lough, A. J. *J. Chem. Soc., Dalton Trans.* **2001**, 1634.

Scheme 4. Syntheses of Fluorous Cobalt Cyclobutadiene Complexes[a]

6a:6b 83:17, 70%

7, 32%
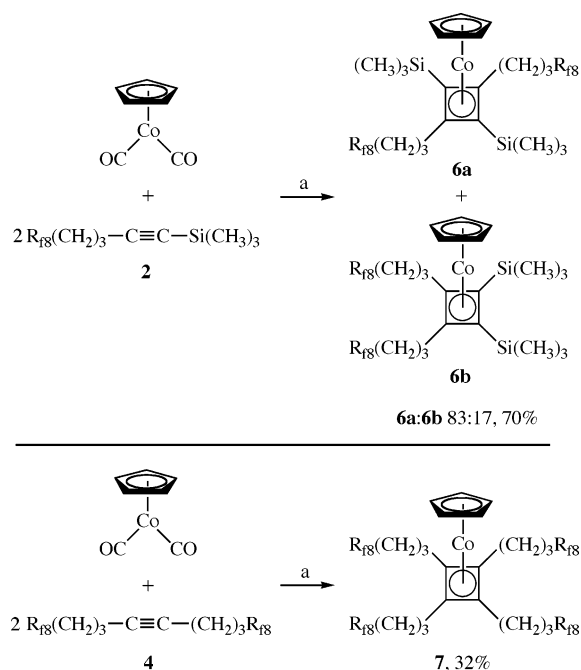
[a] (a) Decane, 150−160 °C, 4 h.

to those found with nonfluorous alkynes, including Si(CH$_3$)$_3$-substituted species (e.g., 2087, 2047, 2024, 2014, 2004 cm^{-1}).[20]

Alkynes are also easily converted into cobalt cyclobutadiene complexes.[6,7a,e] Following a standard procedure,[21] **2** and (η^5-C$_5$H$_5$)Co(CO)$_2$ (2:1) were reacted in decane at 150−160 °C. As shown in Scheme 4, workup gave the fluorous cyclobutadiene complex (η^5-C$_5$H$_5$)Co{η^4-C$_4$[(CH$_2$)$_3$R$_{f8}$]$_2$[Si(CH$_3$)$_3$]$_2$} (**6**) as a yellow oil in 70% yield. Compound **6** was isolated as 83:17 to 78:22 mixtures of two isomers (**6a** (trans), **6b** (cis)), as assayed by integration of the Si(CH$_3$)$_3$ and/or cyclopentadienyl ^{1}H NMR signals. Other ^{1}H and ^{13}C NMR signals (Experimental Section) were assigned on the basis of NMR data for related compounds.[21,22]

The isomers were separated by preparative TLC, and the stereochemistry was assigned from the mass spectrometric data (EI). As established earlier,[23] cis isomers of such cyclobutadiene ligands can fragment to give symmetrically and unsymmetrically substituted alkynes, but trans isomers can give only (in the absence of rearrangements) unsymmetrically substituted alkynes. Accordingly, the most intense peak in the mass spectrum of the minor isomer corresponded to the symmetrical alkyne **4**. Hence, the minor isomer was assigned the cis structure **6b**. Only a trace of this ion was observed in the mass spectrum of **6a**.

Finally, **4** and (η^5-C$_5$H$_5$)Co(CO)$_2$ were similarly reacted. As shown in Scheme 4, workup gave the quadruply ponytailed fluorous cyclobutadiene complex (η^5-C$_5$H$_5$)Co{η^4-C$_4$[(CH$_2$)$_3$R$_{f8}$]$_4$} (**7**) as a yellow solid in 32% yield. Complex **7** was much less soluble than **6** in hexanes and CHCl$_3$, but appreciable concentrations could be realized in THF, CF$_3$C$_6$H$_5$, and fluorous solvents. Other products formed, but were not characterized due to their

much poorer solubilities. The CF$_3$C$_6$F$_{11}$/toluene partition coefficients of **6a** and **7** were determined by both ^{19}F NMR and HPLC. The values were in good agreement, as summarized in Table 2. In both cases, the fluorophilicities were higher than those of the constituent alkynes, despite the incorporation of a nonfluorous (η^5-C$_5$H$_5$)Co moiety (e.g., (98.9−98.5):(1.1−1.5) vs 95.4:4.6 for **7** vs **4**).

Discussion

The preceding data show that the title complexes are very easily accessed, without complications or the need for special methods due to the ponytails or phase properties. Indeed, the (CH$_2$)$_3$R$_{f8}$ substituents appear to exert quite modest electronic effects at the metal centers. In all cases, the perfluoroalkyl segments are insulated by five intervening σ bonds. However, with heteroatom donor ligands of the formula D((CH$_2$)$_3$R$_{f8}$)$_y$L$_z$, electron-withdrawing effects can be easily detected at metal centers.[9]

