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Syntheses and Reactivities of Disubstituted and Trisubstituted Fluorous Pyridines with High Fluorous Phase Affinities: Solid State, Liquid Crystal, and Ionic Liquid-Phase Properties

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Reactions of 2,6-dibromo-, 3,5-dibromo-, and 2,4,6-tribromopyridine with $IZnCH_2CH_2R_{f8}$ ($R_{f8} = (CF_2)_7CF_3$) in THF at 65 °C in the presence of *trans*-$Cl_2Pd(PPh_3)_2$ (5 mol %) gave the fluorous pyridines 2,6- and 3,5-$NC_5H_3(CH_2CH_2R_{f8})_2$ (**1** and **2**; 85%, 31%) and 2,4,6-$NC_5H_2(CH_2CH_2R_{f8})_3$ (**3**, 61%). Reaction of 2,6-pyridinedicarboxaldehyde with $[Ph_3PCH_2CH_2R_{f8}]^+I^-/K_2CO_3$ (*p*-dioxane/H_2O, 95 °C) gave 2,6-$NC_5H_3(CH{=}CHCH_2R_{f8})_2$ (95%; 70:30 *ZZ*/*ZE*), which was treated with H_2 (1 atm, 12 h) and 10% Pd/C to yield 2,6-$NC_5H_3(CH_2CH_2CH_2R_{f8})_2$ (**5**, 95%), a higher homologue of **1**. Longer reaction times afforded piperidine *cis*-2,6-$HNC_5H_8(CH_2CH_2CH_2R_{f8})_2$ (**6**, 98%). The stereochemistry was established by NMR analysis of the *N*-benzylpiperidine. Pyridines **1**−**3** and **5** are low-melting white solids with $CF_3C_6F_{11}$/toluene partition coefficients (24 °C) of 93.8:6.2, 93.9:6.1, >99.7:<0.3, and 90.4:9.6, respectively (**6**, 93.6:6.4). Reaction of **1** and CF_3SO_3H gave a pyridinium salt, and $Cl_2Pd(NCCH_3)_2$ (0.5 equiv) yielded *trans*-$Cl_2Pd(\mathbf{1})_2$. The crystal structure of the former, which also exhibited liquid crystalline and ionic liquid phases, was determined.

Introduction

There has been rapidly increasing interest in the design and synthesis of compounds that exhibit high affinities for "fluorous" phases since the technique of "fluorous biphase chemistry" was described by Horváth and Rábai in 1994.[1,2] This protocol exploits the temperature-dependent miscibility of organic solvents with perfluorocarbons, perfluoroethers, or perfluoroamines.[3] When "pony tails" of the formula $(CH_2)_m(CF_2)_{n-1}CF_3$ (abbreviated $(CH_2)_mR_{fn}$) are added to reagents or catalysts in sufficient numbers, they provide exceptionally high fluorous phase affinities. Reactions can be conducted in mixtures of organic and fluorous solvents under monophasic conditions at higher temperatures. The products, which normally have much greater affinities for the organic solvent, are separated from the fluorous reagent or catalyst under biphasic conditions at lower temperatures. The recovered reagent or catalyst solution is directly reused.

To date, most applications of fluorous chemistry in catalysis involve metal-containing species.[1,2] However, simple aliphatic and aromatic nitrogen donor compounds see extensive use as basic, nucleophilic, or electron-transfer catalysts in organic and inorganic synthesis.[4,5] Of course, nitrogen bases are also used as stoichiometric reagents, and there is an extensive literature on recovery strategies. In view of the many possible applications that

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(4) (a) For an overview, see: *The Chemistry of Amino, Nitroso, Nitro, and Related Groups* (Suppl. F2); Patai, S., Ed.; Wiley: New York, 1996, and similarly titled earlier volumes in this series (1982, 1968). (b) Ragnarsson, U.; Grehn, L. *Acc. Chem. Res.* **1998**, *31*, 494. (c) Fu, G. C. *Acc. Chem. Res.* **2000**, *33*, 412.

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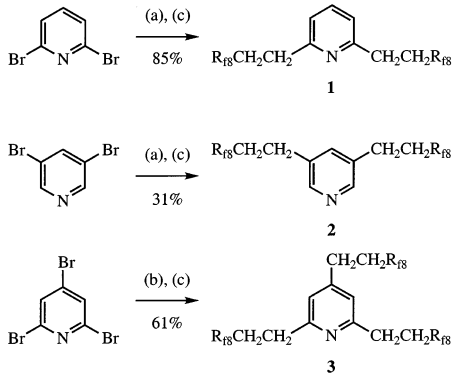
SCHEME 1. Syntheses of Fluorous Pyridines with $(CH_2)_2$ Spacers[a]



[a] $R_{f8} = (CF_2)_7CF_3$. Conditions: (a) 2 $IZnCH_2CH_2R_{f8}$; (b) 3 $IZnCH_2CH_2R_{f8}$; (c) 5.0 mol % *trans*-$Cl_2Pd(PPh_3)_2$, THF, 65 °C.

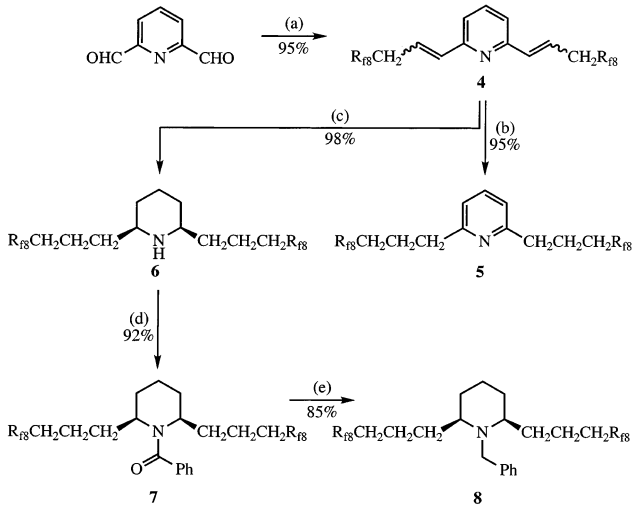
could be envisioned for recyclable fluorous amines, we set out to develop efficient syntheses and characterize their fundamental properties. In our previous paper, we reported high-yield gram-scale preparations of a family of primary, secondary, and tertiary aliphatic amines of the formula $NH_{3-x}[(CH_2)_mR_{f8}]_x$.[6] The length of the methylene spacer (*m* value) could be varied from three to five carbons, allowing donor properties to be fine-tuned.

In this paper, we report convenient gram-scale syntheses of fluorous pyridines with a range of steric and electronic properties, both of which can be systematically varied. Solubility characteristics, reactions with electrophiles, and a crystal structure of a pyridinium salt—which at higher temperatures gives liquid crystalline and ionic liquid phases—are also described. One of the two routes presented is based upon methodology for fluorous arenes published earlier.[7] In this work, it was also shown that a single pony tail imparts only a modest fluorous phase affinity to benzene. Uemura has previously elaborated pyridine carboxaldehydes and acid chlorides to fluorous pyridine acetals and esters.[8] Other researchers have described complementary results involving fluorous bipyridines,[9] as further detailed below.

