

## Preparation of ferrocenes with high fluororous-phase affinities

W. Gary Hollis Jr.<sup>\*,a</sup>, Matthew G. Poferl<sup>a,1</sup>, Michael D. Wolter<sup>a,1</sup>,  
Paul A. Deck<sup>b</sup>, Carla Slebodnick<sup>b</sup>

<sup>a</sup> Department of Chemistry, Roanoke College, Salem, VA 24153, USA

<sup>b</sup> Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, USA

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### Abstract

The reaction of 1,1'-bis(pentafluorophenyl)ferrocene with fluororous alkoxides having the general formula  $\text{NaOCH}_2(\text{CF}_2)_n\text{CF}_3$  ( $n = 0, 2, 5, 7$ , and 8) afforded a series of ferrocenes of general formula  $\{\eta^5\text{-4-}[\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{O}]\text{C}_6\text{F}_4\text{C}_5\text{H}_4\}_2\text{Fe}$  (**1**). The reaction of 1,1'-bis(4-tetrafluoropyridyl)ferrocene with the same fluororous alkoxides afforded a series of ferrocenes of general formula  $(\eta^5\text{-4-}\{2,6\text{-}[\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{O}]\}_2\text{C}_5\text{F}_2\text{N}\}\text{C}_5\text{H}_4)_2\text{Fe}$  (**2**). Perfluoro(methylcyclohexane)/toluene partition coefficients increase with the number (2 or 4) and length ( $n$ ) of the fluororous substituent. Complexes **1a** and **2a** (both  $n = 0$ ) were structurally characterized.

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**Keywords:** Fluororous-phase affinity; Ferrocene; Biphasic; Nucleophilic substitution; UV-vis

### 1. Introduction

Efficient recovery and recycling of both transition metal compounds and organic solvents help decrease the environmental impact of solution catalytic processes. One approach that has attracted considerable recent attention is the use of “fluororous” substituents to confine catalyst components to a secondary fluorocarbon phase [1–6]. The efficiency of this approach clearly depends on high fluororous-phase affinities. These affinities are often expressed in terms of the proportion of a given species that will be present in a fluorocarbon phase (often perfluoromethylcyclohexane, PFMC) after extraction with an equal volume of a hydrocarbon such as hexane or toluene. Alternatively one can express fluororous-phase affinity as a partition coefficient (Eq. (1)), an intensive property of the solute ( $X$ ) that does not depend explicitly on solvent volumes but instead reflects the relative concentrations (more generally activities) of the solute present in the fluorocarbon and hydrocarbon phases at equilibrium ( $[X]_F$  and  $[X]_H$ ,

respectively, in Eq. (1)):

$$Q = \frac{[X]_F}{[X]_H} \quad (1)$$

In coordination chemistry, high fluororous-phase affinities are usually achieved by attaching long perfluorocarbon “ponytails” having the general formula  $(\text{CF}_2)_n\text{CF}_3$  to one or more of the ligands. In catalytic applications, a pragmatic approach uses a fluororous ligand (e.g., a phosphine) that can bind metal fragments *in situ* and retain them in the fluorocarbon phase [7–16]. Cyclopentadienyl (Cp) ligands and complexes bearing one or more fluororous ponytails are a somewhat more recent development with emerging applications. One approach involves attaching the fluororous substituent to a coordinated Cp ligand [17–22], and the other involves preparation of a ponytail-substituted cyclopentadienyl ligand that can, in principle, be used for a wide variety of metal complexes [23–25]. In at least one case, a coordinated Cp ligand is first substituted with ponytails and then detached photochemically to furnish the corresponding cyclopentadiene [17]. Because longer perfluoroalkyl-derived starting materials (halides and alcohols) increase in cost with chain length (prohibitively beyond about  $\text{C}_{12}$ ), attachment of more than one ponytail substituent is needed in practice to attain high fluororous-phase

\* Corresponding author. Tel.: +1 540 375 2437; fax: +1 540 375 2055.

E-mail address: [hollis@roanoke.edu](mailto:hollis@roanoke.edu) (W.G. Hollis Jr.).

