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The First (Ferrocenylmethyl)imidazolium and (Ferrocenylmethyl)triazolium Room Temperature Ionic Liquids

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N-(Ferrocenylmethyl)imidazole (**3a**), 1-(ferrocenylmethyl)-1,2,4-triazole (**3b**), 1,1′-bis[(1*H*-imidazol-1-yl)methyl]ferrocene (**8a**), 1,1′-bis{[1*H*-(2-methyl)imidazol-1-yl]methyl}ferrocene (**8b**), and 1,1′-bis[(1*H*-1,2,4-triazol-1-yl)methyl]ferrocene (**8c**) were synthesized in moderate yields. These compounds were quaternized with methyl iodide to form 1-(ferrocenylmethyl)-3-methylimidazolium iodide (**4a**), 1-(ferrocenylmethyl)-4-methyl-1,2,4-triazolium iodide (**4b**), 1,1′-bis{[1-(2,3-dimethyl)imidazolium]methyl}ferrocene diiodide (**9b**), and 1,1′-bis{[1-(4-methyl)-1,2,4-triazolium]methyl}-ferrocene diiodide (**9c**), respectively, in excellent yields. Compounds **4a**, **4b**, **9b**, and **9c** were metathesized with bis(trifluoromethanesulfonyl)amide to give high yields of **5a**, **5b**, **10b**, and **10c**. With potassium hexafluorophosphate, **9b** forms **10d**. Salts **5a**, **5b**, and **10c** are the first room-temperature ionic liquids with cations containing an organometallic moiety that exhibit T_g values well below room temperature, i.e., –32, –16, and –11 °C. The compounds were characterized by ^{1}H, ^{19}F, and ^{13}C NMR, MS, and elemental analyses. T_g values and melting points were determined by DSC. T_d values (5% weight loss temperature) were recorded by TGA. X-ray single-crystal structures show that **9c** and **10d** crystallize in the triclinic space group $P\bar{1}$.

While the first ionic liquid reported was ethylammonium nitrate in 1914,[1] the current surge in interest stems mainly from the work reported in 1992 when a series of air- and moisture-stable imidazolium salts with anions (nonchloroaluminate-containing), such as [BF_4^-] and [PF_6^-], were synthesized.[2] In the interim, ionic liquids have been suggested for a wide range of applications including in the fields of organic syntheses and biphasic catalysis[3] and in other areas, e.g., surfactants,[4] electrochemistry,[5] separations,[6] and photochemistry.[7] There are a large number of excellent reviews covering syntheses and applications of these versatile liquids.[8−20]

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Ionic liquids are fascinating and exploitable because of their excellent thermal and chemical stability, tolerance to strong acids, wide electrochemical window, high electrical conductivity, wide temperature ranges, and essentially negligible vapor pressure. There appears to be no limit to the number of such liquids that can be designed for specific reactions and processes!

Metal-containing ionic liquids are rather rare (nonchloroaluminate-containing) and most often contain rather complex anions where the metal resides.[21−27] Recently, new organometallic imidazolium salts were reported including the first ionic liquid with a cation composed of an organometallic moiety $[Co_2(CO)_6]$-substituted imidazolium core.[28] The latter melts at 75−77 °C without decomposition. We now report the straightforward syntheses of ferrocene-containing salts including the first room-temperature ionic liquids with ferrocenylmethyl-substituted cations.

Results and Discussion

Synthesis and Characterization. While the acid-catalyzed ferrocenylalkylation reaction using α-ferrocenylcarbinols in aqueous−organic mixtures is one of the most convenient methods for introducing ferrocenylalkyl groups into various nucleophilic substrates including triazoles, this procedure is not applicable for materials with highly basic centers, such as imidazoles, due to protonation of the nitrogen.[29] The latter group can be introduced into ferrocenylalkyl compounds by the ferrocenylalkylation reactions of *N*,*N*′-carbonyldiimidazole. However, ferrocenylmethylation of imidazole and triazole is readily accomplished by reaction of the corresponding nucleophilic heterocycle with (trimethylammonium)methylferrocene iodide, which is an excellent electrophile due to the good leaving group characteristics of trimethylamine.[30] Using this methodology in our work, mono- and disubstitutions on ferrocene rings **1** and **6** were achieved to form **3a,b** and **8a−c,** respectively **(**Scheme 1). Quaternization with methyl iodide occurred readily with **3a**,**b** to form **4a**,**b** and with **8b**,**c** to give **9b**,**c** in excellent yields. However, under all conditions attempted, quaternization of **8a** with CH_3I did not occur. This may arise from the fact that **8a** is insoluble in every solvent tried with the exception of hot DMSO, and not surprisingly, reaction did not occur in that solvent. When the 2-methylimidazole derivative **8b** was dissolved in methanol, **9b** was obtained. Metathesis reactions of iodides **1**, **4a**, **4b**, **6**, **9b**, and **9c** with lithium bis(trifluoromethanesulfonyl)amide gave the respective salts **2**, **5a**, **5b**, **7**, **10b**, and **10c**. With potassium hexafluorophosphate, **9c** formed **10d**. All of the new salts were obtained in excellent isolated yields. For monosubstituted ferrocenes, the melting points of imidazole derivative **3a** and 1,2,4-triazole derivative **3b** are similar, 79−81 and 82.8 °C, respectively, which are higher than that of *N*,*N*-dimethylaminomethylferrocene (Table 1). Comparing their iodide and bis(trifluoromethanesulfonyl)amide, $[NTf_2]^-$, salts, the phase transition temperatures of imidazolium salts **4a** and **5a** were 145−148 °C[30] and −32.2 °C, respectively, which is slightly lower than those of the analogous 1,2,4-triazolium salts at 169.2 °C (**4b)** and −16.4 °C (**5b)**. [(Trimethylammonium)methyl]ferrocene iodide and bis(trifluoromethanesulfonyl)amide salts (**1**, **2**) exhibit the highest melting points at >220 and 84.5 °C.