Results

1. Syntheses. Many halopyridines are readily available, and it has been previously shown that palladium(II) compounds catalyze substitutions of haloarenes by alkylzinc reagents.[10] Accordingly, the fluorous iodozinc compound $IZnCH_2CH_2R_{f8}$ was generated from the commercially available fluorous iodide $ICH_2CH_2R_{f8}$ as described earlier.[11] As shown in Scheme 1, reaction of ≥2 equiv with commercial 2,6-dibromopyridine in the presence of the catalyst *trans*-$Cl_2Pd(PPh_3)_2$ gave the double-pony-tailed pyridine 2,6-$NC_5H_3(CH_2CH_2R_{f8})_2$ (**1**) in 85% yield after workup.

SCHEME 2. Syntheses of Fluorous Pyridine and Piperidines with $(CH_2)_3$ Spacers[a]



[a] Conditions: (a) 2$[R_{f8}CH_2CH_2PPh_3]^+I^-$, K_2CO_3, H_2O, *p*-dioxane, 95 °C; (b) EtOH/hexanes, Pd/C, H_2 (1 atm), 12 h; (c) EtOH/hexanes, Pd/C, H_2 (1 atm), 11 d; (d) PhCOCl, NEt_3, THF; (e) $LiAlH_4$, THF, reflux.

This protocol was repeated with 3,5-dibromopyridine and 2,4,6-tribromopyridine. The latter was prepared by a simple literature procedure.[12] Workups gave the double-pony-tailed 3,5-$NC_5H_3(CH_2CH_2R_{f8})_2$ (**2**) in 31% yield and the triple-pony-tailed 2,4,6-$NC_5H_2(CH_2CH_2R_{f8})_3$ (**3**) in 61% yield. Pyridines **1**−**3** were white solids with relatively low melting points (77−82 °C). Additional characterization is described below.

Our earlier studies of fluorous aliphatic amines showed that the inductive effect of the perfluoroalkyl segments could still be detected through five methylene groups.[6] Aliphatic phosphines show analogous trends.[13,14] Hence, we sought analogues of some the preceding compounds with longer methylene spacer segments. Previously, we showed that various benzaldehydes undergo efficient Wittig reactions with the ylide derived from the phosphonium salt $[Ph_3PCH_2CH_2R_{f8}]^+I^-$.[7] Subsequent hydrogenation leads to arenes with three methylene spacers.

As shown in Scheme 2, commercial 2,6-pyridinedicarboxaldehyde was combined with 2.5 equiv of $[Ph_3PCH_2CH_2R_{f8}]^+I^-$ and the base K_2CO_3 in wet *p*-dioxane at 95 °C. Workup gave the corresponding dialkene 2,6-$NC_5H_3(CH{=}CHCH_2R_{f8})_2$ (**4**) in 95% yield as a 70:30 mixture of *ZZ* and *ZE* isomers, as assayed by ^1H NMR. The dominant *Z* selectivity is typical of unstabilized phosphorus ylides, as analyzed earlier.[7] Hydrogenation over a Pd/C catalyst gave the target pyridine 2,6-$NC_5H_3(CH_2CH_2CH_2R_{f8})_2$ (**5**) in 95% yield after workup.

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TABLE 1. Partition Coefficients (24 °C)

analyte		$CF_3C_6F_{11}$/toluene
2,6-$NC_5H_3(CH_2CH_2R_{f8})_2$	**1**	93.8:6.2[a]
3,5-$NC_5H_3(CH_2CH_2R_{f8})_2$	**2**	93.9:6.1[a]
2,4,6-$NC_5H_2(CH_2CH_2R_{f8})_3$	**3**	>99.7:<0.3[a]
2,6-$NC_5H_3(CH_2CH_2CH_2R_{f8})_2$	**5**	90.4:9.6[a]
cis-2,6-$HNC_5H_8(CH_2CH_2CH_2R_{f8})_2$	**6**	93.6:6.4[a]
cis-2,6-$C_6H_5CH_2NC_5H_8(CH_2CH_2CH_2R_{f8})_2$	**8**	79.3:20.7[a]
$C_6H_4CH_2CH_2CH_2R_{f8}$	**11**	49.5:50.5[b]
1,2-$C_6H_4(CH_2CH_2CH_2R_{f8})_2$	**12**	91.2:8.8[b]
1,3-$C_6H_4(CH_2CH_2CH_2R_{f8})_2$	**13**	90.7:9.3[b]
1,4-$C_6H_4(CH_2CH_2CH_2R_{f8})_2$	**14**	91.1:8.9[b]
1,3,5-$C_6H_3(CH_2CH_2CH_2R_{f8})_3$	**15**	>99.7:<0.3[b]
$HN(CH_2CH_2CH_2R_{f8})_2$	**16**	96.5:3.5[c]
$HN(CH_2CH_2CH_2CH_2R_{f8})_2$	**17**	95.1:4.9[c]
$HN(CH_2CH_2CH_2CH_2CH_2R_{f8})_2$	**18**	93.0:7.0[c]

[a] This work. [b] Reference 7. [c] Reference 6.

2. Physical Properties. Pyridines **1**−**5**, and all other new compounds below, were characterized by microanalysis and ^1H and ^{13}C NMR spectroscopy. All data supported the structural assignments. DSC measurements showed, with a single exception (below), no phase transitions other than melting.

Pyridines **1**−**3** and **5** were very soluble in the fluorinated solvents $CF_3C_6F_{11}$ (perfluoro(methylcyclohexane)), $CF_3C_6F_5$ (perfluorotoluene), and $CF_3C_6H_5$ (α,α,α-trifluorotoluene), as well as ether and THF. They showed significant solubility in hexanes, toluene, $CHCl_3$, CH_2Cl_2, and ethanol. In the last solvent, **5** was more soluble than the others, and **3** always appeared to be the least soluble. All compounds were very poorly soluble in methanol, CH_3CN, DMF, and DMSO.

Quantitative data on fluorous phase affinities were sought. Accordingly, the $CF_3C_6F_{11}$/toluene partition coefficients were determined by GC as previously reported. These reflect *relative* as opposed to *absolute* solubilities and are summarized in Table 1. Values for related arenes and aliphatic amines are also given. Trends are analyzed in the discussion section.

3. Reactions and Derivatives. During the optimization of conditions for the hydrogenation of **4**, traces of a byproduct were sometimes observed. As shown in Scheme 2, longer reaction times gave complete reduction to the fluorous piperidine 2,6-$HNC_5H_8(CH_2CH_2CH_2R_{f8})_2$ (**6**), which was obtained as a white solid in 98% yield.[15] The stereochemistries of symmetrically 2,6-disubstituted piperidines are often assayed via conversion to the corresponding benzylamines.[16] The benzylic methylene protons are enantiotopic in the case of the cis isomer (one ^1H NMR signal), but diastereotopic in the case of the trans (AB system, two signals).