<sup>1</sup> Undergraduate research participant.

affinities. Ideally one can select not only the number of ponytails but also their regiochemistry.

We now report a simple approach to controlled, multiple ponytail attachment by nucleophilic substitution reactions of perfluoroaryl-substituted cyclopentadienyl complexes and alkoxides derived from (*n*-perfluoroalkyl)methanols. The method is illustrated using 1,1'-bis(pentafluorophenyl)-ferrocene [26], which has two aromatic fluorides that are readily displaced by alkoxides [27], and 1,1'-bis(4-tetrafluoropyridyl)-ferrocene [28], which has four labile fluorides. The synthesis and characterization of the resulting ponytail-substituted diarylferrocenes are reported, along with fluorocarbon/hydrocarbon partition constants determined by UV–vis spectrophotometry.

## 2. Results and discussion

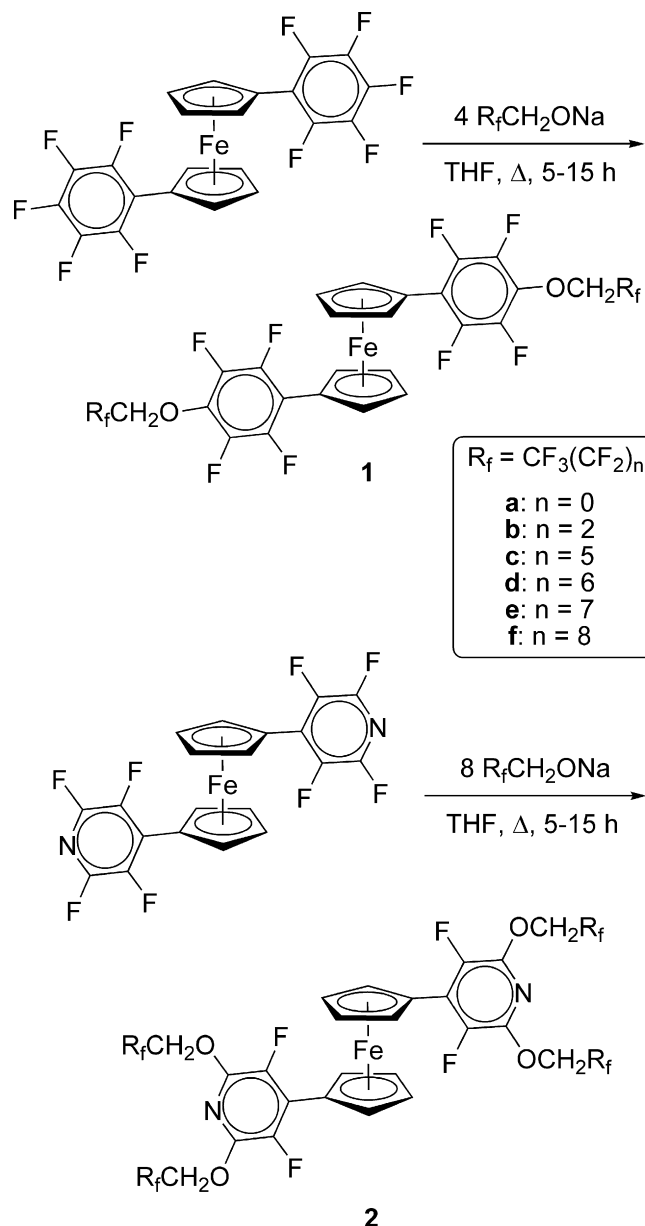
### 2.1. Synthesis

As shown in Scheme 1, reactions of 1,1'-bis(pentafluorophenyl)ferrocene or 1,1'-bis(4-tetrafluoropyridyl)ferrocene with a homologous series of (*n*-perfluoroalkyl)methanols and sodium hydride under relatively mild conditions afforded the corresponding aryl ethers (**1** and **2**). Yields and NMR data are provided in Table 1. NMR spectroscopic analysis of crude product mixtures showed that the pentafluorophenyl substituents underwent cleanly *para* selective reactions. The 4-tetrafluoropyridyl substituents underwent selective displacement of the 2- and 6-fluorines (vicinal to the nitrogen atoms). These selectivities are well precedented [29]. The desired ferrocenes (**1** and **2**) were readily separated from the unreacted alcohols by fractional crystallization from toluene or by silica gel chromatography.