With the exception of the mono- and disubstituted (diquaternized) (ferrencylmethyl)triazolium iodides **4b** and **9c**, the thermal decomposition points of all of the compounds are in excess of 200 °C. Not unexpectedly, the $[NTf_2]^-$ salts are more stable thermally than iodides, with little difference existing between the imidazoles **4a** and **5a** and triazoles **4b** and **5b**. For disubstituted compounds, the order of the melting points was **8a** > **8b** > **8c** > 1,1′-bis(*N*,*N*-dimethylaminomethyl)ferrocene. After quaternization with methyl iodide, the order of the melting points was **6** > **9b** > **9c**, compared with their bis(trifluoromethanesulfonyl)amide salts, where the order was **10c** < **10b** < **7**. All of the melting points decreased dramatically. There is considerable delocalization of the electron cloud over the molecular backbone of this anion, which tends to reduce hydrogen bonding in these liquid systems. However, when iodide **9b** was metathesized with KPF_6 to give **10d**, the decomposition point was reduced only by 3 °C. While the diiodide salts **9b** and **9c** decomposed at their melting points, the $[NTf_2]^-$ salts were considerably more stable. The relative melting points and stabilities of imidazolium and triazolium bis(trifluoromethanesulfonyl)amide analogues are similar to the simpler non-metal-containing ionic liquids; for example, 1-methyl-4-(trifluoropropyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)amide melts at −58 °C and decomposes thermally at 386 °C[32] compared with 1-methyl-3-(trifluoropropyl)imidazolium bis(trifluoromethanesulfonyl)amide melting at −74 °C and decomposing at >300 °C.[33] Similarly 1-methyl-4-