Accordingly, **6** was treated with benzoyl chloride as depicted in Scheme 2. Workup gave the *N*-benzoyl derivative **7** in 92% yield. Reduction with $LiAlH_4$ gave the target *N*-benzylpiperidine 2,6-$(C_6H_5CH_2)NC_5H_8(CH_2CH_2CH_2R_{f8})_2$ (**8**) in 85% yield. The ^1H NMR spectrum showed a sharp singlet for the benzylic protons (δ 3.67, $CDCl_3$), clearly indicting a cis isomer for **8** and, therefore, for **7** and **6** as well.

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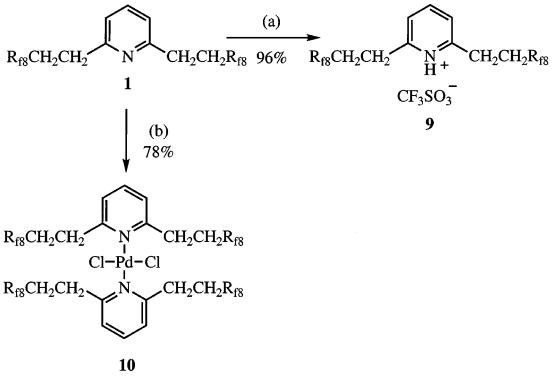
(16) Hill, R. K.; Chan, T.-H. *Tetrahedron* **1965**, *21*, 2015.

SCHEME 3. Derivatives of Fluorous Pyridine 1[a]



[a] Conditions: (a) CF_3SO_3H, ether, room temperature, 0.5 h; (b) $Cl_2Pd(NCCH_3)_2$, $CF_3C_6H_5$, reflux, 2.5 h.

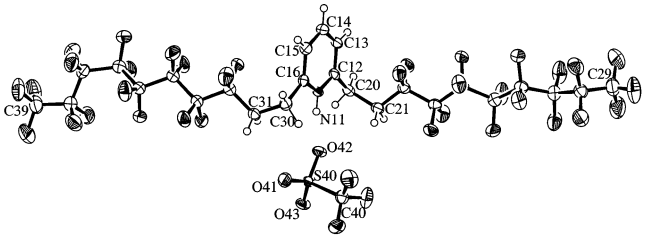


FIGURE 1. Molecular structure of **9**. Key interatomic distances (Å), bond angles (deg), and torsion angles (deg): N(11)−C(16) 1.344(2), N(11)−C(12) 1.350(2), C(12)−C(13) 1.379(3), C(12)−C(20) 1.500(3), C(13)−C(14) 1.381(3), C(14)−C(15) 1.384(3), C(15)−C(16) 1.382(3), C(16)−C(30) 1.500(3), C(20)−C(21) 1.539(3), C(21)−C(22), 1.510(3), C(22)−C(23) 1.545(3), C(30)−C(31) 1.533(3), C(31)−C(32) 1.501(3), C(32)−C(33) 1.549(3), N(11)−O(42) 2.716, N(11)−H 1.844; C(16)−N(11)−C(12) 124.63(16), N(11)−C(12)−C(13) 117.96(18), N(11)−C(12)−C(20) 117.60(16), C(13)−C(12)−C(20) 124.44(18), C(12)−C(13)−C(14) 119.76(19), C(13)−C(14)−C(15) 120.02(19), C(14)−C(15)−C(16) 119.8(2), N(11)−C(16)−C(15) 117.79(18), N(11)−C(16)−C(30) 117.84(16), C(15)−C(16)−C(30) 124.36(18), C(12)−C(20)−C(21) 114.50(17), C(22)−C(21)−C(20) 113.06(16), N(11)−H−O(42) 170.5; C(12)−C(20)−C(21)−C(22) −67.8, C(16)−C(30)−C(31)−C(32) −71.4, N(11)−C(12)−C(20)−C(21) −76.4, N(11)−C(16)−C(30)−C(31) −77.1, C(13)−C(12)−C(20)−C(21) 103.1, C(15)−C(16)−C(30)−C(31) −103.9, C(35)−C(36)−C(37)−C(38) −55.5.

As shown in Scheme 3, an ether solution of pyridine **1** was treated with excess triflic acid, CF_3SO_3H. Workup gave the pyridinium salt $[2,6\text{-}HNC_5H_3(CH_2CH_2R_{f8})_2]^+$ $CF_3SO_3^-$ (**9**) in 96% yield. NMR spectra showed signals shifted from those of **1**, but the NH proton was not readily apparent and tentatively assigned to a very broad signal. When a $CF_3C_6H_5$/ethanol solution of **1** and CF_3SO_3H was allowed to slowly evaporate, single crystals of **9** were obtained.

The crystal structure of **9** was determined as summarized in Table S1 (Supporting Information) and the Experimental Section. The molecular structure is shown in Figure 1. Key bond lengths and angles, as well as torsion angles discussed below, are summarized in the caption. The closest contact between the triflate oxygens and the nitrogen is 2.716 Å. The corresponding value for the pyridinium proton (located but less accurate) is 1.844 Å, and the O−H−N angle is 170.5°. Hence, **9** crystallizes with a hydrogen bond. A packing diagram is given in Figure 2 and is further analyzed below.

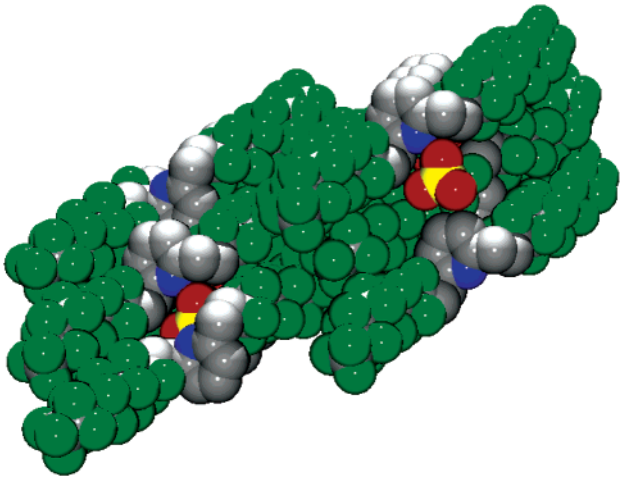


FIGURE 2. Packing diagram of **9**, with color-coded atoms: gray, carbon; green, fluorine; blue, nitrogen; yellow, sulfur; red, oxygen.

Interestingly, DSC measurements established two phase transitions for **9**.[17] As shown in Figure 3, the first occurred slightly above 90 °C. Examination of a sample under a polarizing microscope gave the patterns in Figure 4, confirming the formation of a liquid crystalline phase, most likely smectic B.[18] The second transition, to a liquid or "ionic liquid" state, occurred near 150 °C. The reverse transitions were observed upon cooling (Figure 3), slightly shifted as expected,[18] and a trace equivalent to the first was obtained when the sample was again warmed. The additional small apparent endotherms on the first trace were not observed with other samples.