The methodology used to access fluorous alkynes in Scheme 2 complements that reported by Kvíčala and co-workers.[13] They found that the terminal alkyne HC≡CSiPh(CH$_3$)$_2$ could be deprotonated and alkylated with the fluorous triflate R$_{f6}$(CH$_2$)$_2$-OTf (R$_{f6}$ = (CF$_2$)$_5$CF$_3$). The resulting R$_{f6}$(CH$_2$)$_2$C≡CSiPh(CH$_3$)$_2$ was desilylated, and the deprotonation/alkylation sequence repeated to give the symmetrical alkyne R$_{f6}$(CH$_2$)$_2$C≡C(CH$_2$)$_2$R$_{f6}$. The corresponding iodide R$_{f6}$(CH$_2$)$_2$I gave, in contrast to our results with R$_{f8}$(CH$_2$)$_3$I, little or no reaction. Fluorous alkylating agents R$_{fn}$(CH$_2$)$_m$X with two-methylene spacers are known to be much less electrophilic than those with three-methylene spacers.[9a]

The fluorous cyclobutadiene complex **7** contains a rare example of a "totally ponytailed" or "perfluorous" π ligand. Analogous cyclopentadienyl complexes are known,[5c] but they can be prepared only in low yields. Such molecules possess what might be viewed as a large "fluorous footprint" that may facilitate immobilization of fluorous surfaces. In this context, an obvious question is whether **4** or a similar fluorous alkyne might undergo cyclotrimerization to a hextuply ponytailed benzene.[24] In preliminary experiments using standard catalysts, we have obtained products with extraordinarily low solubilities. These reactions remain under investigation and will be detailed at a later date.

In all of the above compounds, the fluorophilicities increase with increasing numbers of ponytails. In the cases of ligands **a**−**f**, nonfluorous Cr(CO)$_3$ fragments of formula weight 136 can be added without greatly reducing the partition coefficients (Table 1). In contrast, when a hydrogen in **b**−**d** is replaced by iodine, which has an atomic weight of 127, values drop from (91.2−90.7):(8.8−9.3) to (74.7−69.3):(25.3−30.5).[11] Furthermore, in the case of alkynes **2** and **4**, cyclodimerizations followed by additions of nonfluorous (η^5-C$_5$H$_5$)Co fragments of formula weight 124 actually increase the partition coefficients (Table 2). Such phenomena, where the fluorophilicities of molecules are greater than those of the ligand components, are increasingly being recognized. For example, some fluorous metallocenes are more fluorophilic than the corresponding cyclopentadiene ligands,[5c] and the same can be observed with phosphine complexes.[2b,25] A similar relationship is evident with respect to the fluorous alkyne **3** and its cyclotrimer, benzene **e**.

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(24) See for example: Garcia, J. J.; Sierra, C.; Torrens, H. *Tetrahedron Lett.* **1996**, *37*, 6097.

(25) (a) Gladysz, J. A.; Emnet, C.; Rábai, J. In *Handbook of Fluorous Chemistry*; Gladysz, J. A., Curran, D. P., Horváth, I. T., Eds.; Wiley/VCH: Weinheim, 2004, Chapter 6.

In conclusion, families of fluorous alkynes, fluorous cyclobutadiene cobalt complexes, and fluorous arene chromium tricarbonyl complexes with gradated fluorophilicities and solubility properties are now readily available. Applications of these compounds and extensions of this chemistry will be reported in future publications.

Experimental Section

General Data. Reactions were conducted under N_2 atmospheres. Chemicals were treated as follows: THF, dibutyl ether, and toluene, distilled from Na/benzophenone; $CF_3C_6F_{11}$, $CF_3C_6F_5$, and $CF_3C_6H_5$ (Fluorochem or ABCR), distilled from CaH_2; *t*-BuLi (Acros, 1.5 M in pentane), standardized prior to use;[26] DMSO-d_6, benzene-d_6, $CDCl_3$, acetone-d_6, THF-d_8 (5 × Deutero GmbH), $Cr(CO)_6$ (Strem), HC≡CSi(CH$_3$)$_3$ (Acros, 98%), LiC≡CSi(CH$_3$)$_3$ (Acros, 0.5 M in THF), n-Bu$_4$N$^+$ F$^-$·3H$_2$O (Fluka, 1.0 M in THF), DMPU (Fluka, ≥ 99%),[18] Co$_2$(CO)$_8$ (Strem), decane (Aldrich, <0.005% water), (η^5-C$_5$H$_5$)Co(CO)$_2$ (Aldrich, tech.), and C$_6$F$_6$ (ABCR), used as received.

NMR spectra were recorded on standard 400 MHz spectrometers at 27.0 °C and referenced as follows: ^{1}H, residual internal acetone-d_5, $CHCl_3$, or THF-d_7 (δ = 2.05, 7.24, or 1.73 ppm); ^{13}C, internal benzene-d_6, DMSO-d_6, acetone-d_6, CDCl$_3$, or THF-d_8 (δ = 128.0, 39.5, 29.8, 77.0, or 25.2 ppm). Relative ^{1}H NMR integrations are given in the peak assignments (e.g., 3Ar$\textbf{CH}_2$). The highly coupled CF$_2$ and CF$_3$ ^{13}C signals are not listed. IR spectra were recorded with a ASI React-IR 1000 spectrometer. Mass spectra were measured using Micromass Zabspec (FAB) or Finnigan MAT 95 XP (EI) instruments. DSC and TGA data were recorded with a Mettler-Toledo DSC821 apparatus and treated by standard methods.[27] Microanalyses were conducted with a Carlo Erba EA1110 instrument.