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Scheme 1

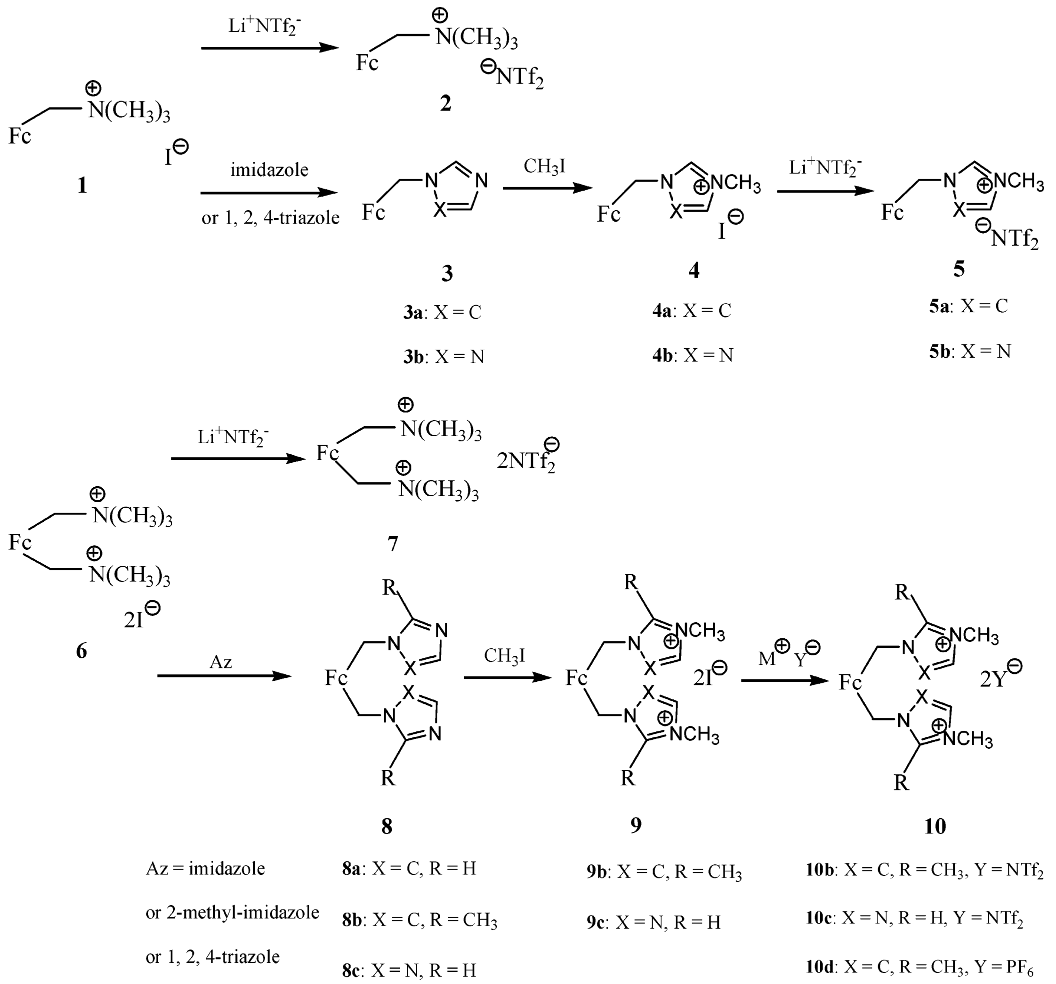

Table 1. Phase Transition and Thermal Decomposition Temperatures

compd	T_m (T_g), °C	T_d,[a] °C	compd	T_m (T_g), °C	T_d,[a] °C
1	220 dec		**7**	195	236
2	85	238	**8a**	292 dec	
3a	79−81[b]		**8b**	181	
3b	83		**8c**	114	
4a	145−148[b]	214	**9b**	248 dec	248
4b	169.2	199	**9c**	199 dec	200
5a	(−32)	248	**10b**	86	305
5b	(−16)	249	**10c**	(−11)	291
6	>300 (210 dec)[c]		**10d**	245 dec	264

[a] T_d was recorded as the 5% weight loss temperature. [b] Reference 30. [c] Reference 31.

(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)amide melts at 62 °C and decomposes at 381 °C compared with 1-methyl-3-(1*H*,1*H*,2*H*,2*H*,1*H*,2*H*,2*H*-perfluorooctyl)imidazolium bis(trifluoromethanesulfonyl)amide[34] melting at −50 °C and decomposing at >375 °C.

The three room-temperature ionic liquids **5a**, **5b**, and **10c** are thermally stable to ~250−290 °C and exhibit T_g values at −32, −16, and −11 °C, respectively. Their densities are 1.68, 1.85, and 1.88 g/cm^3 as determined at 24 °C using a pycnometer. These new heavy-metal-containing liquids have densities of approximately the same magnitude as those of pentafluorosulfanyl-substituted imidazolium and triazolium bis(trifluoromethanesulfonyl)amide salts, e.g., $SF_5(CF_2)_2(CH_2)_4MeIm^+[NTf_2]^-$ at 2.01 g/cm^3 and $SF_5(CF_2)_2(CH_2)_4PrTz^+[NTf_2]^-$ at 1.89 g/cm^3.[34] The SF_5 derivatives exhibit about the same thermal stabilities (>300 °C) as the ferrocenyl ionic liquids.

The UV−vis absorption spectrums of representative compounds showed absorption bands at 429−433 nm in dilute methanol (**8b**, **9b)** and in dilute acetonitrile (**10b**). Bands in this region are typical of iron bis(cyclopentadienyl). These spectra as well as that of ferrocene are shown in Figure 1. The absorption bands are independent of the substituent(s) on the ferrocene ring as well as of the anion.[35]

In the NMR spectrum of **9b**, the 4-H and 5-H of both imidazolium rings were observed at 7.19 and 7.21 ppm. This is a significant downfield shift from 6.74 and 6.82 ppm of **8b** and is typical of quaternized imidazolium species. The protons of the 2-CH_3 of imidazole also shifted from 2.35 to 2.57 ppm. Similaraly the 3-H and 5-H of both 1,2,4-triazolium rings of **9c** were markedly shifted to 8.70 and 9.52 ppm from 7.95 and 8.01 ppm in the nonquaternized rings of **8c**. This phenomenon was also observed in the disubstituted salts.

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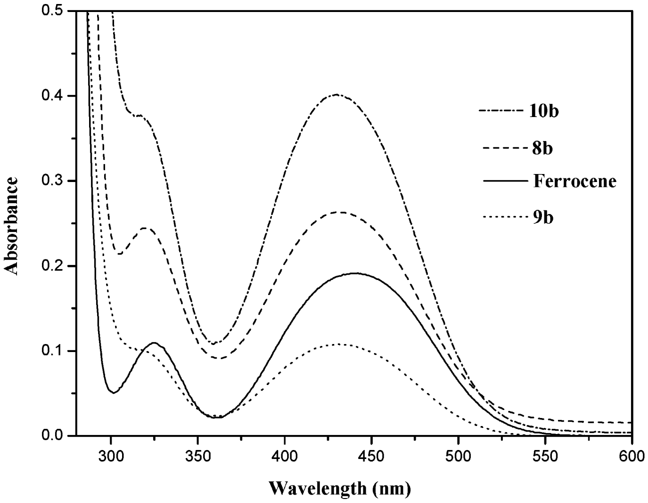

Figure 1. UV−vis spectra of ferrocene and compounds **8b**, **9b**, and **10b** (ferrocene, **8b**, and **9b** in methanol, **10b** in acetonitrile).

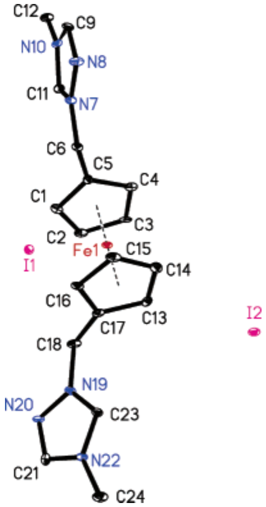

Figure 2. Structure of **9c**. Thermal displacement ellipsoids are shown at 30% probability. Hydrogen atoms and water molecules are omitted for clarity.