To prove the viability of the preceding pyridines as ligands in metal catalysts, a transition-metal adduct was sought. Despite the somewhat congested coordination sites in 2,6-dialkylpyridines, many complexes are known.[19] As shown in Scheme 3, **1** and $Cl_2Pd(NCCH_3)_2$ were reacted in refluxing $CF_3C_6H_5$. Workup gave the target complex *trans*-$Cl_2Pd[2,6\text{-}NC_5H_3(CH_2CH_2CH_2R_{f8})_2]_2$ (**10**) in 78% yield as an analytically pure, high melting (≥200 °C), pale yellow solid. Due to its exceptionally poor solubility, **10** was characterized only by ^{1}H NMR. The trans stereochemistry, although well precedented,[19] must be regarded as tentative. Complex **10** was soluble in the aromatic fluorinated solvents $CF_3C_6F_5$ and $CF_3C_6H_5$ above 50 °C. Highly temperature-dependent solubilities have been noted with other fluorous compounds.[20] However, **10** showed little if any solubility in refluxing $CF_3C_6F_{11}$, CH_2Cl_2, $CHCl_3$, acetone, benzene, and toluene.

Discussion

Schemes 1 and 2 show that fluorous pyridines are easily accessible by two complementary, general methodologies that give families with different numbers of methylene spacers. The first utilizes bromopyridines, and the second pyridine carboxaldehydes. Although only one example of the latter is reported, 3,5-pyridinedicarboxaldehyde[21] and 2,4,6-pyridinetricarboxaldehyde[22] are known compounds, and many examples of related sequences using benzaldehydes have been described.[7,23] We furthermore presume, based upon abundant literature precedent and the specific example of **5** (Scheme 2), that all of these compounds can be hydrogenated to the corresponding fluorous piperidines. The Heck reaction is being increasingly applied in syntheses of aromatic fluorous compounds.[24] However, in exploratory work with 2,6-dibromopyridine,[25] we obtained only low yields or substantial amounts of byproducts.

Table 1 shows that fluorous pyridines **1**−**3** and **5** have partition coefficients very similar to those of related benzenoid compounds. In both series, two R_{f8} pony tails give high fluorous phase affinities (coefficients >90:<10). As would be intuitively expected, **1** shows a slightly greater affinity than **5** (93.8:6.2 vs 90.4:9.6), which has two additional methylene groups. Pyridine **5** can in turn be compared to fluorous benzene **13** (90.4:9.6 vs 90.7:9.3), which differs by only a :N/CH replacement. In both series of compounds, three R_{f8} pony tails give very high fluorous phase affinities (**3**, **15**: >99.7:<0.3), allowing essentially quantitative recovery. The hydrogenation product of **4**, piperidine **6**, has a nearly identical partition coefficient (93.8:6.2 vs 93.6:6.4), indicating a negligible influence of the aromatic π cloud (which, however, plays a major role in other series of compounds[3]). This secondary amine can in turn be compared to $HN((CH_2)_5R_{f8})_2$ (**18**, Table 1),[6] which has one additional methylene group and a very similar fluorous phase affinity (93:0:7.0). Substitution of the NH group in **6** by a benzyl group (**8**, Table 1) significantly diminishes the fluorous phase affinity.

Pyridine **1** would be expected to be the least basic of the *di*substituted pyridines. Only two methylene groups and one sp^2 carbon separate the R_{f8} segments from the nitrogen, and the 2,6-disubstitution pattern is sterically restricting. Nevertheless, **1** readily binds palladium. With phosphines of the formula $P((CH_2)_mR_{f8})_3$, four methylene groups are required to achieve a gas-phase ionization potential and Brønsted basicity close to that of $P(CH_3)_3$. With five methylene groups, ionization and protonation remain thermodynamically less favorable than with $P(CH_2CH_3)_3$.[14] Thus, **1** is certain to be less basic than pyridine and 2,6-dimethylpyridine (2,6-lutidine). Pyridine **3**, which has an additional pony tail, should be slightly less basic than **1**. However, **2**, which has an additional sp^2 carbon between nitrogen and the R_{f8} segment, and **5**, which has an additional methylene group, will be more basic, and closer to pyridine or 2,6/3,5-lutidines. All of these compounds are readily oxidized to pyridine *N*-oxides, as will be described in future papers.[26] Although pK_a values for hundreds of pyridines have been determined, the lack of water solubility precludes analogous measurements with our compounds.

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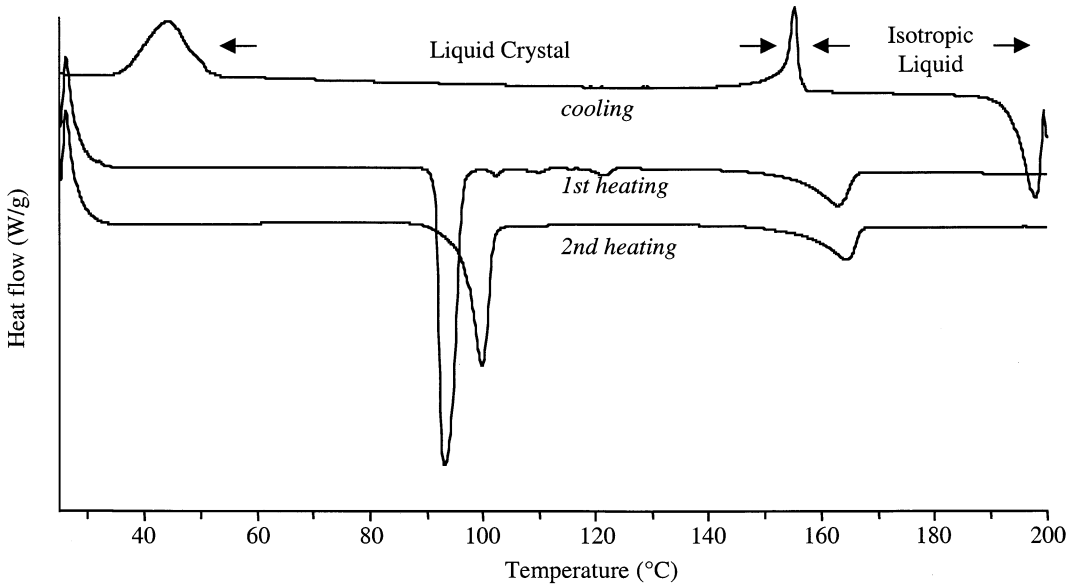

FIGURE 3. DSC thermogram of **9**.