### 2.2. Structural characterization

The regiochemistry shown for **2** is the expected result for a nucleophilic aromatic substitution reaction of a 4-substituted tetrafluoropyridine [29–31]. However, our inability to confirm this result unambiguously by NMR spectroscopy prompted us to attempt the structural characterization of an example. Luckily, inadvertent evaporation of several of our NMR samples afforded crystalline samples of both **1a** and **2a** (both *n* = 0), so these were subjected to single-crystal X-ray diffraction analysis. Subsequent attempts to crystallize other examples with longer ponytail substituents unfortunately failed.

The molecular structure of **1a** (Fig. 1) is unremarkable from the standpoint of the ferrocene core (Fe–C distances are typical). However, the structure does exhibit some phenomena that merit further discussion. First, the two aromatic rings are “slip-stacked” in a manner that has been postulated to enable attractive alignment of individual aromatic C–F dipoles [32]. The C<sub>5</sub>H<sub>4</sub>-aryl torsion angles (12° and 10°) are highly deformable internal coordinates and adjust to accommodate stacking and intermolecular packing forces. The arene–arene centroid-to-centroid distance of 3.52 Å and the distance



Scheme 1.

between the two least squares planes (3.34 Å measured from a centroid) are consistent with those observed in similar ferrocene derivatives [32–34].

Other interesting features of crystalline **1a** are revealed in the packing diagrams. Fig. 2a shows the alignment of molecules along an extended Cp–Fe–Cp axis. The intermolecular distances are probably too long to argue for true “arene stacking,” so we conclude that the observed arrangement simply aligns the Cp–arene dipoles in opposite directions. Within individual “sheets” of molecules, two weak C–H...F–C interactions may be discerned with H...F contact distances of 2.42 and 2.63 Å (Fig. 2b). These parameters are consistent with observations that we made previously with other fluoroarylated ferrocene complexes [34,35], and again we find no reason to argue that these interactions represent “hydrogen bonds” rather than simple dipole–dipole packing alignments [36].

Table 1  
Analytical data for substituted ferrocene complexes

Complex	Yield (%)	<sup>1</sup> H NMR data (δ, 400 MHz, CDCl <sub>3</sub> )			<sup>19</sup> F NMR data (δ, 376 MHz, CDCl <sub>3</sub> )			
		CH <sup>a</sup>	CH <sup>b</sup>	CH <sub>2</sub> <sup>c</sup>	CF <sup>d</sup>	CH <sub>2</sub> CF <sub>2</sub> <sup>e</sup>	(CF <sub>2</sub> ) <sub>n</sub> <sup>f</sup>	CF <sub>3</sub> <sup>g</sup>
<b>1a</b> , <i>n</i> = 0	43	4.82	4.44	4.52	−140.4, −158.3			−75.5
<b>1b</b> , <i>n</i> = 2	65	4.83	4.44	4.64	−140.4, −158.2	−128.0	−122.2	−81.3
<b>1c</b> , <i>n</i> = 5	14	4.83	4.44	4.64	−140.4, −158.2	−126.6	−121.3, −122.6, −123.3, −123.6	−81.2
<b>1d</b> , <i>n</i> = 6	33	4.83	4.45	4.64	−140.3, −158.2	−126.6	−121.3, −122.5 (16 F), −123.2, −123.6	−81.2
<b>1e</b> , <i>n</i> = 7	27	4.83	4.45	4.63	−140.3, −158.2	−126.6	−121.3, −122.4 (24 F), −123.2, −123.6	−81.2
<b>1f</b> , <i>n</i> = 8	24	4.83	4.45	4.63	−140.3, −158.3	−126.6	−121.3, −122.4 (32 F), −123.2, −123.6	−81.2
<b>1g</b> , <i>n</i> = 9	15	4.83	4.45	4.63	−140.3, −158.3	−126.6	−121.3, −122.3 (40 F), −123.2, −123.6	−81.2
<b>2a</b> , <i>n</i> = 0	20	4.92	4.50	4.70	−145.5			−73.7
<b>2b</b> , <i>n</i> = 2	63	4.91	4.51	4.83	−145.5	−127.9	−120.4	−80.9
<b>2c</b> , <i>n</i> = 5	87	4.94	4.53	4.83	−145.3	−126.3	−119.8, −122.3, −122.9, −123.8	−80.9
<b>2d</b> , <i>n</i> = 6	74	4.95	4.54	4.83	−145.3	−126.3	−119.8, −122.1 (16 F), −122.9, −123.9	−80.9
<b>2e</b> , <i>n</i> = 7	74	4.96	4.54	4.82	−145.3	−126.4	−119.8, −122.0 (24 F), −122.9, −124.0	−81.0
<b>2f</b> , <i>n</i> = 8	29	4.97	4.56	4.82	−145.3	−126.4	−119.8, −122.0 (32 F), −122.9, −124.1	−81.0