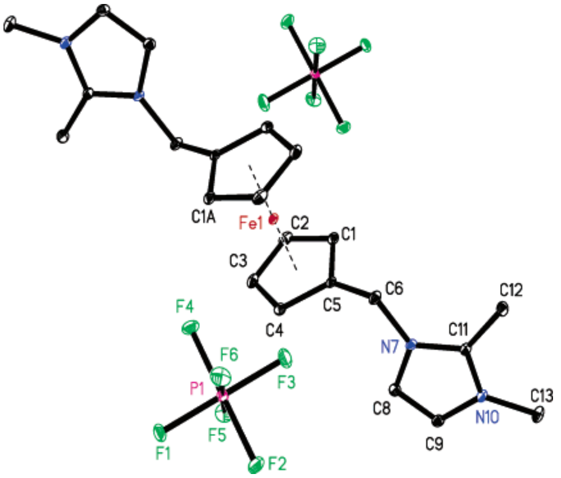

Figure 3. Structure of **10d**. Thermal displacement ellipsoids are shown at 30% probability. Hydrogen atoms are omitted for clarity.

The molecular ion was obtained in the mass spectra of the neutral compounds, but the cations were not found in the mass spectra of salts introduced via the solid probe. However, HRMS (FAB) was utilized to confirm the cations (M^+) for compounds **5a**, **8a**, **8c**, and **10c**.

The qualitative miscibilities of all of the compounds were determined qualitatively in water, methanol, acetone, and chloroform. The monosubstituted ferrocene salts **1**, **2**, **4a**, **4b**, **5a**, and **5b** were easily miscible with methanol, acetone, and chloroform, and only partially or nonmiscible in water. However, the disubstituted compounds **6**, **7**, **9a**, **9b**, and **10b** are all immiscible with chloroform but are somewhat soluble in more polar solvents such as methanol and to a lesser extent water and acetone.

Although we report the first ferrocenyl-containing room-temperature ionic liquids, while this work was in review, new routes to the synthesis of a number of mono-amino-functionalized ferrocenes, ferrocene, and ferrocenium salt counterparts were reported. Structural studies show N−H···O and N−H···F hydrogen bonds.[36] Similar compounds, such as α-(ferrocenylethyl)-1*N*-benzo-1,2,3-triazole, have been demonstrated to inhibit tumor growth and increased life expectancy in animals. Dinuclear ferrocene derivatives, bis(ferrocenyl)benzotriazolium salts, also were effective tumor inhibitors. Both were much less toxic than ferricinium salts. Our new compounds may be equally or more lipophilic and may broaden pharmacokinetic possibilities.[37]

Molecular Structures. Both **9c** (Figure 2) and **10d** (Figure 3) crystallize in the triclinic space group $P\bar{1}$ (Table 2). The iron atom in **10d** is on an inversion center so that half the cation and an anion are symmetry generated; **9c** does not display this internal symmetry. This lack of symmetry in **9c** is also reflected in the cyclopentadienyl (Cp) ring angles. The rings are not coplanar but have a 2° deviation, which is also shown in the Cp−Fe−Cp angle of 178.7°. In **10d** the rings are coplanar and the Cp−Fe−Cp angle is 180°. The arrangement of the substituents on the Cp ring is quite different, with the triazole rings in **9c** 132° to each other instead of the *trans* arrangement in **10d** for the diazole. The azole rings are free to rotate and have different angles to the Cp ring (Table 3). In both compounds the anions I^- and PF_6^- are separate from the cations with no intermolecular interactions. In **9c** the anions of closest approach are in the range I···H = 2.8−3.03 Å. These are extremely weak interactions at best as they are not conventional hydrogen bonds. The more important interaction in **9c** is the hydrogen bonding between a water molecule in the asymmetric unit and the iodide anions (O1−I1 = 3.474(5) Å, O1−I2 = 3.516(5) Å) (Table 3). This prevents any further interaction between the anion and the cation. The anion in **10d** is also separate from the ferrocenyl cation. The absence of a water molecule in this case does not assist in an intermolecular interaction between the cation and anion (F···H distances range from 2.44 to 2.88 Å). This separation of the charges affects the intrinsic properties of the compounds and is reflected in the low melting points.

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Table 2. Data Collection and Refinement Parameters for **9c** and **10d**

	9c	**10d**
empirical formula	$C_{18}H_{24}FeI_2N_6O$	$C_{22}H_{28}F_{12}FeN_4P_2$
fw	650.08	694.27
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.6962(19)	7.9312(16)
b (Å)	11.259(2)	9.5198(19)
c (Å)	11.964(2)	10.575(2)
α (deg)	67.49(3)	97.20(3)
β (deg)	77.62(3)	111.68(3)
γ (deg)	69.99(3)	113.93(3)
V (Å^3)	1128.5(5)	641.6(4)
Z	2	1
T (K)	84 (2)	84 (2)
D_c (g cm^{-3})	1.913	1.797
μ (mm^{-1})	3.424	0.822
F(000)	628	352
color, habit	yellow, fragment	yellow, plate
cryst size (mm)	0.26 × 0.23 × 0.07	0.16 × 0.16 × 0.08
θ range for data collection (deg)	1.85−27.50	2.19−27.50
index ranges (hkl)	$-12 \leq h \leq +12, -14 \leq k \leq +14, -15 \leq l \leq +9$	EnDash10 $\leq h \leq +10, -12 \leq k \leq +12, -13 \leq l \leq +13$
no. of reflns collected	9120	8382
no. of independent reflns (R_{int})	5120 (0.0365)	2933 (0.0302)
no. of reflns with $I > 2\sigma(I)$	3843	2586
max, min transmission	0.783, 0.424	0.9371, 0.8797
no. of data, restraints, params	5120, 36, 255	2933, 0, 189
GOF on F^2	1.058	1.126
final R^a indices [$I > 2\sigma(I)$]	R1 = 0.0514, wR2 = 0.1047	R1 = 0.0454, wR2 = 0.1010
largest diff peak and hole (e Å^{-3})	1.586, −1.461	0.789, −0.427