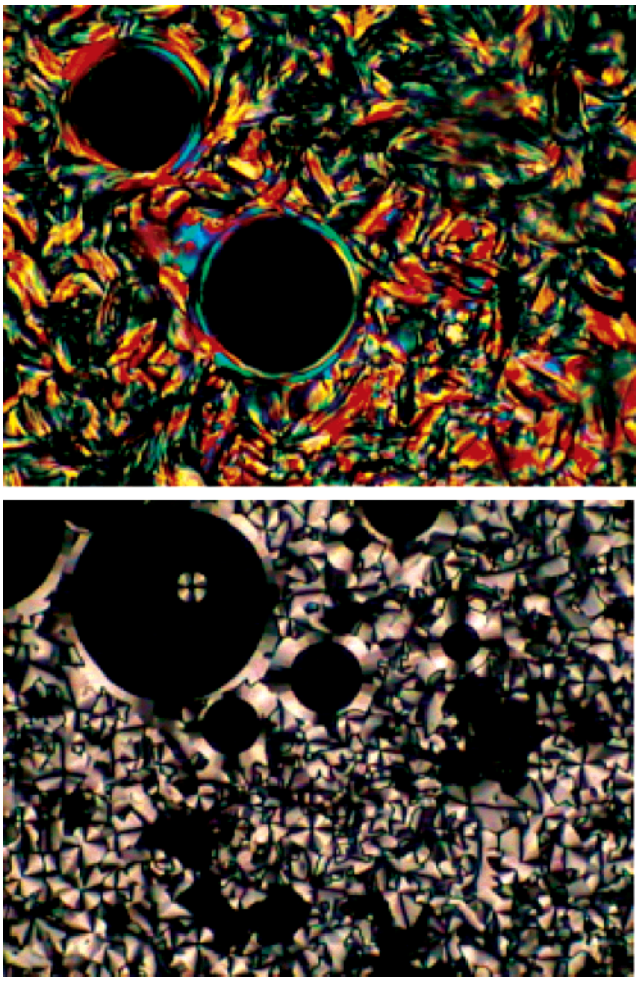

FIGURE 4. Views of the crystalline and liquid crystalline phases of **9** through a polarizing microscope.

The crystal structures of fluorous compounds are of intrinsic interest. As shown in Figure 2, the pony tails of adjacent molecules of **9** segregate into distinct domains, consistent with the "like dissolves like" paradigm that fluorous biphase chemistry was originally based upon.[1] The charged pyridine cores are in turn hydrogen-bonded to the triflate anions, as noted above. One pony tail extends above the plane of the pyridine, and the other below, as is readily visualized when Figure 1 is viewed at a right angle. This is reflected in the X−C(12)−C(20)−C(21) and X′−C(16)−C(30)−C(31) torsion angles (ca. −77°, ±103°; X/X′ are the N/C(13)/C(15) atoms of the pyridine ring), where the twisting originates. Only anti $(CF_2)_4$ segments are found in one pony tail (ending in C(29)), while a single gauche $(CF_2)_4$ segment is found in the other (C(35)−C(36)−C(37)−C(38)). The crystal structures of several protonated 2,6-dialkylpyridines have been determined[27] and exhibit hydrogen bonding to the anion and similar metrical parameters.

We have conducted DSC measurements for all fluorous compounds prepared in our laboratory, and **9** is the first to exhibit a liquid crystalline phase. We speculate that the charges inherent to this salt provide an extra electrostatic driving force for crystal formation, and the packing motif (Figure 2) facilitates an initial phase transition within the fluorous domains. Quaternary phosphonium and ammonium salts are known to be more favorably disposed toward liquid crystalline phases than neutral analogues, but additional, and only partially understood, structural requirements must also be met.[28] Various neutral benzenoid liquid crystalline compounds with R_{f6} and/or $-(OCF(CF_3)CF_2)_n-$ segments have been described,[29] but to our knowledge longer $(CH_2)_m$ segments have always been present. At higher temperatures, **9**

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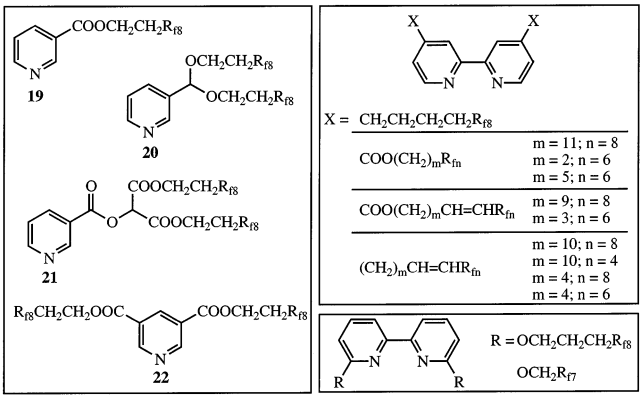
SCHEME 4. Other Fluorous Pyridines and Bipyridines



becomes a fluorous ionic liquid, another type of phase that is presently quite rare.[30]

Some fluorous pyridines and bipyridines reported by other researchers are collected in Scheme 4.[8,9] The structures and synthetic methods employed complement those presented in this work. The functionalized fluorous pyridines **19**−**22** have been elegantly applied as ligands in Pd(II) catalyzed oxidations of alcohols by molecular oxygen.[8] The catalyst can be recovered and reused under fluorous biphase conditions. However, since functional groups can serve as loci of degradation, we believe that the nonfunctionalized fluorous pyridines reported herein should be superior for many catalytic applications.

Conclusion

This study has established convenient and practical syntheses of the first simple, nonfunctionalized fluorous pyridines. There is every reason to anticipate that the gram-level scales can be significantly increased, and that the methodologies can be extended to a variety of homologues as well as fluorous piperidines. The steric and electronic properties of the pyridines, and their fluorous phase affinities, can easily be fine-tuned. With three pony tails, very high levels of immobilization in fluorous solvents are achieved. These compounds exhibit the usual pyridine reactivity modes. The protonation of one gives a salt with a liquid crystalline phase, which upon further heating becomes a fluorous ionic liquid. Our fluorous pyridines are certain to have a useful chemistry, and applications will be reported in due course.

Experimental Section

General Mthods. All reactions were conducted under N_2. Chemicals were treated as follows: THF, ether, toluene, hexanes, distilled from Na/benzophenone; $CF_3C_6F_{11}$, distilled from P_2O_5; $ICH_2CH_2R_{f8}$, 1,2-dibromoethane, 2,6- and 3,5-dibromopyridine, 2,6-$NC_5H_3(CHO)_2$, $(CH_3)_3SiCl$, $LiAlH_4$, CF_3SO_3H, *trans*-$Cl_2Pd(PPh_3)_2$, $CDCl_3$, acetone-d_6, and other chemicals, used as received. NMR spectra were recorded on standard 300 or 400 MHz FT spectrometers at ambient probe temperature and referenced as follows: ^1H, residual internal $CHCl_3$ (δ 7.27) or acetone-d_5 (δ 2.05); ^{13}C, internal $CDCl_3$ (δ 77.2) or acetone-d_6 (δ 29.6). IR spectra were measured on an ASI React IR spectrometer. DSC data were treated by standard methods.[17] Elemental analyses were conducted in-house, or by Atlantic Microlab (Norcross, GA).

