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New Media for Classical Coordination Chemistry: Phase Transfer of Werner and Related Polycations into Highly Nonpolar Fluorous Solvents

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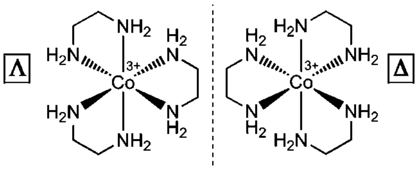
Supporting Information

ABSTRACT: Optimized procedures for the previously reported conversions of 1,3-diiodobenzene and perfluorohexyliodide ($R_{f6}I$; copper, DMSO, 140 °C) to 1,3-$C_6H_4(R_{f6})_2$ (**3**; 86−70%) and **3** to Br(3,5-$C_6H_3(R_{f6})_2$) (**2**; NBS, H_2SO_4/CF_3CO_2H; 88−75%) are described. The latter is converted (*t*-BuLi, BCl_3) to the "fluorous BAr$_f$" salt NaB(3,5-$C_6H_3(R_{f6})_2)_4$ (**1** or NaBAr$_{f6}$; 77−70%), as given earlier. When orange aqueous solutions of [Co(en)$_3$]Cl$_3$ (en = ethylenediamine) are treated with perfluoro(methylcyclohexane) (PFMC) solutions of **1** (1:3 mol ratio), the aqueous phase decolorizes and [Co(en)$_3$](BAr$_{f6}$)$_3$ can be isolated from the fluorous phase (96%). Similar reactions with the *trans*-1,2-cyclohexanediamine analogue [Co(*R,R*−chxn)$_3$]Cl$_3$ and [Ru(bipy)$_3$]Cl$_2$ give [Co−(*R,R*−chxn)$_3$](BAr$_{f6}$)$_3$ (92%) and [Ru(bipy)$_3$](BAr$_{f6}$)$_2$ (95%). All of these salts are isolated as hydrates and exhibit toluene/PFMC partition coefficients of ≤1:≥99, establishing that the anion BAr$_{f6}^-$ can efficiently transport polar polycations into highly nonpolar fluorous phases. When equal volumes of CH_2Cl_2 and PFMC are charged with the "nonfluorous" BAr$_f$ (B(3,5-C_6H_3−$(CF_3)_2)_4$) salt [Co(en)$_3$](BAr$_f$)$_3$ and 3.0 equiv of the fluorous salt NaBAr$_{f6}$, the cobalt trication partitions predominantly into the fluorous phase (64:36). The arene **2** crystallizes in a polar space group (tetragonal, *I*4, *Z* = 8) with fluorous and nonfluorous domains and all eight bromine atoms located essentially on one face of the unit cell.

INTRODUCTION

The chiral octahedral tris(ethylenediamine) cobalt trication [Co(en)$_3$]$^{3+}$ and related Werner systems represent important milestones in the development of inorganic chemistry and stereochemistry.[1−3] As Werner reported in 1912,[2b] the two enantiomers of [Co(en)$_3$]$^{3+}$ can be separated by crystallization of the diastereomeric tartrate salts. As depicted in Scheme 1, the configurations of the cobalt stereocenters are denoted Λ and Δ. Separation is commonly followed by halide anion exchange. Despite the simplicity of this procedure, applications of Werner salts in enantioselective organic reactions remain to be developed.

Scheme 1. Enantiomers of the Trication of [Co(en)$_3$]Cl$_3$



One factor inhibiting progress may be the lack of solubility in organic solvents. The racemic tetraphenylborate salt [Co(en)$_3$](BPh$_4$)$_3$ has been reported and is only soluble in methanol and THF.[4,5] We recently found that the more lipophilic B(3,5-$C_6H_3(CF_3)_2)_4$ "barf" (BAr$_f$) salt could be easily prepared by adding a CH_2Cl_2 solution of NaBAr$_f$ to an aqueous solution of enantiopure Δ-[Co(en)$_3$]I$_3$.[6,7] The trication rapidly transferred into the organic phase, and solvent removal afforded the hydrate Δ-[Co(en)$_3$](BAr$_f$)$_3$·14H$_2$O. This substance was soluble in a wide range of organic solvents, and the water is believed to be associated with a "second" or "outer" coordination sphere involving hydrogen bonding with the NH protons.

Ongoing work in our laboratory has demonstrated the extraordinary utility of such BAr$_f$ salts in enantioselective catalysis.[6,8] Accordingly, we became curious about the possibility of extending this chemistry to fluorous analogues and media.[9] Fluorous catalysts, which often feature ponytails of the formula $(CF_2)_{n-1}CF_3$ (R_{fn}), are easily separated from organic products and recycled by a number of protocols.[10] Furthermore, the "fluorous BAr$_f$" salt NaB(3,5-$C_6H_3(R_{f6})_2)_4$ (**1**, NaBAr$_{f6}$) had previously been reported.[11−13] Hence, we wondered whether it would be possible to render such polycations highly fluorophilic and readily soluble in perfluoroalkanes, which are some of the least-polar solvents known.

In this paper, we describe the facile solubilization of tricationic Werner salts in fluorous media. Because some

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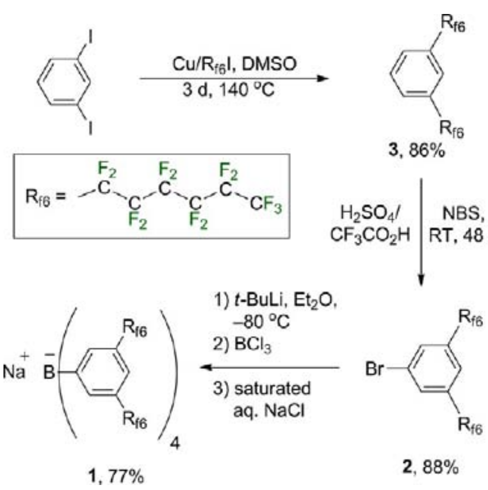
difficulties were encountered in the synthesis of $NaBAr_{f6}$, optimized procedures that have been repeated by several co-workers are provided. In order to confirm that this concept may be extended beyond cobalt hexaamine complexes, the synthesis of a fluorophilic salt of the extensively studied ruthenium dication $[Ru(bipy)_3]^{2+}$ is also detailed.[14] During the course of these efforts, the crystal structure of a fluorous arene could be determined, and it was found to exhibit several unusual features.

RESULTS

1. Synthesis of $NaBAr_{f6}$ (1). The van Koten–Deelman and Bühlmann research groups have reported syntheses of $NaBAr_{f6}$,[11,12] and each of these syntheses requires the fluorous bromoarene precursor $Br(3,5\text{-}C_6H_3(R_{f6})_2)$ (**2**). One route to the latter involves the selective disubstitution of 1,3,5-tribromobenzene using perfluorohexyliodide ($R_{f6}I$) and copper.[12,15,16] However, several co-workers have had difficulty both with stopping this reaction at the optimum stage and with the separation of monosubstitution or trisubstitution byproducts. Thus, we have synthesized **1** by modifying the sequence of van Koten–Deelman,[11] which is summarized in Scheme 2.

Scheme 2. Modified Syntheses of $NaBAr_{f6}$ (1)



First, the copper-mediated cross-coupling of 1,3-diiodobenzene and a slight excess of $R_{f6}I$ was carried out at 140 °C. Only DMSO was used as the solvent, as opposed to DMSO/C_6F_6, which was employed earlier.[11] The co-catalyst 2,2′-bipyridine was also omitted, necessitating a higher temperature. Workup after 3 days gave 1,3-di(perfluorohexyl)benzene or 1,3-$C_6H_4(R_{f6})_2$ (**3**) in 86–70% yields.

Next, **3** was brominated using a procedure developed by Dolbier for the analogous reaction of 1,3-di(trifluoromethyl)-benzene.[17] Thus, **3** was dissolved in 29:71 (v/v) H_2SO_4/CF_3CO_2H, and NBS was added in portions over the course of 6 h. Workup after 2 days gave the aryl bromide $Br(3,5\text{-}C_6H_3(R_{f6})_2$ (**2**) as a spectroscopically pure white solid in 88–75% yields. The literature procedure used a 41:59 (v/v) H_2SO_4/CF_3CO_2H mixture, with a charge of NBS added every 2 days over the course of 7 days.[11] We repeatedly verified that these seemingly minor differences afforded, as reported, a ≈6:1 **2**/**3** mixture in only 54% yield.