[a] $R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **9c** and **10d**

	9c, triazole		**10d**, diazole
$C_d{}^a$−Fe1	1.646(6)		1.645(4)
C_d−Fe1	1.647(6)		
N7−N8	1.364(8)	N7−C8	1.381(3)
N8−C9	1.326(8)	C8−C9	1.345(4)
C9−N10	1.369(8)	C9−N10	1.387(3)
N10−C11	1.336(8)	N10−C11	1.332(3)
C11−N7	1.312(8)	C11−N7	1.346(3)
Cp−Fe1−Cp	178.7		180.0
Cp>Cp	2		0
Cp>azole	87.7		78.7
	83.0		
C6−C5−C17−C18	132.1	C6a−C5a−C5−C6	180

[a] C_d = centroid of the Cp ring.

Substituted triazole structures are rare in the Cambridge database.[38] However, asymmetrically substituted diazoles are more common, and the bonding pattern seen in **10d** (Table 3) is similar in these cases.[39] These structures are unique, and there is only one other similar compound in the Cambridge database, 1,1′-bis(pyridiniomethyl)ferrocene dibromide monohydrate,[40] which is the sole nitrogen-containing arylmethylene-substituted compound. Although this molecule crystallizes in a higher symmetry space group, $P2(1)/n$, the molecule itself is not symmetric. The Cp rings are tilted 3.2° from each other, and the pyridyl rings are more flexible at 105° and 76.6° to the closest Cp ring. The most notable difference between this compound and **9c** and **10d** is the orientation of the substituents on the Cp rings. In this case the pyridylmethylene substituents have an angle of 74°, which is quite different from those of **9c** and **10d**. Part of the reason behind this is probably steric as **9c** and **10d** have methyl substituents on the tri- and diazoles.

Conclusion

Ferrocenes that are mono- and disubstituted with ammonium, imidazolium, and 1,2,4-triazolium moieties have been prepared. The imidazolium and 1,2,4-triazolium bis(trifluoromethanesulfonyl)amides are the first examples of room-temperature ionic liquids with organometal-containing cations. They may prove useful in potential applications in homogeneous catalysis as well as in biological systems. A system in which the ionic liquid is also the catalyst could prove to be a very clean way of conducting reactions.

Experimental Section

General Procedures. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded in acetone-d_6 unless otherwise indicated on a 300 (Bruker AMX 300) (500, Bruker AVANCE 500) MHz spectrometer operating at 300.1, 75.5, and 282.4 MHz, respectively. Chemical shifts are reported in parts per million relative to the peak for the appropriate standard. MS spectra were determined on a Shimadzu GCMS QP 5050A (EI mode) by using the solid probe. HRMS spectra were obtained with a JEOL JMS-AX505HA mass spectrometer. T_m and T_g were determined on a differential scanning calorimeter (TA Instruments Q10) at a scan rate of 10 °C/min. TGA

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(TA Instruments Q50) was recorded as the 5% weight loss temperature at a scan rate of 10 °C/min. IR spectra (BioRad FTS 3000 Excalibur series infrared spectrometer) were obtained using KBr plates for neat liquids and KBr pellets for solids. Densities were measured at 24 °C using a pycnometer. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ, and the Shanghai Institute of Organic Chemistry. The UV absorption spectra of compounds in either Spectrograde methanol or acetonitrile were recorded at ambient temperature using a Shimadzu UV-2501PC spectrophotometer.

Preparation of *N*-(Ferrocenylmethyl)imidazole (3a). *N*-(Ferrocenylmethyl)imidazole was prepared in a manner according to a literature method:[30] 0.77 g, 58% yield; yellow solid; ^{1}H NMR δ 4.18 (s, 5H), 4.21 (s, 4H), 4.88 (s, 2H), 6.92 (s, 1H), 7.04 (s, 1H), 7.50 (s, 1H); ^{13}C NMR δ 137.0, 129.5, 119.2, 83.08, 69.12, 69.07, 68.85, 47.03.

1-(Ferrocenylmethyl)triazole (3b) was prepared similarly to **3a**: 0.87 g, 65% yield; yellow solid; mp 81.2 °C; IR (KBr) 3101, 2978, 1512, 1339, 1272, 1136, 1029, 812 cm^{-1}; ^{1}H NMR δ 4.19 (s, 5H), 4.24 (t, $J = 1.8$ Hz, 2H), 4.30 (t, $J = 1.8$ Hz, 2H), 5.12 (s, 2H), 7.93 (s, 1H), 7.99 (s, 1H); ^{13}C NMR δ 152.5, 143.0, 81.60, 69.92, 69.80, 69.73, 50.49; MS (EI) *m*/*z* 267 (M$^+$, 100). Anal. Calcd for $C_{13}H_{13}N_3Fe$: C, 58.46; H, 4.91. Found: C, 57.86; H, 5.27.