2,6-$NC_5H_3(CH_2CH_2R_{f8})_2$ (1). A three-neck flask was fitted with an addition funnel and charged with Zn turnings (0.980 g, 15.0 mmol) and THF (3 mL). Then 1,2-dibromoethane (0.091 mL, 1.06 mmol) was added with stirring. The mixture was refluxed (heat gun) and allowed to cool to room temperature (4 ×). Then $(CH_3)_3SiCl$ (0.037 mL, 0.29 mmol) was added. After 10 min, a solution of $ICH_2CH_2R_{f8}$ (2.87 g, 5.00 mmol) in THF (3 mL) was added dropwise via the addition funnel. The mixture was stirred for 15 min. A separate Schlenk flask was charged with 2,6-dibromopyridine (0.473 g, 2.00 mmol) and *trans*-$Cl_2Pd(PPh_3)_2$ (0.070 g, 0.100 mmol). The contents of the three-neck flask (estimated as 4.00 mmol of $IZnCH_2CH_2R_{f8}$) were added by cannula. The orange solution was stirred at 65 °C, and after 5 h was cooled to room temperature. Ether (25 mL) was added. The mixture was washed (2 ×) with a solution of KCN (0.050 g) in water (15 mL), dried ($MgSO_4$), and taken to dryness by rotary evaporation. The residue was placed on top of a silica gel pad (10 cm × 2.5 cm ∅, packed in MeOH) and washed with MeOH (1.5−2.0 × the pad volume). The product was eluted with ether and flash chromatographed with hexanes/ether (90:10 v/v). Solvent was removed by oil pump vacuum to give **1** as a white solid (1.650 g, 1.700, 85%). Mp: 77−78 (capillary), 76.9 (DSC) °C. NMR (δ, $CDCl_3$) ^1H 2.54−2.72 (m, $2CH_2CF_2$), 3.07 (t, $^3J_{HH}$ = 7 Hz, $2CH_2CH_2CF_2$), 7.06 (d, $^3J_{HH}$ = 7 Hz, 3,5-NC_5H_3), 7.56 (t, $^3J_{HH}$ = 7 Hz, 4-NC_5H_3); $^{13}C\{^1H\}$ 28.6 (s, $2CH_2CH_2CF_2$), 30.1 (t, $^2J_{CF}$ = 22 Hz, $2CH_2CF_2$), 121.1, 137.4, 158.3 (3s, NC_5H_3).[31] Anal. Calcd for $C_{25}H_{11}F_{34}N$: C, 30.91; H, 1.14. Found: C, 30.83; H, 1.12.

3,5-$NC_5H_2(CH_2CH_2R_{f8})_3$ (2). Zinc turnings (0.980 g, 15.0 mmol), THF (3 mL), 1,2-dibromoethane (0.091 mL, 1.06 mmol), $(CH_3)_3SiCl$ (0.037 mL, 0.29 mmol), $ICH_2CH_2R_{f8}$ (2.870 g, 5.000 mmol), THF (3 mL), 3,5-dibromopyridine (0.473 g, 2.00 mmol), and *trans*-$Cl_2Pd(PPh_3)_2$ (0.070 g, 0.100 mmol, 5 mol %) were combined in a procedure analogous to that given for **1**. An identical workup (initial ether addition: 50 mL) gave **2** as a white solid (0.602 g, 0.618 mmol, 31%). Mp: 117 (capillary), 115.0 (DSC) °C. NMR (δ, $CDCl_3$): ^1H 2.37−2.51 (m, $2CH_2CF_2$), 3.01 (t, $^3J_{HH}$ = 7 Hz, $2CH_2CH_2CF_2$), 7.49 (s, 4-NC_5H_3), 8.43 (s, 2,6-NC_5H_3); $^{13}C\{^1H\}$ 24.1 (s, $CH_2CH_2CF_2$), 33.0 (t, $^2J_{CF}$ = 22 Hz, CH_2CF_2), 135.1, 136.0, 148.5 (3s, NC_5H_3).[31] Anal. Calcd for $C_{25}H_{11}F_{34}N$: C, 30.91; H, 1.14. Found: C, 30.28; H, 1.14.

2,4,6-$NC_5H_2(CH_2CH_2R_{f8})_3$ (3). Zinc turnings (0.820 g, 12.5 mmol), THF (3 mL), 1,2-dibromoethane (0.072 mL, 0.84 mmol), $(CH_3)_3SiCl$ (0.030 mL, 0.24 mmol), $ICH_2CH_2R_{f8}$ (2.40 g, 4.18 mmol), THF (3 mL), 2,4,6-tribromopyridine (0.352 g, 1.115 mmol), and *trans*-$Cl_2Pd(PPh_3)_2$ (0.039 g, 0.056 mmol, 5 mol %) were combined in a procedure analogous to that given for **1**. A similar workup (initial ether addition: 50 mL; silica/MeOH filtration followed by flash chromatography with 20:1 v/v hexanes/ether and then 4:1 v/v hexanes/$CF_3C_6H_5$) gave **3** as a white solid (0.964 g, 0.680 mmol, 61%). Mp: 81−82 (capillary), 79.0 (DSC) °C. NMR (δ, $CDCl_3/CF_3C_6F_5$, 9:1 v/v): ^1H 2.30−2.43 (m, 4-$CH_2CH_2CF_2$), 2.55−2.68 (m, 2,6-CH_2CH_2-CF_2), 2.88 (t, $^3J_{HH}$ = 7 Hz, 4-$CH_2CH_2CF_2$), 3.05 (t, $^3J_{HH}$ = 7 Hz, 2,6-$CH_2CH_2CF_2$), 6.91 (s, 3,5-NC_5H_2); $^{13}C\{^1H\}$ 26.1 (s, 4-$CH_2CH_2CF_2$), 28.7 (s, 2,6-$CH_2CH_2CF_2$), 30.2 (t, $^2J_{CF}$ = 22 Hz, $3CH_2CF_2$), 121.1, 149.6, 159.2 (3s, NC_5H_2).[31] Anal. Calcd for $C_{35}H_{14}F_{51}N$: C, 29.65; H, 0.99. Found: C, 29.83; H, 1.22.

2,6-$NC_5H_3(CH{=}CHCH_2R_{f8})_2$ (4). A flask was charged with 2,6-$NC_5H_3(CHO)_2$ (0.143 g, 1.06 mmol), $[Ph_3PCH_2CH_2R_{f8}]^+I^-$ (2.21 g, 2.64 mmol),[7] K_2CO_3 (0.414 g, 3.00 mmol), *p*-dioxane (15 mL), and water (0.5 mL) and fitted with a condensor. The mixture was stirred at 95 °C (12 h). The solvent was removed by rotary evaporation. Then water (25 mL) and CH_2Cl_2 (50 mL) were added. The organic phase was separated and dried ($MgSO_4$). Solvent was removed by rotary evaporation to give

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(31) The signals of the fluorinated carbons, which are unresolvable and sometimes overlapping multiplets due to extensive fluorine coupling, are omitted. The data are nearly identical for each compound.