Fluorous molecules often resist crystallization, but colorless crystals of **2** were obtained from an acetone-d_6 solution. X-ray data were collected, and the structure was determined, as summarized in Table 1 and the Experimental Section. Two views of the molecular structure and key bond lengths and angles are provided in Figure 1.[18] The perfluorohexyl groups adopt conformations that project "upward" from the plane of the arene ring, as reflected by C2–C3–C7–C8, C4–C3–C7–C8, C4–C5–C13–C14, and C6–C5–C13–C1 torsion angles of 97.6 to 83.1° (Figure 1, bottom). In contrast to first impressions, there is no mirror plane containing the carbon–bromine bond and the *para* carbon atom (Br1, C1, C4). Powder X-ray diffraction data obtained with samples of **2** prior to crystallization agreed well with the single-crystal data. There are several interesting aspects of this crystal structure, but further analyses are deferred to the Discussion section.

Table 1. Crystallographic Data for 2

empirical formula	$C_{18}H_3BrF_{26}$
formula weight	793.11
temperature of collection [K]	110(2)
wavelength [Å]	1.54178
crystal system	tetragonal
space group	*I*4
unit cell dimensions	
a [Å]	29.5335(13)
b [Å]	29.5335(13)
c [Å]	5.5624(3)
α [deg]	90
β [deg]	90
γ [deg]	90
V [Å^3]	4851.7(4)
Z	8
ρ_{calc} [Mg/m^3]	2.172
μ [mm^{-1}]	4.348
F(000)	3040
crystal dimension [mm^3]	0.45 × 0.04 × 0.04
Θ [deg]	2.12–59.92
range/indices (*h, k, l*)	−33,33; −33,33; −6,5
reflections collected	56681
independent reflections	3534 [*R*(int) = 0.0559]
completeness to Θ = 59.92°	98.9%
absorption correction	semiempirical from equivalents
max and min transmission	0.8453, 0.2451
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	3534/1/407
goodness-of-fit on F^2	1.051
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0190$, $wR_2 = 0.0466$
R indices (all data)	$R_1 = 0.0198$, $wR_2 = 0.0470$
absolute structure parameter	0.00(9)
largest diff. peak/hole [e Å^{-3}]	0.187/−0.316

The fluorous BAr_f salt **1** was synthesized according to the literature recipe in Scheme 2,[11] but a chromatographic workup was added (silica gel, ether, and then CH_2Cl_2/CH_3OH) that avoided persistent acetone solvates encountered with the reported purification. White needles were obtained from perfluoro(2-butyltetrahydrofuran) (FC-75) in 77–70% yields. As summarized in Table 2, **1** was soluble in all fluorous solvents investigated, as well as the hybrid solvent $C_6H_5–CF_3$[19] and a number of organic solvents. It was insoluble in benzene, toluene, and hexanes. The NMR properties of **1**–**3** closely agreed with those previously reported. In the case of **1**, a $^{13}C\{^1H,^{19}F\}$NMR spectrum was recorded, which showed a quartet for the *ipso* carbon at 161.8 ppm due to $^{11}B–^{13}C$

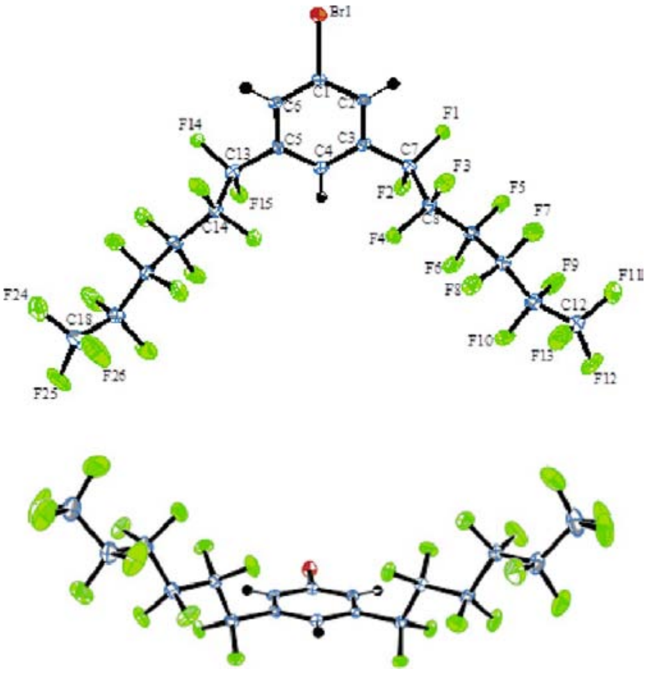


Figure 1. Two views of the molecular structure of **2** with thermal ellipsoids at the 50% probability level. Key bond lengths (Å) and angles (°): C1−Br 1.899(2), C1−C2 1.385(3), C2−C3 1.391(3), C4−C5 1.394(3), C5−C6 1.391(3), C6−C1 1.383(3), C3−C7 1.507(3), C5−C13 1.506(3), average of 10 CF−CF 1.544(5), Br−C1−C2 119.14(17), C1−C2−C3 118.7(2), C2−C3−C4 120.7(2), C3−C4−C5 119.3(2), C4−C5−C6 120.8(2), C5−C6−C1 118.5(2), C6−C1−C2 121.9(2), C6−C1−Br 118.93(17), C2−C3−C7 120.3(2), C4−C3−C7 119.0(2), C4−C5−C13 119.2(2), C6−C5−C13 120.0(2), average of eight CF−CF−CF 115.0(8).

Table 2. Solubility Data (24 °C)

	compound		
solvent	**1**	**4**[a]	**5**[b]
FC-72[c]	soluble	soluble	soluble
FC-75[d]	soluble	soluble	soluble
PFMC[e]	soluble	soluble	soluble
$C_6H_5CF_3$	soluble	soluble	soluble
acetone	soluble	soluble	soluble
Et_2O	soluble	soluble	soluble
CH_3OH	soluble	soluble	soluble
CH_2Cl_2	soluble	soluble	soluble
acetonitrile	soluble	sp soluble	insoluble
ethyl acetate	soluble	soluble	sp soluble
benzene	insoluble	insoluble	insoluble
toluene	insoluble	insoluble	insoluble
hexanes	insoluble	insoluble	insoluble

[a] $\cdot x H_2O$, x = 14−15. [b] $\cdot x H_2O$, x = 4−8. [c] FC-72: Perfluorohexanes. [d] FC-75: Perfluoro(2-butyltetrahydrofuran). [e] PFMC: Perfluoro(methylcyclohexane).

coupling (J = 50.0 Hz) and singlets, as opposed to multiplets, for the CF_2 groups.

2. Syntheses of BAr_{f6} Salts of Werner Complexes. As shown in Scheme 3 (top) and the photographs in Figure 2, a yellow aqueous solution of the racemic trichloride salt $[Co(en)_3]Cl_3\cdot 2.5H_2O$[20] and a colorless perfluoro(methylcyclohexane) (PFMC) solution of $NaBAr_{f6}$ (**1**) were combined (1:3 mol ratio) and were stirred. The lower PFMC phase turned yellow, and the upper aqueous phase decolorized. This suggested that the complete transfer of the trication $[Co(en)_3]^{3+}$ into the fluorous phase had occurred. The phases were separated, and the PFMC was removed. This gave the new, anion-exchanged salt $[Co(en)_3](BAr_{f6})_3\cdot xH_2O$ (**4**$\cdot xH_2O$) as an orange oil in 96% yield, which was characterized by NMR (^1H, ^{13}C) and elemental analysis (Experimental Section). In multiple runs, **4** was reproducibly isolated with 14−15 (x) water molecules of hydration, as assayed by ^1H NMR integrals and supported by microanalyses. In other studies,[8] such tris(diamine) trications have been shown to be superb hydrogen-bond donors.