(η^6-C$_6$H$_5$(CH$_2$)$_3$R$_{f8}$)Cr(CO)$_3$ (1a). A 20 cm Schlenk tube was fitted with a condenser and charged with C$_6$H$_5$(CH$_2$)$_3$R$_{f8}$ (1.00 g, 1.86 mmol),[10] Cr(CO)$_6$ (0.819 g, 3.72 mmol), dibutyl ether (5.0 mL), and THF (1.0 mL). The mixture was degassed and the tube placed in a 140 °C oil bath. After 18 h, the mixture was cooled and yellow flakes formed. The solvents were removed by oil pump vacuum and the excess Cr(CO)$_6$ by sublimation (50 °C, 1 mbar). The remaining yellow solid was washed with pentane. The pentane washings were cooled to −20 °C, giving a second crop of yellow solid. The combined solids were recrystallized from hot hexanes to give **1a** as yellow crystalline flakes (1.15 g, 1.71 mmol, 92%). Mp: 98−102 °C (capillary), 118.4 °C (DSC, T_e). TGA: onset of mass loss 156.5 °C (T_e). Anal. Calcd for C$_{20}$H$_{11}$CrF$_{17}$O$_3$: C, 35.63; H, 1.64. Found: C, 35.68; H, 1.60.

NMR: ^{1}H (δ, acetone-d_6) 5.70 (t, J_{HH} = 6.3 Hz, 2Ar$\textbf{H}_m$), 5.61 (d, J_{HH} = 6.3 Hz, 2Ar$\textbf{H}_o$), 5.52 (t, J_{HH} = 6.3 Hz, Ar$\textbf{H}_p$), 2.60 (t, J_{HH} = 8.1 Hz, Ar$\textbf{CH}_2$), 2.33−2.46 (m, CH$_2$C$\textbf{H}_2$CF$_2$), 1.90−2.01 (m, C$\textbf{H}_2$CH$_2$CF$_2$); ^{13}C{^{1}H} (benzene-d_6) 233.3 (s, 3$\textbf{C}$O), 90.2, 91.9, 93.4, 111.1 (4 s, Ar), 34.0 (s, Ar$\textbf{C}$H$_2$), 30.4 (t, $^2J_{CF}$ = 22 Hz, CH$_2\textbf{C}$H$_2$CF$_2$), 21.9 (s, $\textbf{C}$H$_2$CH$_2$CF$_2$). IR: Table 1. MS (positive FAB, m/z): 674 (M$^+$, 20%), 590 ([M$^+$ − 3CO], 37%), 538 (arene, 100%).

(η^6-1,2-C$_6$H$_4$((CH$_2$)$_3$R$_{f8}$)$_2$)Cr(CO)$_3$ (1b). A 20 cm Schlenk tube was fitted with a condenser and charged with 1,2-C$_6$H$_4$((CH$_2$)$_3$R$_{f8}$)$_2$ (0.502 g, 0.503 mmol),[10] Cr(CO)$_6$ (0.550 g, 2.52 mmol), dibutyl ether (5.0 mL), and THF (1.0 mL). The mixture was degassed and the tube placed in a 140 °C oil bath. After 24 h, the mixture was cooled and greenish yellow flakes (mixed with excess Cr(CO)$_6$) formed. The mixture was loaded onto a silica plug, which was flushed with CF$_3$C$_6$H$_5$. The solvents were removed from the yellow

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eluate by oil pump vacuum and the excess Cr(CO)$_6$ by sublimation (50 °C, 1 mbar). The remaining solid was washed with pentane to remove any free arene and recrystallized from hot CHCl$_3$ to give **1b** as greenish-yellow crystalline flakes (0.374 g, 0.330 mmol, 66%). Mp: 96−97 °C (capillary), 106.9 °C (DSC, T_e). TGA: onset of mass loss 185.3 °C (T_e). Anal. Calcd for C$_{31}$H$_{16}$CrF$_{34}$O$_3$: C, 32.80; H, 1.41. Found: C, 32.72; H, 1.45.

NMR: ^{1}H (δ, acetone-d_6) 5.71−5.73 (m, 2Ar$\textbf{H}$), 5.61−5.64 (m, 2Ar$\textbf{H}$), 2.57−2.61 (m, 2Ar$\textbf{CH}_2$), 2.40−2.51 (m, 2CH$_2$C$\textbf{H}_2$CF$_2$), 1.90−2.01 (m, 2C$\textbf{H}_2$CH$_2$CF$_2$); ^{13}C{^{1}H} (δ, 1:1 v/v benzene-d_6/CF$_3$C$_6$F$_5$) 233.3 (s, 3$\textbf{C}$O), 92.1, 93.5, 109.7 (3 s, Ar), 31.8 (s, 2Ar$\textbf{C}$H$_2$), 31.0−31.4 (m, 2CH$_2$C$\textbf{H}_2$CF$_2$), 22.5 (s, 2$\textbf{C}$H$_2$CH$_2$CF$_2$). IR: Table 1. MS (positive FAB, m/z): 1134 (M$^+$, 25%), 1050 ([M$^+$ − 3CO], 40%), 998 (arene, 100%).