<sup>a</sup> CH proximal to the aryl substituent (pseudopentet  $^3J_{\text{HH}} \sim ^4J_{\text{HH}} \sim ^5J_{\text{FH}} \sim 2$  Hz, 4 H). See Ref. [38] for a discussion of coupling constants in substituted ferrocenes.

<sup>b</sup> CH distal to the aryl substituent (pseudotriplet,  $^3J_{\text{HH}} \sim ^4J_{\text{HH}} \sim 2$  Hz, 4 H).

<sup>c</sup> OCH<sub>2</sub>CF<sub>3</sub> (q,  $^3J_{\text{FH}} = 8$  Hz, 8 H) or OCH<sub>2</sub>CF<sub>2</sub> (t,  $^3J_{\text{FH}} = 14$  Hz, 8 H).

<sup>d</sup> Aromatic CF: two signals (d,  $^3J \sim 20$  Hz, 4 F) for C<sub>6</sub>F<sub>4</sub>OR substituents; one signal for (s, 4 F) for C<sub>5</sub>F<sub>2</sub>(OR)<sub>2</sub>N substituents.

<sup>e</sup> CH<sub>2</sub>CF<sub>2</sub> (m, 8 F).

<sup>f</sup> CH<sub>2</sub>CF<sub>2</sub>(CF<sub>2</sub>)<sub>n</sub>CF<sub>3</sub> (m, 8 F).

<sup>g</sup> CF<sub>3</sub> (t,  $^3J = 9$  Hz, 12 F).

The structure of pyridine derivative **2a** is shown in Fig. 3. The structure is typical of disubstituted ferrocenes. The C<sub>5</sub>H<sub>4</sub>-aryl torsional angle is about 25° (also typical). In this case, no arene stacking or noteworthy C–H...F–C interactions were observed in either the molecular structure or the packing diagrams.