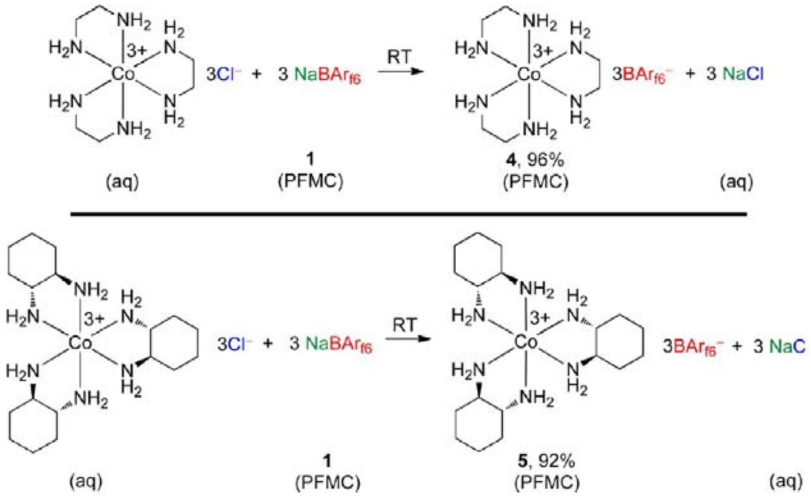
This protocol was extended to a related cobalt complex with somewhat more lipophilic and enantiopure *trans*-1,2-cyclohexanediamine or *R,R*−chxn ligands. As shown in Scheme 3 (bottom) and the photographs in Figure 3, an aqueous solution of the previously reported salt $[Co(R,R\text{−chxn})_3]Cl_3\cdot 4H_2O$[21] was treated with a PFMC solution of $NaBAr_{f6}$. The aqueous phase decolorized, and the cobalt trication transferred to the fluorous phase. An identical workup gave $[Co(R,R\text{−chxn})_3](BAr_{f6})_3\cdot xH_2O$ (**5**$\cdot xH_2O$) in 92% yield, which in multiple runs was isolated as a tetrahydrate to octahydrate (x = 4−8). We note that both the starting material and the product exhibit three chxn ^{13}C NMR signals, strongly suggestive of a single diastereomer (chirality at cobalt). In previous work (lacking ^{13}C NMR data), the Δ or Δ-*lel*$_3$ isomer has been shown to be considerably more stable.[21b]

Finally, to confirm the generality of these phase transfer phenomena, a comparable protocol was applied to the classic ruthenium dication, $[Ru(bipy)_3]^{2+}$.[14] As shown in Scheme 4 and the photographs in Figure 4, an aqueous solution of racemic $[Ru(bipy)_3]Cl_2\cdot 6H_2O$[22] was treated with a PFMC solution of $NaBAr_{f6}$ (1:2 mol ratio). The lower PFMC phase turned red, and the upper aqueous phase decolorized. An identical workup gave $[Ru(bipy)_3](BAr_{f6})_2\cdot xH_2O$ (**6**$\cdot xH_2O$) as a sticky red oil in 95% yield, which was characterized by NMR (^1H, ^{13}C) and elemental analysis (Experimental Section). The latter was best fit by a hemihydrate (x = 0.5), in agreement with the ^1H NMR integral.

3. Additional Physical Characterization of Werner Complexes. The fluorophilicities of substances can be quantified by partition coefficients.[23] These are frequently determined using the biphasic system toluene/PFMC. For example, the lipophilic alkanes *n*-decane through *n*-hexadecane exhibit partition coefficients of 94.6:5.4−98.9:1.1.[23] For this study, data for water/PFMC mixtures were also sought, given the solvents employed in Schemes 3 and 4 and Figures 2−4. Partition coefficients were assayed by ^{19}F NMR and UV−vis spectroscopy, as described in the Experimental Section. The ^{19}F NMR data are summarized in Table 3, and the UV−vis data were in good agreement.

The toluene/PFMC partition coefficients of the precursor salt $NaBAr_{f6}$ (**1**) and the tricationic cobalt salt $[Co(en)_3](BAr_{f6})_3$ (**4**) were 1:99 and <0.1:>99.9, respectively. The 1,2-cyclohexanediamine analogue **5** exhibited a comparable fluorophilicity, at least within the limits of the assay method. The dicationic ruthenium salt **6** appeared to be slightly less fluorophilic than the cobalt complexes (1:99). In a control experiment, it was verified that the nonfluorous analogue of **1**, $NaBAr_f$, exhibited a CH_2Cl_2/PFMC partition coefficient of >99.9:<0.1. The nonfluorous analogue of **4**, $[Co(en)_3](BAr_f)_3$, behaved similarly (neither of these salts are soluble in toluene). None of the salts exhibited an appreciable absolute solubility in

Scheme 3. Syntheses of Fluorous BAr_{f6} Salts of Werner Trications



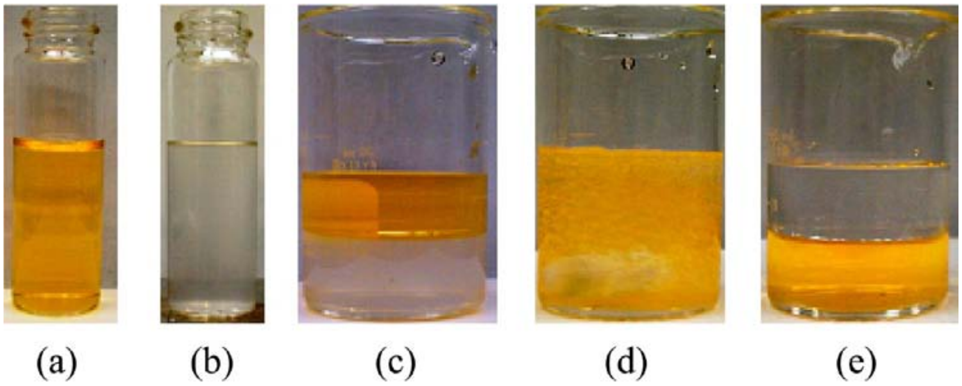


Figure 2. (a) Aqueous solution of $[Co(en)_3]Cl_3$ (2.1×10^{-3} M, 10 mL). (b) $NaBAr_{f6}$ solution in PFMC (6.3×10^{-3} M, 10 mL). (c) Biphasic mixture after gentle addition of (b) to (a). (d) Sample from (c) was stirred (10 min). (e) Sample from (d) after stirring was halted.

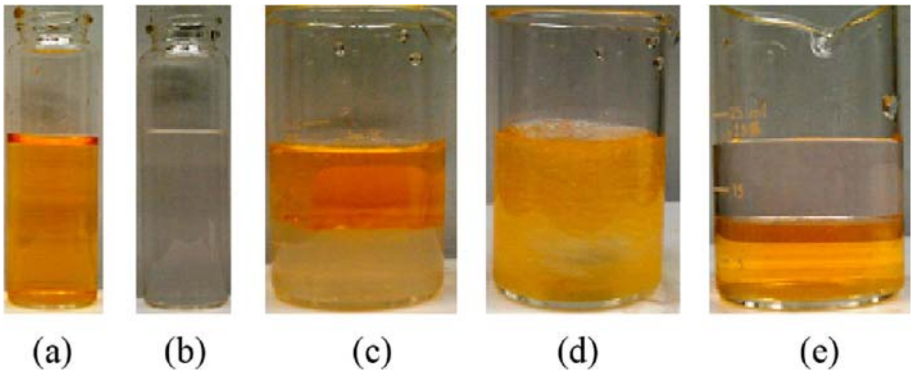
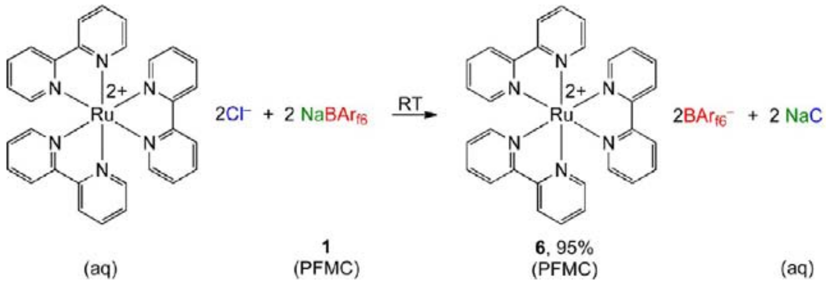


Figure 3. (a) Aqueous solution of $[Co(R,R\text{–}chxn)_3]Cl_3$ (2.1×10^{-3} M, 10 mL). (b) $NaBAr_{f6}$ solution in PFMC (6.3×10^{-3} M, 10 mL). (c) Biphasic mixture after gentle addition of (b) to (a). (d) Sample from (c) was stirred (10 min). (e) Sample from (d) after stirring was halted.

water, although from a partitioning standpoint, water seemed to be a slightly better solvent than toluene.

