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Syntheses and Characterization of Unsymmetric Dicationic Salts Incorporating Imidazolium and Triazolium Functionalities

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A series of both imidazolium- and triazolium-based unsymmetric dicationic salts with alkyl and polyfluoroalkyl substituents were prepared and characterized. Most of them can be classified as ionic liquids (MP < 100 °C). Key physical properties, such as melting point, thermal stability, density, and solubility in common solvents were determined and were compared with those of the related monocationic imidazolium- or triazolium-based salts. The effects of anions and substituents bonded to the triazolium and imidazolium cations on these properties were examined. 1-(3-Butyl-imidazolium-1-yl)methylene-(4-butyl-1,2,4-triazolium diiodide) (**2d**), the precursor of 1-(3-butylimidazolium-1-yl)methylene-(4-butyl-1,2,4-triazolium) bi[bis(trifluoromethanesulfonyl)amide] (**3d),** reacted with $Pd(OAc)_2$ at 120 °C to generate a binuclear palladium(II) dicarbene complex. The palladium(II) complex was characterized by single-crystal X-ray diffraction analysis and was used as a catalyst precursor for palladium-catalyzed Heck cross-coupling reactions in **3d**. Preliminary results show that **3d** could serve as both the solvent and catalyst support in the catalytic reactions.

Introduction

Ionic liquids have received considerable attention as green solvents for organic synthesis and catalysis.[1−5] This is mainly because of their superior properties compared with conventional organic solvents, such as nonvolatility, nonflammability, low toxicity, high thermal stability, wide liquid range, and reusability.[1,2] In addition to these favorable properties, they can immobilize transition metal catalysts and provide an excellent reaction medium for the recovery and recycling of catalysts.[3] Both the cationic and anionic components of ionic liquids can be varied and modified for desirable qualities and special applications. Of a variety of these liquids available, most of cations are monoquaternary species with only one quaternization center. However, just as conventional organic solvents, not all ionic liquids are appropriate for a particular application, and a single ionic liquid will not always be the best in every respect. Further development of ionic liquids and their applications to other important processes often require the syntheses of new ionic liquids with suitable properties.[4−7] Our experience[5,6] and that of others[4] in symmetric di- and polycationic ionic liquids suggested that they usually have different chemical and physical properties from monocationic ionic liquids, such as higher densities and viscosities, greater thermal stabilities, and longer liquid ranges. Recent advances in task-specific ionic liquids further increase their chemical applications.[7] Despite such a rapidly growing effort, the correlation between their structures and properties is still not well understood. Hence, a great deal of work is necessary to extend the

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knowledge of relevant types of ionic liquids through controlling and adjusting the cationic, anionic, or both components.

Imidazolium-based ionic liquids are excellent reaction media for transition metal-catalyzed coupling reactions which are considered to involve in situ formation of N-heterocyclic transition metal−carbene complexes.[8] In most cases, the presence of bulky phosphine ligands was required to immobilize catalysts and to enhance catalytic activities.[8,9] Many phosphine ligands are sensitive to air and moisture which may result in operational difficulty and catalyst decomposition. Moreover, the reductive elimination of 2-arylimidazolium salts from transition metal−monocarbene complexes is a facile reaction and represents a potential route to catalyst deactivation.[9a,10] In such cases, the reuse of catalysts would be difficult. Subsequent experimental and theoretical evidence suggested that chelating carbenes can better resist the degradation, even under phosphine-free catalytic conditions, by benefiting from the chelating effect and stereoelectronic barriers to undesirable degradation pathways.[11−13] Thus, various chelating dicarbene−transition metal complexes have been synthesized and successfully applied in catalytic reactions. Furthermore, some of their precursors were excellent candidates for ionic liquids, which can show different performances from monoimidazolium-based ionic liquids.[4,5b]

It is well-known that the introduction of the third nitrogen atom into the 1,2,4-triazolium ring makes the species slightly more acidic than the 1,3-imidazolium ring, resulting in derived ionic liquids with very different chemical and physical properties.[13,14a] Therefore, it was anticipated that ionic liquids, based on the combination of triazolium and imidazolium rings, not only would incorporate interesting properties of both functional groups but would also be more inclined toward the modification of ionic liquids through changing the substituents on either of them. This allows the production of a much larger collection of ionic liquids.[15] As an extension of our research in fluorine-containing triazolium- or imidazolium-based ionic liquids,[14] we became interested in di- or polycationic ionic liquids and their applications in recyclable catalytic systems.[5] In this paper, we wish to report the syntheses and characterization of a series of both imidazolium- and triazolium-based unsymmetric dicationic salts with alkyl and polyfluoroalkyl substituents. The preliminary application in the Heck cross-coupling reaction was evaluated using ionic liquid **3d** as the reaction medium.