(η^6-1,3-C$_6$H$_4$((CH$_2$)$_3$R$_{f8}$)$_2$)Cr(CO)$_3$ (1c). The compounds 1,3-C$_6$H$_4$((CH$_2$)$_3$R$_{f8}$)$_2$ (0.502 g, 0.503 mmol),[10] Cr(CO)$_6$ (0.550 g, 2.52 mmol), dibutyl ether (5.0 mL), and THF (1.0 mL) were combined in a procedure analogous to that for **1b**. An identical workup gave **1c** as yellowish crystalline flakes (0.524 g, 0.463 mmol, 92%). Mp: 128−130 °C (capillary), 131.2 °C (DSC, T_e). TGA: onset of mass loss 197.2 °C (T_e). Anal. Calcd for C$_{31}$H$_{16}$CrF$_{34}$O$_3$: C, 32.80; H, 1.41. Found: C, 32.30; H, 1.47.

NMR: ^{1}H (δ, acetone-d_6) 5.76 (t, J_{HH} = 6.5 Hz, 1Ar$\textbf{H}$), 5.60 (s, 1Ar$\textbf{H}$), 5.48 (dd, J_{HH} = 6.5 Hz, J_{HH} = 1.2 Hz, 2Ar$\textbf{H}$), 2.55−2.67 (m, 2Ar$\textbf{CH}_2$), 2.29−2.41 (m, 2CH$_2$C$\textbf{H}_2$CF$_2$), 1.88−2.02 (m, 2C$\textbf{H}_2$CH$_2$CF$_2$); ^{13}C{^{1}H} (δ, 1:1 v/v DMSO-d_6/CF$_3$C$_6$F$_5$) 233.4 (s, 3$\textbf{C}$O), 92.6, 94.7, 96.5, 114.6 (4 s, Ar), 34.4 (s, 2Ar$\textbf{C}$H$_2$), 30.3 (m, 2CH$_2$C$\textbf{H}_2$CF$_2$), 22.2 (s, 2$\textbf{C}$H$_2$CH$_2$CF$_2$). IR: Table 1. MS (positive FAB, m/z): 1134 (M$^+$, 21%), 1050 ([M$^+$ − 3CO], 38%), 998 (arene, 100%).

(η^6-1,4-C$_6$H$_4$((CH$_2$)$_3$R$_{f8}$)$_2$)Cr(CO)$_3$ (1d). The compounds 1,4-C$_6$H$_4$((CH$_2$)$_3$R$_{f8}$)$_2$ (1.005 g, 1.06 mmol),[10] Cr(CO)$_6$ (1.170 g, 5.30 mmol), dibutyl ether (5.0 mL), and THF (1.0 mL) were combined in a procedure analogous to that for **1b**. An identical workup gave **1d** as yellowish crystalline flakes (0.510 g, 0.445 mmol, 42%). Mp: 103−107 °C (capillary), 120.1 °C (DSC, T_e). TGA: onset of mass loss 196.0 °C (T_e). Anal. Calcd for C$_{31}$H$_{16}$CrF$_{34}$O$_3$: C, 32.80; H, 1.41. Found: C, 32.71; H, 1.65.

NMR: ^{1}H (δ, acetone-d_6) 5.67 (s, 4Ar$\textbf{H}$), 2.55 (t, J_{HH} = 8.03 Hz, 2Ar$\textbf{CH}_2$), 2.28−2.42 (m, 2CH$_2$C$\textbf{H}_2$CF$_2$), 1.89−1.99 (m, 2C$\textbf{H}_2$CH$_2$CF$_2$); ^{13}C{^{1}H} (δ, 1:1 v/v DMSO-d_6/CF$_3$C$_6$F$_5$) 234.3 (s, 3$\textbf{C}$O), 95.2, 112.0 (2 s, Ar), 33.6 (s, 2Ar$\textbf{C}$H$_2$), 30.3 (m, 2CH$_2$C$\textbf{H}_2$CF$_2$), 22.4 (s, 2$\textbf{C}$H$_2$CH$_2$CF$_2$). IR: Table 1. MS (positive FAB, m/z): 1134 (M$^+$, 23%), 1050 ([M$^+$ − 3CO], 40%), 998 (arene, 100%).

(η^6-1,3,5-C$_6$H$_3$((CH$_2$)$_3$R$_{f8}$)$_3$)Cr(CO)$_3$ (1e). A 20 cm Schlenk tube was fitted with a condenser and charged with 1,3,5-C$_6$H$_3$-((CH$_2$)$_3$R$_{f8}$)$_3$ (0.250 g, 0.173 mmol),[10] Cr(CO)$_6$ (0.190 g, 0.865 mmol), dibutyl ether (5 mL), THF (1.0 mL), and CF$_3$C$_6$H$_5$ (1.0 mL). The mixture was degassed and the tube placed in a 140 °C oil bath. After 24 h, the darkened mixture was cooled. Some Cr-(CO)$_6$ precipitated. The mixture, except for as much Cr(CO)$_6$ as possible, was loaded onto a silica plug, which was flushed with CF$_3$C$_6$H$_5$. The solvents were removed by oil pump vacuum to give a greenish-yellow solid. The remaining Cr(CO)$_6$ was removed by sublimation (50 °C, 1 mbar), and the excess arene by washing with pentane. The residue was recrystallized from hot CHCl$_3$ to give **1e** as greenish crystalline flakes (0.130 g, 0.081 mmol, 47%). Mp: 108−111 °C (capillary), 119.9 °C (DSC, T_e). TGA: onset of mass loss 230.1 °C (T_e). Anal. Calcd for C$_{42}$H$_{21}$CrF$_{51}$O$_3$: C, 31.64; H, 1.33. Found: C, 31.89; H, 1.67.