Ferrocene-1,1′-diylbis(methyltrimethylammonium iodide) (6) was prepared as described.[31] **1,1′-Bis((1*H*-imidazol-1-yl)methyl)ferrocene (8a)** was obtained from **6** by a published method[30] as modified by us: 5 mmol of **6** and 14 mmol of imidazole (2-methylimidazole and 1,2,4-triazole, respectively) were dissolved in 30 mL of DMF. The solution was heated at 150 °C for 8 h. **8a** precipitated as a yellow powder and was filtered, washed with methanol, and then dried in vacuo at room temperature for 24 h: 1.38 g, 80% yield; yellow solid; mp 292.1 °C dec; IR (KBr) 3092, 2971, 1503, 1345, 1219, 1076, 1019, 928 cm^{-1}; ^{1}H NMR (D_2O/DCl) δ 4.15 (s, 4H), 4.27 (s, 4H), 4.93 (s, 4H), 7.11 (s, 2H), 7.18 (s, 2H), 8.37 (s, 2H); ^{13}C NMR (D_2O/DCl) δ 134.4, 122.1, 120.2, 81.60, 71.65, 71.21, 49.13; MS (EI) *m*/*z* 346 ($C_{18}H_{18}N_4Fe^+$, 10); HRMS *m*/*z* calc 346.0881, found 346.0884.

1,1′-Bis{[1*H*-(2-methyl)imidazol-1-yl]methyl}ferrocene (8b). The reaction procedure is the same as for **8a**. The brown solution was hydrolyzed with 300 mL of water and extracted with 3 × 50 mL of methylene chloride. The combined organic layer was washed with 3 × 50 mL of water, dried with Na_2SO_4, evaporated on a Rotavap, and heated in vacuo at 50 °C for 3 h. Then the crude product was purified by column chromatography (Al_2O_3) using methylene chloride/acetone (7:3) as an eluent, affording **8b**: 0.84 g, 45% yield; yellow solid; mp181.3 °C; IR (KBr) 3088, 2931, 1500, 1423, 1264, 1041, 980, cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 6H), 4.12 (s, 8H), 4.66 (s, 4H), 6.74 (s, 2H), 6.82 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 144.9, 127.9, 119.8, 84.75, 70.38, 70.04, 46.26, 14.17; MS (EI) *m*/*z* 374 ($C_{20}H_{22}N_4Fe^+$, 30). Anal. Calcd for $C_{20}H_{22}N_4Fe$: C, 64.18; H, 5.92, Found: C, 64.20; H, 6.03.

1,1′-Bis[(1*H*-1,2,4-triazol-1-yl)methyl]ferrocene (8c). The preparation is the same as for **8b**: 0.84 g, 48% yield; yellow solid; mp 114.3 °C; IR (KBr) 3105, 2993, 1508, 1442, 1333, 1271, 1138, 1018, 878 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.23 (t, $J = 1.8$ Hz, 4H), 4.28 (t, $J = 1.8$ Hz, 4H), 5.09 (s, 4H), 7.95 (s, 2H), 8.01 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 152.7, 143.3, 82.98, 70.74, 70.43, 49.93; MS (EI) *m*/*z* 348 ($C_{16}H_{16}N_6Fe^+$, 10); HRMS (FAB) *m*/*z* calcd 348.0786, found 348.0782.

Preparation of 1-(Ferrocenylmethyl)-3-methylimidazolium Iodide (4a).[30] A 1 mmol sample of **3a** was dissolved in 2 mL of methyl iodide and refluxed for 2 h. The resulting precipitate was filtered and washed with ether until the ether fraction was colorless: 0.40 g, 98% yield; yellow solid; ^{1}H NMR δ 4.04 (s, 3H), 4.21 (t, $J = 1.7$ Hz, 2H), 4.27 (s, 5H), 4.73 (t, $J = 1.7$ Hz, 2H), 5.59 (s, 2H), 7.86 (s, 1H), 8.02 (s, 1H), 9.70 (s, 1H); ^{13}C NMR δ 137.0, 124.5, 123.0, 81.91, 70.66, 70.01, 69.95, 49.72, 37.45.

Data for 1-(ferrocenylmethyl)-4-methyltriazolium iodide (4b): 0.39 g, 95% yield; yellow solid; mp 169.2 °C; IR (KBr) 3120, 3060, 1578, 1482, 1359, 1229, 1159, 1096, 813, cm^{-1}; ^{1}H NMR (D_2O) δ 3.87 (s, 3H), 4.31 (s, 5H), 4.36 (s, 2H), 4.47 (s, 2H), 5.38 (s, 2H), 8.70 (s, 1H), 9.51 (s, 1H); ^{13}C NMR (D_2O) δ 145.6, 141.9 (t, $J = 34.3$ Hz), 77.92, 70.33, 70.13, 69.62, 52.72, 34.31.