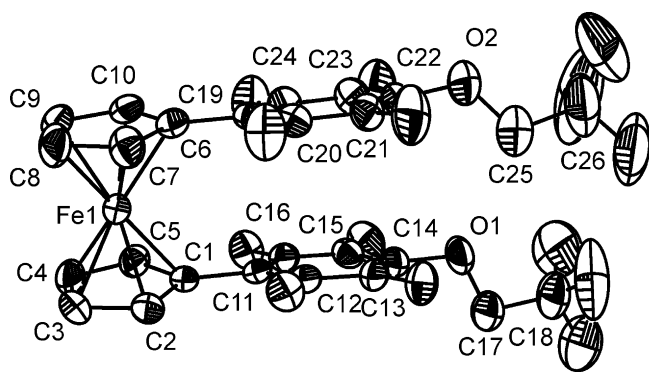


Fig. 1. Thermal ellipsoid plot (50% probability) of the molecular structure of **1a** with numbering scheme. Hydrogens are omitted for clarity. Fluorine atoms are numbered the same as the carbon atoms to which they are attached. Selected bond lengths (Å), bond angles (°), and torsional angles (°): Fe–Cp centroid (C1–C5), 1.644(4); Fe–Cp centroid (C6–C10), 1.641(4); C1–C11, 1.469(4); C11–C12, 1.394(4); C12–C13, 1.372(4); C13–C14, 1.380(4); C14–C15, 1.378(4); C15–C16, 1.366(4); C16–C11, 1.395(4); C14–O1, 1.377(3); O1–C17, 1.416(4); C17–C18, 1.464(5); C6–C19, 1.468(4); C19–C20, 1.391(4); C21–C21, 1.368(4); C21–C13, 1.372(4); C22–C23, 1.377(4); C23–C24, 1.361(4); C24–C19, 1.396(4); C22–O2, 1.361(4); O2–C25, 1.379(5); C25–C26, 1.451(6); C14–O1–C17, 114.4(2); O1–C17–C18, 107.4(3); C22–O2–C25, 118.3(4); O2–C25–C26, 109.9(4); C2–C1–C11–C12, −12.4(4); C7–C6–C19–C20, −10.1(4); C14–O1–C17–C19, 179.5(3); C22–O2–C25–C26, 178.3(4).

### 2.3. Fluorous affinity (partition) studies

Because ferrocene derivatives exhibit strong absorbances ( $\epsilon \sim 5 \times 10^5$  L mol<sup>−1</sup> cm<sup>−1</sup>) in the visible region, we used UV–vis spectrophotometry to determine the coefficients of partition between the hydrocarbon (hexane or toluene) and fluorous (perfluoromethylcyclohexane or PFMC) phases. The coefficients (Table 2) were determined by dissolving a small quantity of the solid substituted ferrocene in a vigorously agitated mixture of the two solvents, measuring the total absorptivity of each phase, and calculating their ratio. This approach embodies the assumption that the extinction coefficients are independent of solvent, which we have verified to within 5% error. Moreover, the basic characteristics of the spectra (the  $\lambda_{\text{max}}$  and full-width-at-half-maximum of the visible bands) are strikingly independent not only of solvent but also of the length of the perfluoroalkyl substituents.

The data in Table 2 reveals two key trends. First, the ferrocenes having four ponytail groups (**2**) have much higher fluorous-phase affinities than those having two ponytail groups (**1**). Second, fluorous-phase affinities increase with longer ponytail chain lengths. Neither of these results is surprising, considering the trends observed by others in analogous systems [18,19,21,23,37]. One feature that did surprise us was the decrease in *Q* going from *n* = 8 to *n* = 9. We observed this phenomenon in both series of compounds and cannot find a satisfactory explanation. Although additional experimentation (with longer chains) would be needed to confirm this hypothesis, we speculate that above a certain chain length the chains are able to coil into configurations in which they solvate themselves or one another rather than interacting with solvent molecules.

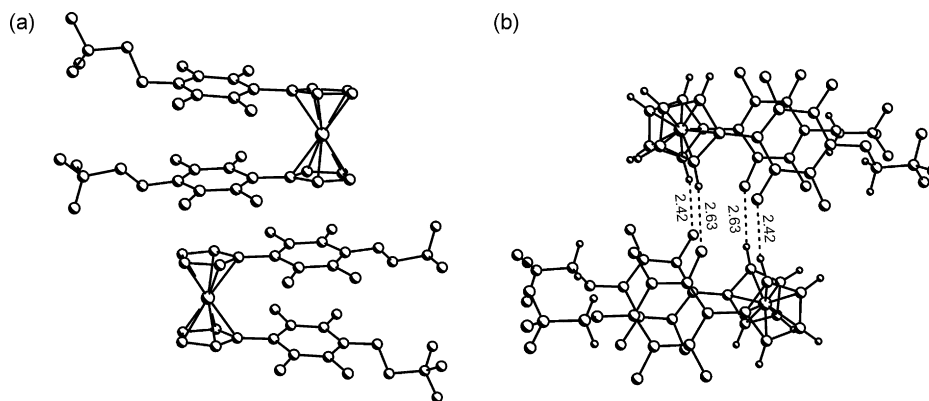


Fig. 2. (a) Packing diagram of **1a** showing intermolecular arene stacking alignment. Hydrogen atoms are removed for clarity. (b) Packing diagram of **1a** showing intermolecular C–H...F–C contacts.