NMR: ^{1}H (δ, acetone-d_6) 5.52 (s, 3Ar$\textbf{H}$), 2.65 (t, J_{HH} = 8.0 Hz, 3Ar$\textbf{CH}_2$), 2.28−2.41 (m, 3CH$_2$C$\textbf{H}_2$CF$_2$), 1.99−2.03 (m, 3C$\textbf{H}_2$CH$_2$CF$_2$); ^{13}C{^{1}H} (δ, 1:1 v/v benzene-d_6/CF$_3$C$_6$F$_5$) 234.7 (s, 3$\textbf{C}$O), 93.1, 115.3 (2 s, Ar), 34.4 (s, 3Ar$\textbf{C}$H$_2$), 30.3 (m, 3CH$_2$C$\textbf{H}_2$CF$_2$), 22.7 (s, 3$\textbf{C}$H$_2$CH$_2$CF$_2$). IR: Table 1. MS (positive FAB, m/z): 1594 (M$^+$, 20%), 1510 ([M$^+$ − 3CO], 35%), 1458 (arene, 100%).

[η⁶-(p-R$_{f8}$(CH$_2$)$_3$C$_6$H$_4$CH(S(CH$_2$)$_3$R$_{f8}$)(CH$_2$)$_2$R$_{f8}$)]Cr(CO)$_3$ (1f). The compounds p-R$_{f8}$(CH$_2$)$_3$C$_6$H$_4$CH(S(CH$_2$)$_3$R$_{f8}$)(CH$_2$)$_2$R$_{f8}$ (0.500 g, 0.335 mmol),[11] Cr(CO)$_6$ (0.369 g, 1.68 mmol), dibutyl ether (5.0 mL), THF (1.0 mL), and CF$_3$C$_6$H$_5$ (1.0 mL) were combined in a procedure analogous to that for **1e**. An identical workup gave **1f** as yellowish crystalline flakes (0.256 g, 0.157 mmol, 47%). Mp: 89−94 °C (capillary), 95.0 °C (DSC, T_e). TGA: onset of mass loss 204.0 °C (T_e). Anal. Calcd for C$_{42}$H$_{21}$CrF$_{51}$O$_3$S: C, 31.01; H, 1.30. Found: C, 30.91; H, 1.26.

NMR (δ, acetone-d_6): ¹H 5.92−5.94 (m, 2Ar*H*), 5.58−5.60 (m, 2Ar*H*), 3.74 (m, SC*H*CH$_2$CH$_2$CF$_2$), 2.80−2.83 (m, ArC*H$_2$*CH$_2$-CH$_2$CF$_2$), 2.60−2.62 (m, SC*H$_2$*CH$_2$CH$_2$CF$_2$), 2.54−2.56 (m, SCH$_2$C*H$_2$*CH$_2$CF$_2$), 2.32−2.37 (m, 3CH$_2$C*H$_2$*CF$_2$), 1.98−2.00 (m, ArCH$_2$C*H$_2$*CH$_2$CF$_2$), 1.86−1.90 (m, SCHC*H$_2$*CH$_2$CF$_2$); ¹³C{¹H} 234.3 (s, 3*C*O), 93.2, 93.3, 95.0, 97.2, 113.7, 114.7 (6 s, Ar), 47.5 (s, CH$_2$S*C*HCH$_2$CH$_2$CF$_2$), 47.4 (s, S*C*H$_2$CH$_2$CH$_2$CF$_2$), 34.4 (s, *C*H$_2$-CH$_2$CH$_2$CF$_2$), 30.8 (m, CH$_2$CH$_2$*C*H$_2$CF$_2$), 30.4 (m, CH$_2$SCHCH$_2$*C*H$_2$-CF$_2$), 26.8 (m, SCH$_2$CH$_2$*C*H$_2$CF$_2$), 23.0 (s, CH$_2$*C*H$_2$CH$_2$CF$_2$), 21.3 (s, CH$_2$SCH*C*H$_2$CH$_2$CF$_2$), 14.2 (s, SCH$_2$*C*H$_2$CH$_2$CF$_2$). IR: Table 1. MS (positive FAB, m/z): 1627 (M⁺, 18%), 1543 ([M⁺ − 3CO], 30%), 997 ([arene − SCH$_2$CH$_2$CH$_2$CF$_2$], 100%).