A final question involves how the cobalt trication $[Co(en)_3]^{3+}$ would partition between organic and fluorous phases in the presence of both the nonfluorous and the fluorous anions, BAr_f^- and BAr_{f6}^-. In other words, would this species prefer fluorous or nonfluorous environs? Of course, a second cation is required to set up the equilibrium. Hence, the result will reflect the weighted partitioning preference of both species. As shown in Scheme 5 and Figure 5, equal volumes of CH_2Cl_2 and PFMC were charged with the nonfluorous salt $[Co(en)_3](BAr_f)_3$ and 3.0 equiv of the fluorous sodium salt $NaBAr_{f6}$, respectively. The trication $[Co(en)_3]^{3+}$ partitioned predominantly into the fluorous phase (64:36), as assayed by ^1H NMR. By inference, the sodium monocation partitioned predominantly into the more polar organic phase. When an analogous experiment was carried out with 4.0 equiv of $NaBAr_{f6}$, the $[Co(en)_3]^{3+}$ concentration ratio increased to 73:27. Similar data were obtained by UV–vis spectroscopy.

Scheme 4. Synthesis of a Fluorous BAr_{f6} Salt of the Dication $[Ru(bipy)_3]^{2+}$



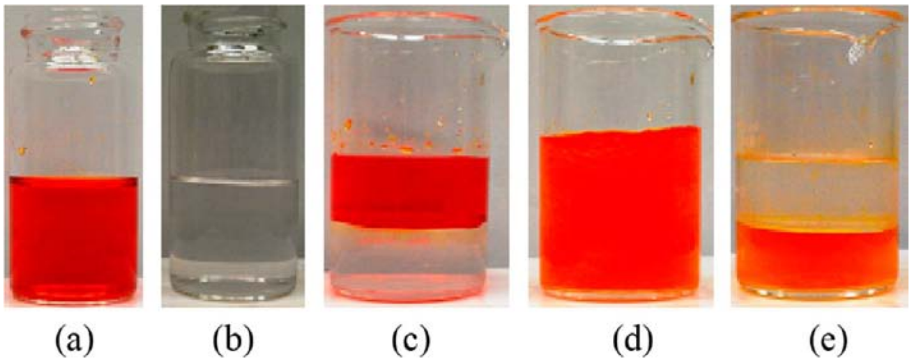


Figure 4. (a) Aqueous solution of $[Ru(bipy)_3]Cl_2{\cdot}6H_2O$ (2.1×10^{-3} M, 10 mL). (b) $NaBAr_{f6}$ solution in PFMC (4.20×10^{-3} M, 10 mL). (c) Biphasic mixture after gentle addition of (b) to (a). (d) Sample from (c) was stirred (10 min). (e) Sample from (d) after stirring was halted.

Table 3. Partition Coefficients Measured by ^{19}F NMR (24 °C)

compound	biphasic system	partition coefficients
$NaBAr_{f6}$ (**1**)[a]	water/PFMC	0.2:99.8
	toluene/PFMC	1:99
$NaBAr_f$[b]	CH_2Cl_2/PFMC	>99.9:<0.1
4[c]	water/PFMC	<1:>99
	toluene/PFMC	<0.1:>99.9
$[Co(en)_3](BAr_f)_3$[d]	CH_2Cl_2/PFMC	>99.9:<0.1
5[e]	water/PFMC	<1:>99
	toluene/PFMC	<0.1:>99.9
6[f]	water/PFMC	1:99
	toluene/PFMC	1:99

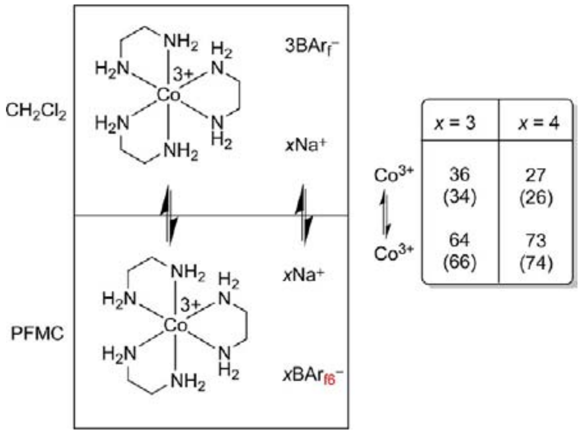
[a] $\cdot 2.5H_2O$. [b] $\cdot 2H_2O$. [c] $\cdot xH_2O$, x = 14–15. [d] $\cdot 7H_2O$. [e] $\cdot xH_2O$, x = 4–8. [f] $\cdot xH_2O$, x = 0.5–2.0.

Given the great interest in the photophysical properties of the ruthenium dication $[Ru(bipy)_3]^{2+}$,[14] the UV–vis spectrum of **6** was measured in PFMC. A strong UV absorption tailed into the visible region, which exhibited a characteristic band at 446 nm (ε 15 310 M^{-1} cm^{-1}). This λ_{max} is slightly lower than that found for other salts of $[Ru(bipy)_3]^{2+}$ in aqueous and organic solutions (average ≈450 nm),[14a] as well as another fluorous salt described in the Discussion section.[24] When the PFMC solution of **6** was irradiated at 446 nm, the fluorescence spectrum exhibited a λ_{max} at 594 nm. This Stokes shift (148 nm) is to our knowledge the largest observed for a $[Ru(bipy)_3]^{2+}$ salt to date.[14a,24]

DISCUSSION

The preceding results, together with other recently reported data,[6] establish that it is possible to selectively solubilize tris(1,2-diamine) cobalt trications in aqueous, organic, and fluorous solvents depending upon the counteranion selected.

Scheme 5. Partitioning of $[Co(en)_3]^{3+}$ between a CH_2Cl_2 Solution of $3BAr_f^-$ and a PFMC Solution of $xBAr_{f6}^-$ in the Presence of xNa^+ (x = 3, 4) As Determined by ^1H NMR and UV–Vis Spectroscopy (Unbracketed and Bracketed Values)



Similar results can be expected with a variety of other tris(diamine) Werner complexes, which are generally di- to tetracations derived from middle to late transition metals.[25] Thus, chemistry that has been largely limited to aqueous solutions for over a century can now be explored in less polar media that allow a much broader range of solutes.