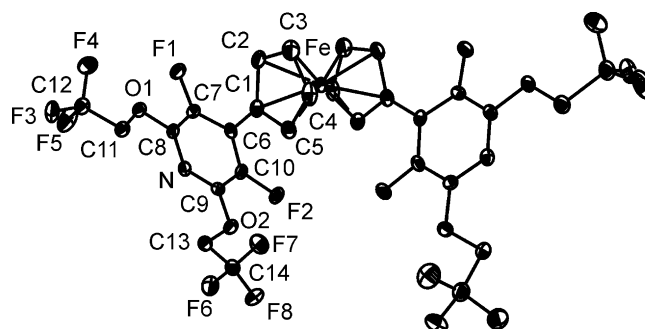


Fig. 3. Thermal ellipsoid plot (50% probability) of the molecular structure of **2a** with numbering scheme. Selected bond lengths (Å), bond angles (°), and torsional angles (°): Fe–Cp (centroid), 1.642(3); C1–C6, 1.475(3); C6–C7, 1.392(3); C7–C8, 1.380(3); C8–N, 1.324(3); N–C9, 1.332(3); C9–C10, 1.377; C10–C6; 1.389(4); C8–O1, 1.364(3); O1–C11, 1.427(3); C11–C12, 1.500(3); C7–F1, 1.346(3); C10–F2, 1.360(3); C8–O1–C11, 115.9(2); O1–C11–C12, 105.3(2); C2–C1–C6–C7, –24.6(2); N–C8–O1–C11, 4.4(3); C8–O1–C11–C12, 167.9(2); N–C9–O2–C13, 5.9(3); C9–O2–C13–C14, 151.0(3).

Table 2  
Fluorocarbon/hydrocarbon partition coefficients for substituted ferrocene complexes

Entry	Complex	$Q^a$	Percent ratio	Ref.
1	<b>3a</b> , $n = 0$	0.0068	<1:99	This work
2	<b>3b</b> , $n = 2$	0.051	5:95	This work
3	<b>3c</b> , $n = 5$	0.32	24:76	This work
4	<b>3d</b> , $n = 6$	0.58	27:63	This work
5	<b>3e</b> , $n = 7$	1.31	57:43	This work
6	<b>3f</b> , $n = 8$	1.80	85:15	This work
7	<b>3g</b> , $n = 9$	1.51	60:40	This work
8	<b>4a</b> , $n = 0$	<sup>e</sup>	<1:99	This work
9	<b>4b</b> , $n = 2$	0.25	80:20	This work
10	<b>4c</b> , $n = 5$	13.3	93:7	This work
11	<b>4d</b> , $n = 6$	34.6	97:3	This work
12	<b>4e</b> , $n = 7$	<sup>f</sup>	>99:1	This work
13	<b>4f</b> , $n = 8$	<sup>f</sup>	>99:1	This work
14	<b>4g</b> , $n = 9$	18.1	95:5	This work
14	[CF <sub>3</sub> (CF <sub>2</sub> ) <sub>9</sub> CH <sub>2</sub> CH <sub>2</sub> C <sub>5</sub> H <sub>4</sub> ] <sub>2</sub> Fe	20 <sup>b</sup>	95:5	[25]
15	{[CF <sub>3</sub> (CF <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ] <sub>2</sub> C <sub>5</sub> H <sub>3</sub> ] <sub>2</sub> Fe <sup>c</sup>	10 <sup>d</sup>	91:9	[19]
16	{[CF <sub>3</sub> (CF <sub>2</sub> ) <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> C <sub>5</sub> H <sub>3</sub> ] <sub>2</sub> Fe <sup>c</sup>	72 <sup>d</sup>	99:1	[19]
17	{[CF <sub>3</sub> (CF <sub>2</sub> ) <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub> ][CF <sub>3</sub> (CF <sub>2</sub> ) <sub>7</sub> (CH <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> C <sub>5</sub> H <sub>3</sub> ] <sub>2</sub> Fe <sup>c</sup>	22 <sup>d</sup>	96:4	[19]

<sup>a</sup> Ratio defined in Eq. (1); measured by UV–vis spectrophotometry at 25 °C unless otherwise indicated.