R$_{f8}$(CH$_2$)$_3$C≡CSi(CH$_3$)$_3$ (2). A Schlenk flask was charged with a THF solution of LiC≡CSi(CH$_3$)$_3$ (0.5 M; 10 mL, 5 mmol)[28] and cooled to −10 °C. A solution of R$_{f8}$(CH$_2$)$_3$I (1.50 g, 2.56 mmol)[17] in THF (6.0 mL) was added. The mixture was stirred for 12 h while warming to room temperature. The clear brown solution was diluted with hexanes (10 mL), washed with aqueous NH$_4$Cl (2 × 40 mL) and brine (40 mL), and dried (MgSO$_4$). The solvent was removed by rotary evaporation. The brown oil (pure by NMR; >90%) was distilled under oil pump vacuum to give **2** as a colorless oil (0.917 g, 1.64 mmol, 63%). Bp: 56 °C, 0.0054 mbar. Anal. Calcd for C$_{16}$H$_{15}$F$_{17}$Si: C, 34.42; H, 2.71. Found: C, 34.45; H, 2.52.

NMR (δ, CDCl$_3$): ¹H 2.35 (t, ³J_{HH} = 6.9 Hz, C*H$_2$*C≡), 2.22 (m, CF$_2$C*H$_2$*), 1.82 (m, 2H, CF$_2$CH$_2$C*H$_2$*), 0.15 (s, Si(C*H$_3$*)$_3$); ¹³C{¹H} 104.9 (s, ≡*C*Si), 86.4 (s, CH$_2$*C*≡), 29.9 (t, ²J_{CF} = 22 Hz, CF$_2$*C*H$_2$), 19.7 (s, *C*H$_2$C≡), 19.3 (CF$_2$CH$_2$*C*H$_2$), 0.0 (s, Si(*C*H$_3$)$_3$). IR (cm⁻¹, film): $\nu_{C≡C}$ 2181 w; ν_{CF} 1239−1116 s br.

R$_{f8}$(CH$_2$)$_3$C≡CH (3). A round-bottom flask was charged with a solution of **2** (0.6002 g, 1.075 mmol) in THF (5.0 mL) and n-Bu$_4$N⁺F⁻·3H$_2$O (1.0 M in THF, 1.6 mL, 1.6 mmol). The mixture was stirred and immediately turned deep brown. After 12 h, water (10 mL) was added. The mixture was extracted with hexanes (3 × 10 mL). The extract was washed with brine (20 mL) and dried (MgSO$_4$). The solvent was removed by rotary evaporation, and the yellow oil was distilled under oil pump vacuum to give **3** as a colorless oil (0.369 g, 0.759 mmol, 71%). Bp: 28 °C, 0.0055 mbar.

NMR (δ, CDCl$_3$): ¹H 2.32 (td, ³J_{HH} = 6.8 Hz, ⁴J_{HH} = 2.6 Hz, C*H$_2$*C≡), 2.20 (m, CF$_2$C*H$_2$*), 2.01 (t, ⁴J_{HH} = 2.6 Hz, ≡C*H*), 1.84 (m, CF$_2$CH$_2$C*H$_2$*); ¹³C{H} 82.3 (s, CH$_2$*C*≡), 69.8 (s, ≡*C*H), 29.9 (t, ²J_{CF} = 22 Hz, CF$_2$*C*H$_2$), 19.3 (s, CF$_2$CH$_2$*C*H$_2$), 17.9 (s, *C*H$_2$C≡). IR (cm⁻¹, film): $\nu_{C≡H}$ 3320 w; ν_{CF} 1235−1116 s br.

R$_{f8}$(CH$_2$)$_3$C≡C(CH$_2$)$_3$R$_{f8}$ (4). A Schlenk flask was charged with a solution of **3** (0.450 g, 0.926 mmol) in THF (4.0 mL) and cooled to −78 °C. Then t-BuLi (1.58 M in pentane, 0.63 mL, 1.0 mmol) was added with stirring. The solution was allowed to warm to room temperature. Then DMPU (0.12 mL, 0.13 g, 1.0 mmol)[18] and a solution of R$_{f8}$(CH$_2$)$_3$I (0.600 g, 1.02 mmol)[17] in THF (4.0 mL) were added. The mixture was refluxed for 7 h and cooled to room temperature. Then HCl (3 M, 5.0 mL) was added. The mixture was extracted with hexanes (3 × 30 mL). The extract was washed with water and dried (MgSO$_4$). The solvent was removed by rotary evaporation. The brown oil was chromatographed on silica gel with hexanes and hexanes/ether (1:1 v/v). The solvent was removed from the product-containing fractions by rotary evaporation to give **4** as

a white solid (0.506 g, 0.535 mmol, 58%). Mp: 33.8 °C (DSC, T_e). Anal. Calcd for C$_{24}$H$_{12}$F$_{34}$: C, 30.46; H, 1.28. Found: C, 30.62; H, 1.02.

NMR (δ, CDCl$_3$): ¹H 2.28 (t, ³J_{HH} = 6.6 Hz, 2C*H$_2$*C≡), 2.24−2.11 (m, 2CF$_2$C*H$_2$*), 1.81−1.74 (m, 2CF$_2$CH$_2$C*H$_2$*); ¹³C{¹H} 79.7 (s, 2CH$_2$*C*≡), 29.9 (t, ²J_{CF} = 22 Hz, 2CF$_2$*C*H$_2$), 19.7 (2CF$_2$-CH$_2$*C*H$_2$), 18.1 (s, 2*C*H$_2$C≡). IR (cm⁻¹, film): ν_{CF} 1239−1112 s br. MS (EI, m/z): 946 ([M]⁺, 100% vs peaks with m/z >600), 927 ([M − F]⁺, 19%), 907 ([M − 2F − H]⁺, 5%).