For example, Table 2 shows that the fluorous Werner salts **4** and **5** are soluble in the usual fluorous (FC-72, FC-75, PFMC) and hybrid ($C_6H_5CF_3$) solvents, as well as a range of more polar organic solvents (acetone, Et_2O, CH_3OH, CH_2Cl_2, ethyl acetate). Thus, it is now possible to employ them as homogeneous catalysts in organic and fluorous media. Furthermore, Table 3 establishes that these salts markedly prefer to partition into fluorous over organic solvents (PFMC

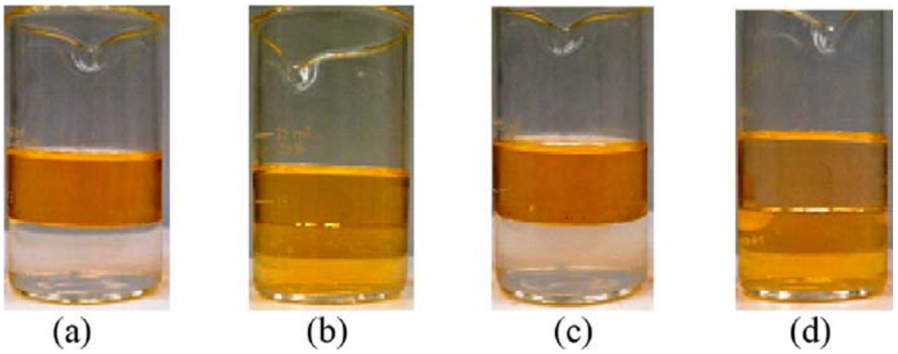
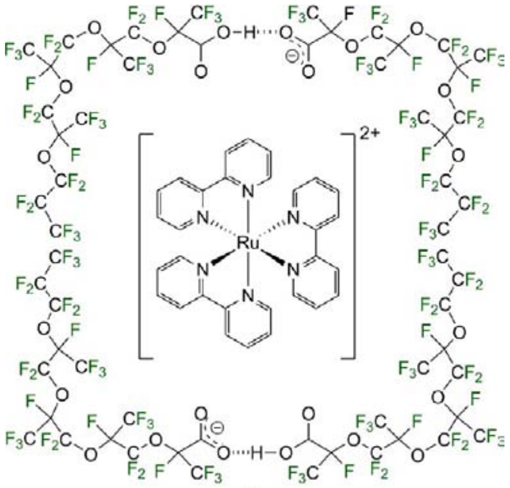


Figure 5. (a) Biphasic mixture after gentle addition of a 1.74 × 10^{-3} M CH_2Cl_2 solution of $[Co(en)_3](BAr_f)_3$ (10 mL, upper layer) to a 5.22 × 10^{-3} M PFMC solution of $NaBAr_{f6}$ (10 mL, bottom layer). (b) Sample from (a) after stirring was halted. (c) Biphasic mixture after gentle addition of a 1.74 × 10^{-3} M CH_2Cl_2 solution of $[Co(en)_3](BAr_f)_3$ (10 mL, upper layer) to a 6.96 × 10^{-3} M PFMC solution of $NaBAr_{f6}$ (10 mL, bottom layer). (d) Sample from (c) after stirring was halted.

vs toluene). Hence, it should be possible to extract, recover, and recycle such salts using fluorous solvents or supports.

In this context, we have found that the nonfluorous Werner salt $[Co(en)_3](BAr_f)_3$ catalyzes the Michael additions of malonates to enones in the presence of tertiary amines.[6,7] The trication is believed to function as a second coordination-sphere chiral hydrogen-bond donor toward the enone, activating it toward addition. Although enantioselectivities are modest (up to 33% ee), two classes of newer generation catalysts have recently been developed that afford Michael adducts with 80−95% ee.[8] Obviously, fluorous analogues could have attractive features, and catalysis data will be reported in due course.

Important and related work of Vincent and co-workers deserves emphasis.[24] He first prepared a salt of the ruthenium dication, $[Ru(bipy)_3]^{2+}$, with fluorous carboxylate anions, $[Ru(bipy)_3](O_2CCF(CF_3)(OCF_2CF(CF_3))_3OCF_2CF_2CF_3)_2$ (**7**). When taken up in CH_2Cl_2/perfluorodecalin mixtures, **7** partitioned exclusively into the organic phase. However, when 2 equiv of the carboxylic acid $HO_2CCF(CF_3)(OCF_2CF(CF_3))_3OCF_2CF_2CF_3)_2$ was added, the ruthenium was found exclusively in the fluorous phase. This was attributed to the generation of the salt **8** (Figure 6), which features two more fluorophilic monoanions derived from hydrogen-bonded carboxylate ions and carboxylic acids. It should be noted that it is also possible to solubilize polyanions—even dodecaanions—in fluorous media with suitable fluorous cations.[26]



8

Figure 6. Fluorophilic salt of $[Ru(bipy)_3]^{2+}$ prepared by Vincent and coauthors.

The UV−vis spectrum of **8** exhibited a band at 450 nm (perfluorodecalin; ε 14 100 M^{-1} cm^{-1}), a very slightly longer wavelength than our fluorophilic analogue **6** (Scheme 4; 446 nm and ε 15 300). In contrast, the λ_{max} in the fluorescence spectrum of **8** was at a somewhat shorter wavelength (585 vs 594 nm), making for a slightly reduced Stokes shift (135 vs 148 nm) and suggestive of a marginally less polar environment. Salts of $[Ru(bipy)_3]^{2+}$ mediate a number of photochemically triggered processes with a range of substrates.[14,27] There are possibilities for new selectivities or chemistries in fluorous media, for example, due to the much higher solubilities of small gaseous molecules as compared to aqueous media.[28] Vincent and co-workers established that **8** is an efficient photosensitizer for singlet oxygen, and enhanced $^1O_2$ lifetimes were observed.

Additional features of the crystal structure of bromoarene **2** (Figure 1) merit analysis. First, as noted in Table 1, **2** crystallizes in a chiral, polar space group ($I4$) as a tetragonal crystal system with α, β, and γ equal to 90°. As represented in Figure 7 (top), the unit cell dimensions are markedly skewed, with a and b equal to 29.5335(13) Å and c being >80% less at 5.5624(3) Å. The perfluorohexyl groups associated with the eight molecules in the unit cell lie roughly in a plane defined by the a/b axes. They exhibit C−C−C−C and F−C−C−F torsion angles characteristic of perfluoroalkyl groups, with the values for *anti* segments distinctly less than 180° (165.8(3.4) and 164.3(1.8)°, respectively).[29] They also segregate, as found for most fluorous molecules, into fluorous domains.[29]

Next, consider the eight aryl rings. Figure 7 shows that (1) they are oriented distinctly out of the plane defined by the a/b axes, with plane/plane angles of 48.1°, and (2) all of the bromine atoms are found on the same "side", or a/b face, of the unit cell. The bromine atoms from one unit cell nest approximately into the centroids of the arene rings of the adjacent unit cell (c direction) with bromine−centroid and centroid−centroid distances of 3.850 and 5.562 Å, respectively. The planes of the nesting rings are parallel, with separations of 3.71 Å.

The features in the preceding paragraph are manifestations of the polar nature of the crystal. Such crystals are sometimes observed to give nonlinear optical phenomena such as frequency doubling.[30,31] However, when a powdered sample of **2** is irradiated with a Nd:YAG laser (1064 nm; "Kurtz

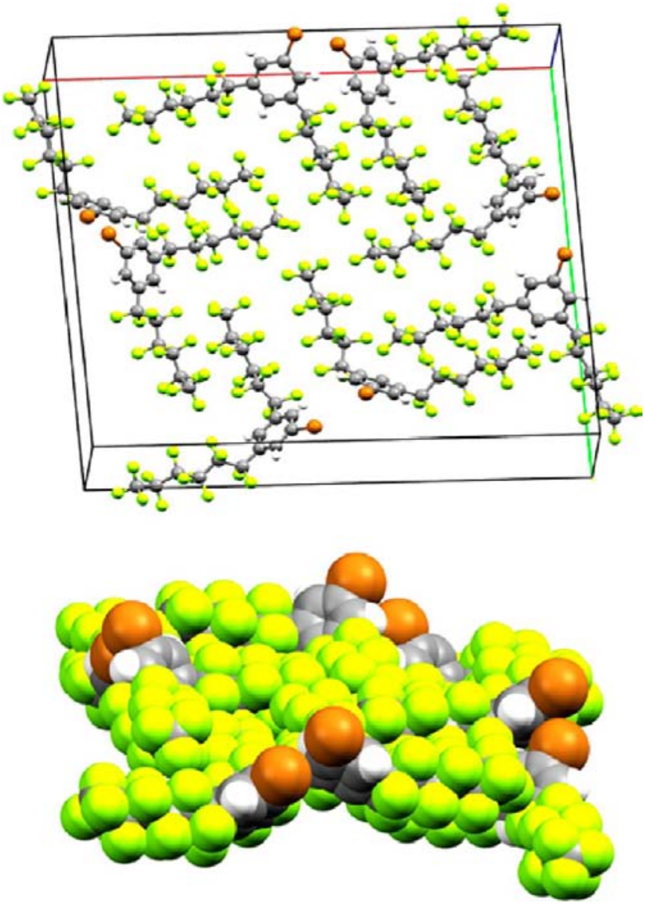


Figure 7. Packing of **2** in the unit cell (Z = 8). (Top) Ball-and-stick representation, (bottom) space-filling representation.