a yellowish oil that was chromatographed (silica gel column, 9:1 v/v hexanes/ether). Solvent was removed from the product fraction to give **4** as a white solid (1.010 g, 1.014 mmol, 95%; 70:30 *ZZ*/*ZE*). NMR (δ, $CDCl_3$): ^1H 3.06 (dt, $^3J_{HF}$ = 18 Hz, $^3J_{HH}$ = 7 Hz, $1CH_2CF_2$; *ZE*), 3.66 (dt, $^3J_{HF}$ = 18 Hz, $^3J_{HH}$ = 7 Hz, $2CH_2CF_2$; *ZZ*), 3.97 (dt, $^3J_{HF}$ = 18 Hz, $^3J_{HH}$ = 7 Hz, $1CH_2CF_2$; *ZE*), 5.90−6.03 (m, 2C*H*=CHCH$_2$; *ZZ* and *ZE*), 6.64−6.76 (m, 2CH=C*H*CH$_2$; *ZZ* and *ZE*), 7.10 (d, $^3J_{HH}$ = 8 Hz, 3,5-NC_5H_3; *ZZ*), 7.18 (d, $^3J_{HH}$ = 8 Hz, 3,5-NC_5H_3; *ZE*), 7.67 (t, $^3J_{HH}$ = 8 Hz, 4-NC_5H_3; *ZE*), 7.70 (t, $^3J_{HH}$ = 8 Hz, 4-NC_5H_3; *ZZ*); $^{13}C\{^1H\}$ 31.0 (t, $^2J_{CF}$ = 22 Hz, *C*H$_2$CF$_2$; *ZZ*), 122.0, 123.8 (2s, *C*H=*C*HCH$_2$; *ZZ*), 133.2, 137.1, 154.9 (3s, NC_5H_3).[31] Anal. Calcd for $C_{27}H_{11}F_{34}N$: C, 32.58; H, 1.11. Found: C, 32.41; H, 1.08.

2,6-$NC_5H_3(CH_2CH_2CH_2R_{f8})_2$ (5). A Schlenk flask was charged with **4** (0.974 g, 0.978 mmol), 10% Pd/C (0.124 g), hexanes (10 mL), and ethanol (10 mL), purged with H_2, and fitted with a thick-walled balloon filled with H_2. The mixture was stirred (12 h) and filtered through a silica gel plug, which was eluted with ether (100 mL). Solvent was removed from the combined filtrates by rotary evaporation to give **5** as a white solid (0.935 g, 0.935 mmol, 95%). Mp: 48−49 (capillary), 48.0 (DSC) °C. NMR (δ, $CDCl_3$): ^1H 1.94−2.25 (m, 2C*H*$_2$C*H*$_2$-CF_2), 2.86 (t, $^3J_{HH}$ = 7 Hz, 2C*H*$_2$CH$_2$CH$_2$CF$_2$), 7.00 (d, $^3J_{HH}$ = 8 Hz, 3,5-NC_5H_3), 7.55 (t, $^3J_{HH}$ = 8 Hz, 4-NC_5H_3); $^{13}C\{^1H\}$ 20.3 (s, 2*C*H$_2$CH$_2$CF$_2$), 30.5 (t, $^2J_{CF}$ = 22 Hz, 2*C*H$_2$CF$_2$), 37.2 (s, 2*C*H$_2$CH$_2$CH$_2$CF$_2$), 120.7, 137.2, 160.2 (3s, NC_5H_3).[31] Anal. Calcd for $C_{27}H_{15}F_{34}N$: C, 32.45; H, 1.51. Found: C, 32.48; H, 1.48.

***cis*-2,6-$HNC_5H_8(CH_2CH_2CH_2R_{f8})_2$ (6).** Compound **4** (0.970 g, 0.974 mmol), 10% Pd/C (0.240 g), hexanes (20 mL), ethanol (20 mL), and H_2 were combined as in the preceding procedure. The sample was periodically monitored by ^1H NMR. After 11 days, an identical workup gave **6** as a white solid (0.961 g, 0.955 mmol, 98%). Mp: 72 (capillary), 66.6 (DSC) °C. NMR (δ, $CDCl_3$): ^1H 0.98−1.90 (m, 7CH$_2$ and NH), 2.01−2.17 (m, 2CH$_2$CF$_2$), 2.49−2.55 (m, 2NCH); $^{13}C\{^1H\}$ 16.8 (s, 2*C*H$_2$CH$_2$-CF_2), 24.7 (s, C-4), 31.1 (t, $^2J_{CF}$ = 22 Hz, 2*C*H$_2$CF$_2$), 32.7 (s, C-3, C-5), 36.9 (s, 2*C*H$_2$CH$_2$CH$_2$CF$_2$), 56.7 (s, C-2, C-6).[31] Anal. Calcd for $C_{27}H_{15}F_{34}N$: C, 32.25; H, 2.10. Found: C, 32.38; H, 2.32.

***cis*-2,6-$C_6H_5C(=O)NC_5H_8(CH_2CH_2CH_2R_{f8})_2$ (7).** A Schlenk flask was charged with **6** (0.500 g, 0.497 mmol) and THF (15 mL). Then NEt_3 (0.115 mL, 0.994 mmol) and PhCOCl (0.138 mL, 0.994 mmol) were immediately added by syringe. The mixture was stirred overnight, water (25 mL) was added, and the pH adjusted to ca. 8 (solid $KHCO_3$). The sample was extracted with CH_2Cl_2 (2 × 25 mL). The extracts were dried ($MgSO_4$), and solvent was removed. The light brown oil was chromatographed (silica gel column; 20:80 v/v EtOAc/hexanes) to give **7** as a colorless oil (0.506 g, 0.456 mmol, 92%). IR (cm^{-1}, thin film): ν_{CO} 1629. NMR (δ, $CDCl_3$): ^1H 1.12−1.90 (m, 7CH$_2$), 2.11−2.33 (m, 2CH$_2$CF$_2$), 3.80 (br s, 1NCH), 4.77 (br s, 1NCH′), 7.19 (m, 2H of C_6H_5), 7.36 (m, 3H of C_6H_5); $^{13}C\{^1H\}$ 14.2 (s, 2CH$_2$CH$_2$CF$_2$), 17.9, 18.1 (2s, C-4), 27.7, 27.8 (2s, C-3, C-5), 29.0 (m, 2CH$_2$CF$_2$), 33.6, 34.4 (2s, 2CH$_2$CH$_2$CH$_2$CF$_2$), 48.3, 53.5 (2s, C-2, C-6), 126.0, 128.6, 129.1, 137.3 (4s, C_6H_5), 172.1 (s, C=O).[31] Anal. Calcd for $C_{34}H_{25}F_{34}NO$: C, 36.80; H, 2.27. Found: C, 36.58; H, 2.34.