<sup>b</sup>  $Q$  determined gravimetrically.

<sup>c</sup> Mixture of regioisomers.

<sup>d</sup>  $Q$  determined by acid digestion and atomic absorption spectroscopy.

<sup>e</sup> Concentration in fluorous-phase was too small to measure.

<sup>f</sup> Concentration in non-fluorous-phase was too small to measure.

### 3. Conclusions

Fluorous “ponytail” substituted ferrocenes are readily prepared by chemo- and regioselective nucleophilic aromatic substitution reactions of pentafluorophenyl- or perfluoropyridyl-substituted ferrocenes. Increasing the number and length of the ponytails increases fluoruous-phase affinities.

### 4. Experimental

#### 4.1. General experimental procedures

NMR spectra were recorded on a Varian Inova 400 instrument. The starting diarylferrocene complexes were prepared as described elsewhere [26,28]. Toluene and perfluoro(methylcyclohexane) were used as received from commercial sources. Microanalyses were performed by Desert Analytics (Tucson, AZ, USA). Mass spectra were obtained using a JEOL HX-110 with FAB ionization. The crystal structure of **1a** was obtained at 100 K using an Oxford Diffraction Gemini Diffractometer. The structure of **2a** was obtained at 100 K using an Oxford Diffraction Xcalibur 2 Diffractometer. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 669270 and 669271.

#### 4.2. Preparation of **1** (general procedure)

The reaction was conducted under an atmosphere of dry nitrogen at a nominal scale of 0.2 mmol with the diarylated ferrocene as the limiting component. A dry flask was flushed with nitrogen and charged with sodium hydride (about 8 equiv.). After rinsing the sodium hydride with pentane (3 × 25 mL) to remove the mineral oil dispersant, 20 mL of THF was added to form a suspension. With stirring, the (*n*-perfluoroalkyl)methanol (8 equiv.) was added, and the mixture was stirred at 25 °C for 2 h. Bis(pentafluorophenyl)ferrocene was then added as a solution in 10 mL of THF. A condenser was fitted, and the mixture was stirred under reflux for 5–15 h. The mixture was cooled, and the THF was evaporated. The product was isolated by crystallization from hot toluene (rather inefficient for **1a**) and subjected to NMR spectroscopic analysis. The most commonly observed impurity was unreacted (*n*-fluoroalkyl)methanol, which was readily separated on a short column of silica gel. Isolated product yields and NMR data are provided in Table 1. Analysis was obtained for **1a**: Calcd (found) for C<sub>26</sub>H<sub>12</sub>F<sub>14</sub>FeO<sub>2</sub>C, 46.05 (46.97); H, 1.78 (2.01). The identities of the remaining homologues were confirmed by obtaining HRMS data within 10 ppm of calculated values.

#### 4.3. Preparation of **2** (general procedure)

The procedure is the same as for **1** (see above) except that only 4 equiv. of NaH and 4 equiv. of the (*n*-fluoroalkyl)methanol were used. Isolated product yields and NMR data are

provided in Table 1. Analysis was obtained for **2a**: calcd (found) for C<sub>28</sub>H<sub>16</sub>F<sub>16</sub>FeN<sub>2</sub>O<sub>4</sub>C, 41.81 (41.96); H, 2.01 (1.90); N, 3.48 (3.48). The identities of the remaining homologues were confirmed by obtaining HRMS data within 10 ppm of published values.

#### 4.4. Partition coefficients

A small sample (typically 2–3 mg) of the substituted ferrocene was placed in a flask with 2.0 mL of toluene and 2.0 mL of PFMC. The flask was shaken until the ferrocene dissolved and then allowed to stand for 2 min, allowing the layers to separate. The lower and upper layers were separated and analyzed directly by UV–vis spectrophotometry using a Shimadzu UV-2401PC instrument. The absorbance at λ<sub>max</sub> at 460(5) nm was recorded. Each experiment was run in triplicate.

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