test"[32]), no detectable visible light is scattered. Crystals of **2** are highly piezoelectric (qualitative plastic comb test), and the space group ($I4$) is 1 of 10 that can exhibit spontaneous polarization without mechanical stress.[31]

In summary, this study has extended previous efforts to bring the chemistry of Werner cations from aqueous solutions into the full spectrum of modern liquid phases. Toward this end, an improved, scalable synthesis of $NaBAr_{f6}$ (**1**), a sodium salt of a highly fluorophilic anion, has been developed. Based upon the successful demonstration with the salts **4**−**6**, it can be anticipated that metal polycations can generally be solubilized in fluorous phases with the anion BAr_{f6}^-. The toluene/PFMC partition coefficients establish very high fluorophilicities (≤1:≥99) and provide a valuable foundation for the design of future applications. Finally, an intermediate in the synthesis of **1**, the fluorous bromoarene **2**, crystallizes in an uncommon polar space group and exhibits a range of interesting properties.

■ EXPERIMENTAL SECTION

General. All reactions were carried out under air unless noted. All workups were carried out in air. The Et_2O was dried and degassed using a Glass Contour solvent purification system. Fluorous chemicals were used as received from the following suppliers: perfluorohexyliodide ($R_{f6}I$; SynQuest Laboratories, 98%), C_6F_6 (TCI, 99%), FC-75 (perfluoro(2-butyltetrahydrofuran); Alfa Aesar, 99%), FC-72 (perfluorohexanes; Apollo Scientific, 98%), PFMC (perfluoro(methylcyclohexane); Alfa Aesar, 94%). Nonfluorous solvents and starting materials were used as received from common commercial sources, as summarized in the Supporting Information. NMR spectra were recorded at ambient probe temperatures and referenced as follows. ^1H: residual internal $CHCl_3$ (δ, 7.26 ppm), acetone-d_5 (2.05 ppm), or CHD_2CN (1.94 ppm). ^{13}C: internal acetone-d_6 (29.8 ppm), $CDCl_3$ (77.0 ppm), or CD_3CN (1.3 ppm). Instrumentation that was utilized is summarized in the Supporting Information.

1,3-$C_6H_4(R_{f6})_2$ (3).[11] An oven-dried Schlenk tube was charged with copper (7.02 g, 110 mmol), 1,3-diiodobenzene (7.09 g, 21.5 mmol), and DMSO (60 mL) and was stirred under N_2. Then perfluorohexyliodide ($R_{f6}I$; 10.2 mL, 47.1 mmol) was added dropwise over 5 min. The tube was sealed and kept at 140 °C (with stirring). After 3 days, the mixture was cooled to room temperature, and water (100 mL) was added. Some solid precipitated. The mixture was transferred to a separatory funnel and extracted with CH_2Cl_2 (3 × 150 mL; most of the solid was retained on the sides of the funnel). The combined extracts were filtered, washed with water (100 mL) and brine (100 mL), and dried (Na_2SO_4). The solvent was removed by rotary evaporation. The yellow oil was dissolved in FC-72 (15 mL), which was washed with acetone (2 × 20 mL; separatory funnel). The solvent was removed from the fluorous phase by rotary evaporation to give **3** as a light yellow oil (13.27 g, 18.58 mmol, 86%), the properties of which agreed with those previously reported.[11] ^1H NMR (δ (ppm), 500 MHz, $CDCl_3$ or $C_6F_6/CDCl_3$ mixture): 7.83 or 7.89 (s, 1H, doubly *o* to R_{f6}), 7.82 or 7.88 (s, 2H, singly *o* to R_{f6}), 7.69 or 7.78 (m, 1H, doubly *m* to R_{f6}).

Br(3,5-$C_6H_3(R_{f6})_2$) (2).[11,15] A round-bottomed flask was charged with **3** (11.4 g, 16.0 mmol). A mixture of H_2SO_4 (13.0 mL) and CF_3CO_2H (34.0 mL) was added with stirring. Then, solid NBS (4.42 g, 24.8 mmol) was added over the course of 6 h (one portion/h). After an additional 48 h (with stirring), the mixture was poured into a beaker of ice (300 g). Aqueous NaOH was added dropwise until a pH of 7−9 was reached. The mixture was extracted with CH_2Cl_2 (3 × 200 mL; separatory funnel). The combined extracts were dried (Na_2SO_4). The solvent was removed by rotary evaporation to give **2** as a white solid (11.23 g, 14.14 mmol, 88%), mp 44−42 °C, which was pure by GLC (Shimadzu SHRXI-5MS column) and which had previously been characterized as a mixture by a related route[11] and a pure compound by a different route.[15] ^1H NMR (δ (ppm), 500 MHz, $CDCl_3$ or $C_6F_6/CDCl_3$ mixture): 7.96 or 8.02 (s, 2H, *o*-BrC_6H_3), 7.74 or 7.84 (s, 1H, *p*-BrC_6H_3). $^{13}C\{^1H,^{19}F\}$ NMR (δ (ppm), 125 MHz, $CDCl_3$): 133.6 (s), 131.7 (s), 124.3 (s), 123.4 (s), 117.1 (s), 114.6 (s), 111.1 (s), 110.5 (s), 110.2 (s), 108.4 (s). UV−vis (nm, 1.94×10^{-3} M in PFMC (ε, $M^{-1}\ cm^{-1}$)): 274 (995), 281 (969).

$NaB(3,5-C_6H_3(R_{f6})_2)_4$ (1; $NaBAr_{f6}$).[11,12] A Schlenk flask was charged with **2** (3.70 g, 4.64 mmol) and Et_2O (170 mL) under a positive N_2 pressure and transferred to a −78 °C cold bath. After 20 min, *t*-BuLi (1.70 M in pentane; 6.00 mL, 10.2 mmol) was added dropwise over 10 min with stirring. After an additional hour, BCl_3 (1.00 M in hexane, 1.00 mL, 1.00 mmol) was added. After an additional 2 h, the cold bath was removed. After 2−3 h, the solution was poured into water (200 mL), which was saturated with NaCl with stirring. The mixture was extracted with Et_2O (3 × 150 mL). The combined extracts were dried ($MgSO_4$). The solvent was removed by rotary evaporation. The brown oil was chromatographed on a silica gel column (3 × 16 cm) packed in hexanes. The column was eluted with Et_2O, and a brown band was collected. The column was then eluted with CH_2Cl_2/CH_3OH (98:2 to 80:20 v/v). The fractions were monitored by thin-layer chromatography. The product-containing fractions were combined, and the solvent was removed by rotary evaporation. The off-white solid was recrystallized from FC-75, and the white solid was dried by oil pump vacuum to give $\mathbf{1}\cdot 2.5H_2O$ as a white solid (2.26 g, 0.771 mmol, 76%), mp 89−86 °C, the properties of which agreed with those previously reported.[11,12] ^1H NMR (δ (ppm), 500 MHz, acetone-d_6): 7.71 (s, 8H, *o*-BC_6H_3), 7.58 (s, 4H, *p*-BC_6H_3), 2.86−2.82 (m, 5H, H_2O). $^{13}C\{^1H,^{19}F\}$ NMR (δ (ppm), 125 MHz, acetone-d_6):[33] 161.8 (q, $^1J_{BC}$ = 50.0 Hz, *i*-BC_6H_3), 137.5 (s, *o*-BC_6H_3), 128.2 (s, *m*-BC_6H_3), 121.4 (s, *p*-BC_6H_3), 118.1 (s, CF_3), 116.8 (s, $BCC\underline{C}F_2$), 112.1 (s, CF_2), 111.8 (s, CF_2), 111.2 (s, CF_2), 109.3 (s, CF_2). Anal. Calcd for $C_{72}H_{12}BF_{104}Na\cdot 2.5H_2O$: C, 29.50; H, 0.58; F, 67.40. Found: C, 29.23; H, 0.49; F, 67.50.