Co$_2$(CO)$_6$(η²-μ-R$_{f8}$(CH$_2$)$_3$CCSi(CH$_3$)$_3$) (5). A Schlenk flask was charged with Co$_2$(CO)$_8$ (0.444 g, 1.29 mmol) and hexane (5 mL) and cooled to −10 °C. A solution of **2** (0.502 g, 0.899 mmol) in hexane (5.0 mL) was slowly added with stirring. The mixture was allowed to warm to room temperature. After 24 h, the solvent was removed under vacuum and the residue chromatographed on silica gel with hexanes. The solvent was removed from the first fraction to give **5** as a red oil (0.670 g, 0.794 mmol, 88%). Anal. Calcd for C$_{22}$H$_{15}$F$_{17}$O$_6$SiCo$_2$: C, 31.30; H, 1.79. Found: C, 31.11; H, 2.52.

NMR (δ, CDCl$_3$): ¹H 3.02 (t, ³J_{HH} = 8.1 Hz, CF$_2$CH$_2$CH$_2$C*H$_2$*), 2.27 (m, CF$_2$CH$_2$C*H$_2$*CH$_2$), 1.97 (m, CF$_2$C*H$_2$*), 0.30 (s, Si(C*H$_3$*)$_3$); ¹³C{¹H} 200.0 (br s, 6*C*O), 110.2 (s, *C*Si(CH$_3$)$_3$), 79.2 (s, CF$_2$CH$_2$-CH$_2$CH$_2$*C*), 34.5 (s, CF$_2$CH$_2$CH$_2$*C*H$_2$), 30.6 (t, ²J_{CF} = 22 Hz, CF$_2$*C*H$_2$), 22.9 (s, CF$_2$CH$_2$*C*H$_2$CH$_2$), 0.6 (s, Si(*C*H$_3$)$_3$). IR (cm⁻¹, film): ν_{CO} 2088 s, 2050 s, 2007 s; ν_{CF} 1239−1112 s br. MS (positive FAB, m/z): 828 (M⁺ − CH$_3$, 31%), 815 ([M⁺ − CO], 48%), 787 ([M⁺ − 2CO], 71%), 759 ([M⁺ − 3CO], 100%), 731 ([M⁺ − 4CO], 84%), 703 ([M⁺ − 5CO], 56%), 675 ([M⁺ − 6CO], 28%), 617 ([M⁺ − 6CO − Co], 23%).

(η⁵-C$_5$H$_5$)Co{η⁴-C$_4$[(CH$_2$)$_3$R$_{f8}$]$_2$[Si(CH$_3$)$_3$]$_2$} (6). A Schlenk flask was charged with (η⁵-C$_5$H$_5$)Co(CO)$_2$ (0.0872 g, 0.484 mmol), decane (5 mL), and a solution of **2** (0.602 g, 1.07 mmol) in decane (5 mL) and fitted with a condenser. The mixture was kept at 150−160 °C for 6 h, during which time N$_2$ was bubbled through the solution. The sample was cooled, and the decane was removed by oil pump vacuum (40−50 °C). The brown oily residue was flash chromatographed on silica gel with hexanes to give a yellow oil (0.425 g, 0.342 mmol, 70%), which ¹H NMR (CDCl$_3$) showed to be a 83:17 mixture of **6a** (trans isomer) and **6b** (cis isomer; see text for assignments). A portion of the mixture (0.208 g) was chromatographed (preparative TLC, hexanes) to give **6a** (0.142 g, 0.114 mmol) and **6b** (0.0315 g, 0.0254 mmol) as viscous yellow oils.

Data for **6a**. Anal. Calcd for C$_{37}$H$_{35}$F$_{34}$Si$_2$Co: C, 35.82; H, 2.84. Found: C, 35.65; H, 3.09. NMR (δ, CDCl$_3$): ¹H 4.75 (s, C$_5$*H$_5$*), 2.09 (m, 2C*H$_2$*CH$_2$C*H$_2$*CF$_2$), 1.68 (m, 2CH$_2$C*H$_2$*CH$_2$CF$_2$), 0.13 (s, 2Si(C*H$_3$*)$_3$); ¹³C{¹H} 90.2 (s, 2C of cyclobutadiene), 79.4 (s, C$_5$*H$_5$*), 64.4 (s, 2C of cyclobutadiene), 30.9 (t, ²J_{CF} = 24 Hz, 2*C*H$_2$CF$_2$), 28.8 (s, 2CH$_2$CH$_2$*C*H$_2$CF$_2$), 21.6 (s, 2CH$_2$CH$_2$CH$_2$CF$_2$), 1.0 (s, 2Si-(*C*H$_3$)$_3$). IR (cm⁻¹, film): ν_{CF} 1239−1112 s br. MS (positive FAB, m/z): 1240 (M⁺, 100%). MS (EI, m/z): 1240 (M⁺, 100%), 1221 ([M − F]⁺, 12%), 1168 ([M − Si(CH$_3$)$_3$]⁺, 18%), 946 ([R$_{f8}$-(CH$_2$)$_3$C≡C(CH$_2$)$_3$R$_{f8}$]⁺, 2%).