1,1-Bis((1-(2,3-dimethyl)imidazolium)methyl)ferrocene Diiodide (9b). The preparation is the same as for **4a** except methanol is used as solvent: 0.64 g, 97% yield; yellow solid; mp 248.1 °C dec; IR (KBr) 3046, 2907, 1574, 1526, 1231, 1138, 1040, cm^{-1}; ^{1}H NMR (D_2O) δ 2.57 (s, 6H), 3.67 (s, 6H), 4.36 (t, $J = 1.9$ Hz, 4H), 4.47 (t, $J = 1.9$ Hz, 4H), 5.08 (s, 4H), 7.19 (d, $J = 2.2$ Hz, 2H), 7.21 (d, $J = 2.2$ Hz, 2H); ^{13}C NMR (D_2O) δ 144.6, 122.9, 121.0, 81.62, 71.47, 71.00, 48.34, 35.43, 10.08.

1,1-Bis((1-(4-methyl)-1,2,4-triazolium)methyl)ferrocene Diiodide (9c). The preparation is the same as for **9b** except acetonitrile is used as solvent: 0.60 g, 95% yield; yellow solid; mp 199.3 °C dec; IR (KBr) 3098, 2923, 1596, 1430, 1321, 1108, 996 cm^{-1}; ^{1}H NMR (D_2O) δ 3.86 (s, 6H), 4.43 (t, $J = 1.8$ Hz, 4H), 4.53 (t, $J = 1.8$ Hz, 4H), 5.39 (s, 4H), 8.70 (s, 2H), 9.52 (s, 2H); ^{13}C NMR (D_2O) δ 145.4 (t, $J = 6.29$ Hz), 141.8 (t, $J = 34.3$ Hz), 78.62, 71.18, 70.86, 52.08, 34.13.

Preparation of (Ferrocenylmethyl)trimethylammonium Bis(trifluoromethanesulfonyl)amide (2). To a magnetically stirred solution of **1** (0.5 mmol) in methanol/water (1:1) (8 mL) in a 15 mL flask was added lithium bis(trifluoromethanesulfonyl)amide ($LiNTf_2$, 0.6 mmol). After 8 h at 40 °C, the yellow solid was filtered and washed with water (2 × 2 mL) and dried in vacuo (0.3 mmHg) at 40 °C for 24 h: 0.24 g, 89% yield; yellow solid; mp 84.5 °C; IR (KBr) 3098, 3044, 1477, 1352, 1194, 1140, 1056, 872 cm^{-1}; ^{1}H NMR δ 3.22 (S, 9H), 4.27 (S, 5H), 4.45 (t, $J = 1.8$ Hz, 2H), 4.61 (t, $J = 1.8$ Hz, 2H), 4.68 (s, 2H); ^{13}C NMR δ 121.0 (q, $J = 321.2$ Hz), 73.75, 73.01, 71.33, 69.99, 67.76 (t, $J = 2.1$ Hz), 52.72 (t, $J = 4.2$ Hz); ^{19}F NMR δ −79.88 (s, 6F). Anal. Calcd for $C_{16}H_{20}N_2S_2O_4F_6Fe$: C, 35.70; H, 3.74. Found: C, 35.78; H, 3.85.

Data for 1-(ferrocenylmethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (5a): 0.27 g, 96% yield; orange liquid; $d = 1.68$ g/cm^{-3}; $T_g = -32.2$ °C; IR (KBr) 3154, 3109, 1564, 1353, 1194, 1140, 1057, 829, cm^{-1}; ^{1}H NMR δ 4.03 (s, 3H), 4.26 (s, 5H), 4.30 (t, $J = 1.7$ Hz, 2H), 4.51 (t, $J = 1.7$ Hz, 2H), 5.39 (s, 2H), 7.66 (s, 1H), 7.71 (s, 1H), 8.95 (s, 1H); ^{13}C NMR (75 MHz) δ 136.7, 124.7, 123.0, 121.0 (q, $J = 321.3$ Hz), 80.95, 70.24, 70.18, 69.74, 50.13, 36.66; ^{19}F NMR δ −79.89 (s, 6F); HRMS (FAB) *m*/*z* calcd 281.0741, found 281.0730.

Data for 1-(ferrocenylmethyl)-4-methyltriazolium bis(trifluoromethanesulfonyl)amide (5b): 0.27 g, 96% yield; orange liquid; $d = 1.85$ g/cm^{-3}; $T_g = -16.4$ °C; IR (KBr) 3140, 3032, 1582, 1352, 1193, 1137, 1056, 827 cm^{-1}; ^{1}H NMR δ 4.12 (s, 3H), 4.28 (s, 5H), 4.31 (t, $J = 1.9$ Hz, 2H), 4.49 (t, $J = 1.9$ Hz, 2H), 5.55 (s, 2H), 8.98 (s, 1H), 9.78 (s, 1H); ^{13}C NMR δ 145.7, 142.4, 120.5 (q, $J = 321.3$ Hz), 78.66, 69.93, 69.78, 69.31, 52.81, 34.45; ^{19}F NMR δ −79.81 (s, 6F). Anal. Calcd for $C_{16}H_{16}N_4S_2O_4F_6Fe$: C, 34.18; H, 2.87. Found: C, 34.22; H, 2.97.