$[\mathrm{Co(en)_3}](\mathrm{BAr_{f6}})_3$ (4). A beaker was charged with a solution of **1**·2.5H_2O in PFMC (0.0063 M; 10.0 mL, 0.0630 mmol). An aqueous solution of racemic $[\mathrm{Co(en)_3}]\mathrm{Cl_3}\cdot2.5\mathrm{H_2O}$ (0.0021 M; 10.0 mL, 0.0210 mmol)[20] was added. The biphasic mixture was vigorously stirred for 10 min. Stirring was halted, and the lower fluorous phase was separated and dried ($MgSO_4$). The solvent was removed by rotary evaporation and oil pump vacuum to give **4**·$x$$H_2O$ (x = 14–15) as an orange oil (0.0183 g, 0.020 mmol, 96%). ^{1}H NMR (δ (ppm), 500 MHz, acetone-d_6): 7.71 (s, 24H, o-BC_6H_3), 7.58 (s, 12H, p-BC_6H_3), 5.70 (br s, 6H,[34] N$\underline{H}$H′), 5.29 (br s, 6H,[34] NH$\underline{H}$′), 3.31 (br s, 12H, CH_2), 2.83 (s, 28–30H, H_2O). ^{13}C{^{1}H,^{19}F} NMR (δ (ppm), 125 MHz, acetone-d_6):[33] 161.9 (q, $^{1}J_{BC}$ = 50.0 Hz, i-BC_6H_3), 137.5 (s, o-BC_6H_3), 128.3 (s, m-BC_6H_3), 121.4 (s, p-BC_6H_3), 118.1 (s, CF_3), 116.8 (s, BCC$\underline{C}F_2$), 112.1 (s, CF_2), 111.8 (s, CF_2), 111.2 (s, CF_2), 109.3 (s, CF_2), 46.2 (s, CH_2). Anal. Calcd for $C_{222}H_{60}CoB_3F_{312}N_6\cdot14.5H_2O$: C, 29.33; H, 0.99; N, 0.92; F, 65.20. Found: C, 29.43; H, 0.91; N, 0.88; F, 64.63.[35]

$[\mathrm{Co}(\mathit{R,R}\text{–}\mathrm{chxn})_3](\mathrm{BAr_{f6}})_3$ (5). A beaker was charged with a solution of **1** in PFMC (0.0063 M; 10.0 mL, 0.0630 mmol). Then, an aqueous solution of $[\mathrm{Co}(R,R\text{–}\mathrm{chxn})_3]\mathrm{Cl_3}\cdot4\mathrm{H_2O}$ (0.0021 M; 10.0 mL, 0.0210 mmol)[6,21] was added. The biphasic mixture was vigorously stirred for 10 min. Stirring was halted, and the lower fluorous phase was separated and dried ($MgSO_4$). The solvent was removed by rotary evaporation and oil pump vacuum to give **5**·$x$$H_2O$ (x = 4–8) as an orange oil (0.175 g, 0.019 mmol, 92%). ^{1}H NMR (δ (ppm), 500 MHz, acetone-d_6): 7.70 (s, 24H, o-BC_6H_3), 7.57 (s, 12H, p-BC_6H_3), 5.53 (br s, 4H,[34] N$\underline{H}$H′), 5.16 (br s, 4H, NH$\underline{H}$′), 3.00 (br s, 6H, CHN), 2.84 (s, 8–16H, H_2O), 2.35 (m, 6H of $(CH_2)_4$), 1.74 (m, 6H of $(CH_2)_4$), 1.62 (m, 6H of $(CH_2)_4$), 1.22 (m, 6H of $(CH_2)_4$). ^{13}C{^{1}H,^{19}F} NMR (δ (ppm), 125 MHz, acetone-d_6):[33] 161.8 (q, $^{1}J_{BC}$ = 50 Hz, i-BC_6H_3), 137.5 (s, o-BC_6H_3), 128.3 (s, m-BC_6H_3), 121.4 (s, p-BC_6H_3), 118.1 (s, CF_3), 116.8 (s, BCC$\underline{C}F_2$), 112.1 (s, CF_2), 111.8 (s, CF_2), 111.2 (s, CF_2), 109.3 (s, CF_2), 61.5 (s, C$\underline{H}NH_2$), 33.6 (s, CH_2), 24.6 (s, CH_2). Anal. Calcd for $C_{234}H_{78}CoB_3F_{312}N_6\cdot4H_2O$: C, 31.01; H, 0.96; N, 0.93; F, 65.40. Found: C, 31.05; H, 0.86; N, 0.95; F, 63.97.[35]

$[\mathrm{Ru(bipy)_3}](\mathrm{BAr_{f6}})_2$ (6). A beaker was charged with a solution of **1** in PFMC (0.0130 M; 10.0 mL, 0.13 mmol). Then, an aqueous solution of $[\mathrm{Ru(bipy)_3}]\mathrm{Cl_2}\cdot6\mathrm{H_2O}$ (0.00650 M, 10.0 mL, 0.065 mmol)[22] was added. The biphasic mixture was vigorously stirred for 10 min. Stirring was halted, and the lower fluorous phase was separated and dried ($MgSO_4$). The solvent was removed by rotary evaporation and oil pump vacuum to give **6**·$x$$H_2O$ (x = 0.5–2.0) as a sticky red oil (0.391 g, 0.062 mmol, 95%). ^{1}H NMR (δ (ppm), 500 MHz, acetone-d_6): 8.86 (d, J = 10.0 Hz, 6H of 3bipy), 8.24 (t, J = 7.50 Hz, 6H of 3bipy), 8.10 (d, J = 5.00 Hz, 6H of 3bipy), 7.72 (s, 16H, o-BC_6H_3), 7.61 (m, 6H of 3bipy), 7.58 (s, 8H, p-BC_6H_3), 2.81 (m, 1–4H, H_2O). ^{13}C{^{1}H,^{19}F} NMR (δ (ppm), 125 MHz, acetone-d_6): 161.5 (q, $^{1}J_{BC}$ = 50 Hz, i-BC_6H_3)), 158.2 (s), 152.7 (s), 139.0 (s), 137.5 (s), 128.8 (s), 128.2 (s), 125.3 (s), 121.4 (s), 118.1 (s, CF_3), 116.8 (s), 112.0 (s), 111.8 (s), 111.2 (s), 109.3 (s). UV–vis (nm, 6.77×10^{-5} M in PFMC (ε, M^{-1} cm^{-1})): 446 (15300). Fluorescence (nm, 3.05×10^{-6} M in PFMC, λ_{ex} = 446 nm): 594. Anal. Calcd for $C_{174}H_{48}RuB_2F_{208}N_6\cdot0.5H_2O$: C, 33.14; H, 0.78; N, 1.33; F, 62.66. Found: C, 33.08; H, 0.68; N, 1.42; F, 59.80.[35]

$[\mathrm{Co(en)_3}](\mathrm{BAr_f})_3$.[36] A beaker was charged with a solution of $NaBAr_f\cdot2H_2O$ (0.510 g, 0.557 mmol)[37] in CH_2Cl_2 (20 mL). Then, a solution of racemic $[\mathrm{Co(en)_3}]\mathrm{Cl_3}\cdot2.5\mathrm{H_2O}$ (0.073 g, 0.186 mmol)[20] in water (20 mL) was added. The heterogeneous mixture was vigorously stirred for 15 min. The orange CH_2Cl_2 phase was separated from the colorless aqueous phase. The CH_2Cl_2 was allowed to evaporate in a fume hood overnight to give $[\mathrm{Co(en)_3}](\mathrm{BAr_f})_3\cdot7\mathrm{H_2O}$ as an orange powder (0.514 g, 0.173 mmol, 93%).[38] ^{1}H NMR (δ (ppm), 500 MHz, CD_3CN): 7.70 (m,[39] 24H, o-BC_6H_3), 7.67 (s, 12H, p-BC_6H_3), 4.20 (br s, 6H, N$\underline{H}$H′), 3.76 (br s, 4H, NH$\underline{H}$′), 2.75 (br s, 6H, C$\underline{H}$H′), 2.70 (br s, 6H, CH$\underline{H}$′), 2.27 (s, 14H, H_2O). ^{13}C{^{1}H} NMR (δ (ppm), 125 MHz, CD_3CN):[40] 162.6 (q, $^{1}J_{BC}$ = 50.0 Hz, i-BC_6H_3), 135.7 (s, o-BC_6H_3), 130.1 (q, $^{2}J_{CF}$ = 31.3 Hz, $\underline{C}CF_3$), 125.5 (q, $^{1}J_{CF}$ = 270 Hz, CF_3), 118.7 (t, $^{3}J_{CF}$ = 3.8 Hz, p-BC_6H_3), 45.6 (s, CNH_2). Anal. Calcd. for $C_{102}H_{60}B_3CoF_{72}N_6\cdot7H_2O$: C, 41.46; H, 2.52; N, 2.84. Found: C, 41.45; H, 2.54; N, 2.76.