***cis*-2,6-$C_6H_5CH_2NC_5H_8(CH_2CH_2CH_2R_{f8})_2$ (8).** A Schlenk flask was charged with $LiAlH_4$ (0.035 g, 0.92 mmol) and THF (1 mL), and a solution of **7** (0.450 g, 0.405 mmol) in THF (5 mL) was added dropwise with stirring. The flask was fitted with a condenser and placed in an oil bath (85 °C). After 12 h, the mixture was allowed to cool to room temperature, and water (5 mL) was slowly added. The sample was extracted with ether (3 × 20 mL). The extracts were dried ($MgSO_4$), and solvent removal by oil pump vacuum gave a yellowish oil that eventually solidified. The oil was flash chromatographed (silica gel column; 9:1 v/v hexanes/ether) to give **8** as a white solid (0.379 g, 0.346 mmol, 85%). Mp: 53 (capillary), 52.4 (DSC) °C. NMR (δ, $CDCl_3$): ^1H 1.19−1.62 (m, 7CH$_2$), 1.71−1.82 (m, 2CH$_2$CF$_2$), 2.60 (br s, 2NCH), 3.67 (s, C*H*$_2$C$_6$H$_5$), 7.19 (t, $^3J_{HH}$ = 7 Hz, 1H of C_6H_5), 7.27−7.30 (m, 2H of C_6H_5), 7.37 (d, $^3J_{HH}$ = 7 Hz, 2H of C_6H_5); $^{13}C\{^1H\}$ 17.6 (s, 2*C*H$_2$CH$_2$CF$_2$), 24.0 (s, C-4), 27.5 (s, C-3, C-5), 31.1 (t, $^2J_{CF}$ = 22 Hz, 2*C*H$_2$CF$_2$), 34.4 (s, 2*C*H$_2$CH$_2$CH$_2$CF$_2$), 51.9 (s, *C*H$_2$C$_6$H$_5$), 126.4, 127.6, 128.2, 142.8 (4s, C_6H_5).[31] Anal. Calcd for $C_{34}H_{27}F_{34}N$: C, 37.27; H, 2.48. Found: C, 37.41; H, 2.69.

[2,6-$HNC_5H_3(CH_2CH_2R_{f8})_2$]$^+CF_3SO_3^-$ (9). A flask was charged with **1** (0.200 g, 0.206 mmol) and ether (5 mL), and CF_3SO_3H (0.050 mL, 0.56 mmol) was slowly added with stirring. The precipitate was isolated by filtration, washed with ether (3 × 10 mL), and dried by oil pump vacuum to give **9** as a white powder (0.222 g, 0.198 mmol, 96%). Mp: 140−150 °C (capillary), DSC (Figure 3) $T_i/T_e/T_p/T_c/T_f$[17] 86.56/91.28/92.89/96.17/99.30 (crystal to liquid crystal) and 134.31/155.30/162.75/166.00/170.14 °C (liquid crystal to liquid). IR (cm^{-1}, thin film, selected bands): 2883−2798 w, 1660 m, 1629 m, 1247 s, 1200 vs/br, 1170 s, 1146 vs, 1112 s, 1031 s. NMR (δ, acetone-d_6): ^1H 2.91−3.02 (m, 2CH$_2$CF$_2$), 3.62 (t, $^3J_{HH}$ = 7 Hz, 2C*H*$_2$CH$_2$-CF_2), 4.00−5.00 (br s, NH), 8.22 (d, $^3J_{HH}$ = 7 Hz, 3,5-NC_5H_3), 8.71 (t, $^3J_{HH}$ = 7 Hz, 4-NC_5H_3); $^{13}C\{^1H\}$ 25.3 (t,$^3J_{CF}$ = 5 Hz, *C*H$_2$CH$_2$CF$_2$), 30.3 (t, $^2J_{CF}$ = 22 Hz, *C*H$_2$CF$_2$), 128.7, 148.6, 155.7 (3s, NC_5H_3).[31] Anal. Calcd for $C_{26}H_{12}F_{37}O_3N$: C, 27.85; H, 1.08. Found: C, 28.12; H, 1.05.

***trans*-$Cl_2Pd[2,6\text{-}NC_5H_3(CH_2CH_2CH_2R_{f8})_2]_2$ (10).** A Schlenk was charged with $Cl_2Pd(NCCH_3)_2$ (0.060 g, 0.231 mmol),[32] $CF_3C_6H_5$ (10 mL), and **1** (0.550 g, 0.566 mmol), fitted with a condenser, and placed in an oil bath (110 °C). The orange solution was stirred (2.5 h) and allowed to cool to room temperature. The precipitate was collected by filtration, washed with ether (3 × 10 mL), and dried by oil pump vacuum to give **10** as a pale yellow solid (0.383 g, 0.180 mmol, 78%). Mp: 203−204 dec (capillary), 199.2 (DSC) °C. NMR (δ, $CDCl_3$/$CF_3C_6F_5$, 1/1 v/v): ^1H 2.94−3.04 (m, 2CH$_2$CF$_2$), 4.73 (t, $^3J_{HH}$ = 7 Hz, 2C*H*$_2$CH$_2$CF$_2$), 7.39 (d, $^3J_{HH}$ = 7 Hz, 3,5-NC_5H_3), 7.90 (t, $^3J_{HH}$ = 7 Hz, 4-NC_5H_3). Anal. Calcd for $C_{50}H_{22}Cl_2F_{68}N_2Pd$: C, 28.32; H, 1.04. Found: C, 28.24; H, 1.07.

Partition Coefficients. The following is representative.[3] A 1 dram vial was charged with **1** (0.0215 g, 0.0222 mmol), $CF_3C_6F_{11}$ (2.000 mL), and toluene (2.000 mL), fitted with a mininert valve, and vigorously shaken (2 min). After 12−24 h (24 °C), an aliquot of each layer (0.500 mL) was added to a hexane solution of octadecane (0.500 mL, 0.0177 M). Then ether (0.50 mL) was added. GC analyses (OPTIMA-5−0.25 μm capillary column (25 m × 0.32 mm), average of seven to eight injections) showed 0.00495 mmol of **1** in the $CF_3C_6F_{11}$ aliquot and 0.00033 mmol in the toluene aliquot (93.8:6.2; a 2.000/0.500 scale factor gives a mass balance of 0.0211 g, 95%). Typical retention times (compound/standard): **1**/octadecane, 3.1/4.5 min, 200 °C; **2**/hexadecane, 8.8/4.9 min, 175 °C, **3**/eicosane, 3.1/2.6 min, 250 °C, **5**/hexadecane 4.5/2.9 min, 200 °C, **6**/eicosane, 5.1/7.5 min, 200 °C; **8**/eicosane, 8.5/3.8 min, 225 °C.

Crystallography. To a solution of **1** (0.202 g, 0.208 mmol) in ethanol/$CF_3C_6H_5$ (10 mL, 9:1 v/v) was added CF_3SO_3H (0.075 mL, 0.847 mmol). The solvents were allowed to slowly evaporate (25 °C). After 3 weeks, colorless prisms of **9** had formed. Data were collected as summarized in Table S1 (Supporting Information). Cell parameters were obtained from 10 images using a 10° scan and refined with 8418 reflections. The space group was determined from systematic absences and subsequent least-squares refinement. Lorenz, polarization, and empirical absorption corrections were applied.[33] The structure was solved by direct methods (SHELXS-97).[34] The parameters were refined with all data by full-matrix-least-squares on F^2

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(SHELXL-97).[34] Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined freely and isotropically. Scattering factors were taken from literature.[35] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 176600. Copies of this information can be obtained free on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (int) + 44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk].

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Supporting Information Available: Table of general crystallographic data for **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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