Data for **6b**. Anal. Calcd for C$_{37}$H$_{35}$F$_{34}$Si$_2$Co: C, 35.82; H, 2.84. Found: C, 34.95; H, 3.63. NMR (δ, CDCl$_3$): ¹H 4.76 (s, C$_5$*H$_5$*), 2.13 (m, 2C*H$_2$*CH$_2$C*H$_2$*CF$_2$), 1.63 (m, 2CH$_2$C*H$_2$*CH$_2$CF$_2$), 0.16 (s, 2Si(C*H$_3$*)$_3$); ¹³C{¹H} 92.1 (s, 2C of cyclobutadiene), 79.9 (s, C$_5$*H$_5$*), 68.8 (s, 2C of cyclobutadiene), 30.7 (t, ²J_{CF} = 24 Hz, 2*C*H$_2$CF$_2$), 29.9 (s, 2CH$_2$CH$_2$*C*H$_2$CF$_2$), 19.5 (s, 2CH$_2$CH$_2$CH$_2$CF$_2$), 0.4 (s, 2Si-(*C*H$_3$)$_3$). IR (cm⁻¹, film): ν_{CF} 1239−1112 s br. MS (positive FAB, m/z): 1240 (M⁺, 100%). MS (EI, m/z): 1240 (M⁺, 78%), 1221 ([M − F]⁺, 8%), 1168 ([M − Si(CH$_3$)$_3$]⁺, 15%), 946 ([R$_{f8}$(CH$_2$)$_3$C≡C(CH$_2$)$_3$R$_{f8}$]⁺, 100%).

(η⁵-C$_5$H$_5$)Co{η⁴-C$_4$[(CH$_2$)$_3$R$_{f8}$]$_4$} (7). Decane (5 mL), (η⁵-C$_5$H$_5$)-Co(CO)$_2$ (0.0571 g, 0.311 mmol), and a suspension of **4** (0.605 g, 0.642 mmol) in decane (5 mL) were combined in a procedure analogous to that for **6**. After decane removal, the brown oily residue was chromatographed on silica gel with hexanes and hexanes/ether

(9:1 v/v). The solvent was removed from the product-containing fractions by rotary evaporation to give **7** as a yellow solid (0.201 g, 0.0997 mmol, 32%). Mp: 61.3 °C (DSC, T_e). Anal. Calcd for $C_{53}H_{29}F_{68}Co$: C, 31.57; H, 1.45. Found: C, 31.38; H, 1.25.

NMR: ^1H (δ, THF-d_8) 4.67 (s, C_5H_5), 2.09 (m, 4CH_2CH$_2$CH_2-CF$_2$), 1.72 (m, 4CH_2CH$_2$CF$_2$); $^{13}C\{^1H\}$ (δ, THF-d_8) 80.8 (s, C_5H$_5$), 78.2, (s, 4C of cyclobutadiene), 31.4 (t, $^2J_{CF}$ = 22 Hz, 4CH_2CF$_2$), 26.9 (s, 4CH_2CH$_2$CH$_2$CF$_2$), 21.9 (s, 4CH_2CH$_2$CF$_2$). IR (cm^{-1}, film): ν_{CF} 1239−1116 s br. MS (positive FAB, *m/z*): 2016 (M$^+$, 100%).

Partition Coefficients. The following are representative. **A**. A 10 mL vial was charged with **1d** (0.105 g, 0.093 mmol), CF$_3$C$_6$F$_{11}$ (2.000 mL), and toluene (2.000 mL), fitted with a mininert valve, and gently heated until **1d** dissolved. The vial was vigorously shaken (2 min) to ensure good phase mixing and kept 12−24 h in a darkened location at room temperature (23 °C). An aliquot (0.500 mL) was removed from each layer and taken to dryness (oil pump vacuum). Then CF$_3$C$_6$F$_{11}$ (1.000 mL) was 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). The relative peak areas were 90.5:9.5. **B**. A 10 mL vial was charged with **2** (0.1168 g, 0.2093 mmol) and CF$_3$C$_6$F$_{11}$ (2.000 mL). After complete dissolution, toluene (2.000 mL) was added. The vial was vigorously shaken (2 min) and kept for 12 h in a darkened location at room temperature (23 °C). An aliquot (0.500 mL) was removed from each layer and added to a stock solution of C$_6$F$_6$ in CF$_3$C$_6$H$_5$ (0.200 mL, 0.1897 M). A DMSO-d_6 capillary was added, and ^{19}F NMR spectra were recorded. The area of the (CF$_2$)$_7$CF_3 signal was integrated versus that of C$_6$F$_6$. The procedure was repeated, giving an average partition coefficient of 57.4:42.6 (0.0171 g of **2** in 0.500 mL of CF$_3$C$_6$F$_{11}$; 0.0126 g of **2** in 0.500 mL of toluene). The total amount of **2** calculated from these data (0.119 g after a 2.000/0.500 scale factor) closely agrees with that utilized.