Partition Coefficients. The following are representative: (**A**) (UV–vis) A standard solution of **1**·2.5H_2O (0.0591 g, 0.0200 mmol) in PFMC (20.00 mL volumetric flask) was prepared (1.00×10^{-3} M). This was diluted in a series of volumetric flasks to give 6.25×10^{-5}, 1.25×10^{-4}, and 2.50×10^{-4} M solutions. The three solutions gave UV–vis absorbances (A, 271 nm) of 0.33450, 0.60840, and 1.2424, indicating good agreement with Beer's law and an extinction coefficient (ε) of 4968 M^{-1} cm^{-1} (R = 0.999). (**B**) A standard solution of $[\mathrm{Co(en)_3}](\mathrm{BAr_f})_3\cdot7\mathrm{H_2O}$ (0.0503 g, 0.0170 mmol) in CH_2Cl_2 (10.00 mL volumetric flask) was prepared (1.70×10^{-3} M). This was diluted in a series of volumetric flasks to give 8.0×10^{-4}, 1.2×10^{-3}, and 1.70×10^{-3} M solutions. The three solutions gave UV–vis absorbances (A, 468 nm) of 0.0643, 0.1026, and 0.1423, indicating good agreement with Beer's law and an extinction coefficient (ε) of 82.99 M^{-1} cm^{-1} (R = 0.998). (**C**) (Partitioning, UV–vis) Water (4.0 mL) and a 1.00×10^{-3} M PFMC solution of **1**·2.5H_2O (4.0 mL) were combined in a vial (20 mL) at room temperature (24 °C) and were vigorously stirred (10 min). Stirring was halted. After 15 min, an aliquot (3.0 mL) was removed from the aqueous phase. An aliquot (0.50 mL) was removed from the PFMC phase and was diluted to 2.0 mL. Aliquots were assayed by UV–vis, and the absorbances (0.02160 and 1.1735) indicated 4.30×10^{-6} and 2.36×10^{-4} M concentrations, respectively (see data from **A**). This corresponds to a concentration ratio of $4.30 \times 10^{-6}/9.45 \times 10^{-4}$ (1.72×10^{-5} mmol of **1** in the aqueous phase and 3.78×10^{-3} mmol of **1** in the fluorous phase), or ≈1:99 (Table 3). (**D**) (Partitioning, NMR) A 20 mL vial was charged with a PFMC solution of **1**·2.5H_2O (5.0×10^{-4} M, 4.0 mL) and toluene (4.0 mL) and was capped and vigorously stirred. After 10 min at room temperature (24 °C), aliquots were removed from the fluorous (2.0 mL) and organic (2.0 mL) phases. The solvent was evaporated from each, and the residues were dried under vacuum. A solution of $C_6H_5CF_3$ (internal standard; 0.020 mL) in acetone-d_6 (5.0 mL) was prepared. Each residue was dissolved in this solution, and ^{19}F NMR spectra were recorded. The relative peak integrations gave the ratios in Table 3. For nonfluorous BAr_f, CF_3CH_2OH was used as the internal standard. (**E**) A 30 mL beaker was charged with a PFMC solution of **1**·2.5H_2O (5.22×10^{-3} M, 10.0 mL, 0.0522 mmol) and a CH_2Cl_2 solution of $[\mathrm{Co(en)_3}](\mathrm{BAr_f})_3\cdot7\mathrm{H_2O}$ (1.74×10^{-3} M, 10.0 mL, 0.0174 mmol). The mixture was vigorously stirred. After 10 min at room temperature (24 °C), aliquots were removed from the fluorous (7.0 mL) and organic (7.0 mL) phases. The solvent was evaporated from each, and the residues were dried by oil pump vacuum. A solution of cyclohexane (internal standard; 0.020 mL) in acetone-d_6/$C_6H_5CF_3$ (5.0 mL, 4:1 v/v) was prepared. Each residue was dissolved in this solution, and ^{1}H NMR spectra were recorded. The relative peak integrations gave the ratios in Scheme 5. (**F**) (UV–vis) A beaker was charged with a solution of **1**·2.5 H_2O in PFMC (5.7×10^{-3} M; 6.0 mL, 0.0342 mmol) and a solution of $[\mathrm{Co(en)_3}](\mathrm{BAr_f})_3\cdot7\mathrm{H_2O}$ (1.9×10^{-3} M, 6.0 mL, 0.0114 mmol) in CH_2Cl_2. The mixture was vigorously stirred. After 10 min at room temperature (24 °C), aliquots were removed from the organic (3.0 mL) and fluorous (3.0 mL) phases. These were assayed by UV–vis, and the absorbances (0.0520 and 0.1314) indicated 6.3×10^{-4} M (see data from **B**) and 1.21×10^{-3} M (see data from **A**) concentrations, respectively. This corresponds to a concentration ratio of $6.3 \times 10^{-4}/1.21 \times 10^{-3}$ (0.0038 mmol of $[\mathrm{Co(en)_3}]^+$ in the CH_2Cl_2 phase and 0.0073 mmol of $[\mathrm{Co(en)_3}]^+$ in the fluorous phase).

Crystallography. A small vial was charged with **2** (0.025 g) and acetone-d_6 (0.15 mL), and the solution was kept at room temperature. After a few days, colorless crystals had formed and were analyzed as outlined in Table 1. Cell parameters were obtained from 180 data frames using a 0.5° scan.[41] No supercell or erroneous reflections were observed. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.[42] Data were corrected for Lorentz and polarization factors, as well as for crystal decay and (using SADABS)[43] absorption effects. The space group was determined by systematic reflection conditions and statistical tests. The structure was solved by direct methods using SHELXTL (SHELXS).[44] The absence of additional symmetry was verified using PLATON (ADDSYM).[45] The hydrogen atoms were fixed in idealized positions using a riding model. Non-hydrogen atoms were refined with anisotropic thermal parameters. The parameters were refined by weighted least-squares refinement on F^2 to convergence.[44,46] The absolute structure parameter was estimated as 0.00(9) (Table 1).[47]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Data on starting materials and instrumentation, NMR spectra, and a CIF file with crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The MS Thesis of this author, upon which this manuscript is in part based, was submitted under the name of Ann R. Sullivan.

The authors declare no competing financial interest.

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(7) A reviewer has questioned our characterization of the salt $NaBAr_f$ or the corresponding anion as nonfluorous. Although this compound contains 24 sp^3 carbon−fluorine bonds, significantly fluorophilic molecules that feature only isolated trifluoromethyl groups (as opposed to compact arrays such as $OC(CF_3)_3$) are rare. Given the >99.9:<0.1 CH_2Cl_2/PFMC partition coefficients for $NaBAr_f$ and $[Co(en)_3](BAr_f)_3$ in Table 3, we hesitate to even refer to such salts as "light fluorous".

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(35) The fluorine analysis does not closely correspond to the calculated value, but in view of the excellent C/H/N agreement, it is believed to result from an analytical artifact.

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