Data for ferrocene-1,1′-diylbis(methyltrimethylammonium bis(trifluoromethanesulfonyl)amide) (7): 0.43 g, 96% yield; yellow solid; mp 195.3 °C; IR (KBr) 3107, 3044, 1478, 1354, 1195, 1141, 1056, 872, cm^{-1}; ^{1}H NMR δ 3.21 (s, 18H), 4.56 (t, $J = 1.8$ Hz, 4H), 4.69 (s, 4H), 4.75 (t, $J = 1.8$ Hz, 4H); ^{13}C NMR (125

MHz) δ 121.5 (q, $J = 321.3$ Hz), 75.51, 74.52, 73.01, 67.51 (t, $J = 2.5$ Hz), 53.20 (t, $J = 4.2$ Hz); ^{19}F NMR δ −79.84 (s, 6F). Anal. Calcd for $C_{22}H_{30}N_4S_4O_8F_{12}Fe$: C, 29.67; H, 3.40. Found: C, 29.81; H, 3.37.

Data for 1,1′-bis((1-(2,3-dimethyl)imidazolium)methyl)ferrocene bis[bis(trifluoromethanesulfonyl)amide] (10b): 0.47 g, 98% yield; yellow solid; mp 86.2 °C; IR (KBr) 3150, 2977, 1535, 1352, 1194, 1141, 1056, 842, cm^{-1}; ^{1}H NMR δ 2.82 (s, 6H), 3.93 (s, 6H), 4.43 (t, $J = 1.8$ Hz, 4H), 4.64 (t, $J = 1.8$ Hz, 4H), 5.38 (s, 4H), 7.50 (d, $J = 2.0$ Hz, 2H), 7.54 (d, $J = 2.0$ Hz, 2H); ^{13}C NMR δ 145.1, 123.3, 121.3, 121.0 (q, $J = 321.3$ Hz), 81.98, 71.41, 71.22, 48.54, 35.49, 9.97; ^{19}F NMR δ −79.79 (s, 6F). Anal. Calcd for $C_{26}H_{28}N_6S_4O_8F_{12}Fe$: C, 32.37; H, 2.93. Found: C, 32.56; H, 2.97.

Data for 1,1′-bis((1-(4-methyl)-1,2,4-triazolium)methyl)ferrocene bis[bis(trifluoromethanesulfonyl)amide] (10c): 0.45 g, 96% yield; orange liquid; $d = 1.88$ g/cm^{-3}; $T_g = -11.0$ °C; IR (KBr) 3142, 2985, 1583, 1435, 1351, 1189, 1139, 1056, 886, cm^{-1}; ^{1}H NMR δ 4.10 (s, 6H), 4.45 (t, $J = 1.8$ Hz, 4H), 4.62 (t, $J = 1.8$ Hz, 4H), 5.60 (s, 4H), 8.97 (s, 2H), 9.76 (s, 2H); ^{13}C NMR δ 146.3, 143.0, 120.9 (q, $J = 321.1$ Hz), 80.27, 71.61, 71.55, 52.83, 34.97; ^{19}F NMR δ −79.80 (s, 6F). Anal. Calcd for $C_{22}H_{22}N_8S_4O_8F_{12}Fe$: C, 28.15; H, 2.36. Found: C, 28.98; H, 2.60.

Data for 1,1′-bis{[1-(2,3-dimethyl)imidazolium]methyl}ferrocene bis(hexafluorophosphate) (10d): 0.33 g, 95% yield; yellow solid; mp 245 °C dec; IR (KBr) 3153, 3101, 1587, 1523, 1445, 1330, 1230, 836, cm^{-1}; ^{1}H NMR δ 2.80 (s, 6H), 3.92 (s, 6H), 4.41 (t, $J = 1.8$ Hz, 4H), 4.62 (t, $J = 1.8$ Hz, 4H), 5.35 (s, 4H), 7.49 (s, 2H), 7.52 (s, 2H); ^{13}C NMR δ 144.7, 122.8, 120.8, 81.59, 70.79, 70.72, 47.93, 34.94, 9.35; ^{19}F NMR δ −72.21 (d, $J = 708.0$ Hz, 12F). Anal. Calcd for $C_{22}H_{28}N_4F_{12}P_2Fe$: C, 38.06; H, 4.07. Found: C, 38.21; H, 4.11.

X-ray Crystal Structures. Single crystals of **9c** and **10d** suitable for X-ray analysis were obtained by slow crystallization from water or acetone/methanol. Crystals of each compound were covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream.[41] Data for **9c**, and **10d** were collected at 84(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using ω scans of 0.3° per frame for 5 (**9c**) and 10 (**10d**) s, and a half sphere (**9c**) and a full sphere (**10d**) of data were collected. A total of 1471 (**9c**) and 2132 (**10d**) frames were collected with a final resolution of 0.77 Å for both. The first 50 frames were recollected at the end of the data collection to monitor for decay. Cell parameters were retrieved using SMART[42] software and refined using SAINTPlus[43] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[44] The structure was solved by direct methods and refined by the least-squares method on F^2 using the SHELXTL program package.[45] The structures were solved in the space group $P\bar{1}$ (No. 2) by analysis of systematic absences. All atoms were refined anisotropically. The hydrogen atoms associated with the water molecule (**9c**) were located on the difference map and fixed in place. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 2. Further details are provided in the Supporting Information.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. The data have also been deposited in the Cambridge database. CCDC 228122 and 228123 can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, U.K., fax +44 1223 336033, deposit@ccdc.cam.ac.uk).

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