Results and Discussion

The syntheses of the diquaternary salts followed different routes. The synthetic pathway to the compounds with the same substituents on both the imidazolium and triazolium rings (**3a**−**e**) is summarized in Scheme 1. The reaction of 1-(chloromethyl)-1H-1,2,4-triazole with imidazole in the presence of base produced the neutral compound **1**. In this molecule, there are two basic nitrogen atoms available to participate in quaternization reactions. Diquaternary compounds, **2a**−**e**, were prepared by reactions of **1** with 3 equiv of alkyl halide at 100 °C for 24 h. A small amount of DMF was added to solubilize the monoquaternary intermediates to ensure that the diquaternization reactions would go to completion. Subsequent metathetical reactions with $LiNTf_2$ led to the formation of the diquaternary salts (**3a**−**e)** in excellent yields. In the course of preparing these diquaternary salts, we assumed that the dicationic salts with different substituents on triazolium and imidazolium rings could be obtained from simple quaternization of the monoquaternary compounds. Treatment of 1-methylimidazole or 1-butylimidazole with 1-(chloromethyl)-1H-1,2,4-triazole gave the corresponding monoquaternary compounds **4a** and **4b (**Scheme 2). Salts **5a**−**h** were prepared by the quaternization reactions of **4a** or **4b** with alkyl halides followed by metathesis with $LiNTf_2$ or KPF_6.

All the unsymmetric diquaternary salts were stable in air. They were characterized by ^1H, ^{13}C, and ^{19}F NMR, IR, and elemental analyses. The triazolium and imidazolium rings in all of salts display the same pattern in their ^1H and ^{13}C spectra. However, the alkyl substituents on the imidazolium and triazolium rings showed two sets of signals in their ^1H and ^{13}C NMR spectra, even for the salts bearing the same substituents, which indicated the nonequivalence of the alkyl groups and confirmed the proposed asymmetry of the salts. The chemical shifts of the protons of the methylene bridge ($-NCH_2N-$) are in the range from 6.86 to 7.29 ppm, which are comparable to those of related bistriazolium and bisimidazolium ionic salts.[5b,11,13a] The chemical shift of the acidic proton H5 ($-NCHN-$) in the triazolium ring is at 10.21−10.55 ppm which is much higher than the value of 9.15−9.38 ppm for H2 ($-NCHN-$) in the imidazolium ring; this clearly supported the higher acidity of the triazolium ring.

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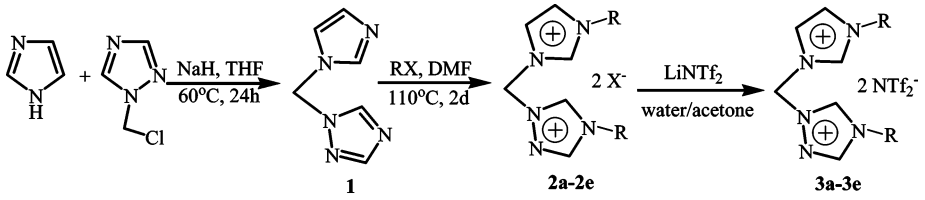
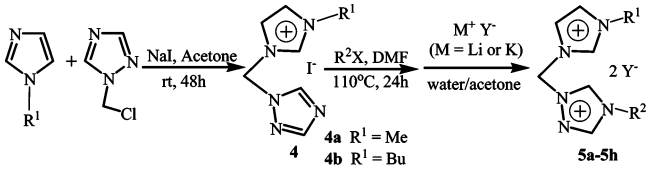
Scheme 1



Compd	R	T_m (°C) [a]	T_d (°C) [b]	Density ($g \cdot cm^{-3}$)[c]
3a	CH_3	95	371	1.76
3b	CH_2CH_3	52	360	1.71
3c	$(CH_2)_2CH_3$	43	329	1.68
3d	$(CH_2)_3CH_3$	–45	334	1.64
3e	$(CH_2)_3CF_3$	65	323	1.76

[a] Melting point or glass transition temperature. [b] Thermal degradation. [c] 25 °C.

Scheme 2



compd	R^1	R^2	Y	T_m (°C)[a]	T_d (°C)[b]	Density ($g \cdot cm^{-3}$)[c]
5a	CH_3	CH_2CH_3	NTf_2	65	348	1.73
5b	CH_3	$(CH_2)_3CH_3$	NTf_2	–32	319	1.64
5c	CH_3	$(CH_2)_3CH_3$	PF_6	150	282	1.66
5d	CH_3	$(CH_2)_3CF_3$	NTf_2	72	319	1.75
5e	$(CH_2)_3CH_3$	CH_3	NTf_2	–37	330	1.69
5f	$(CH_2)_3CH_3$	CH_3	PF_6	145	269	1.70
5g	$(CH_2)_3CH_3$	CH_2CH_3	NTf_2	–41	348	1.67
5h	$(CH_2)_3CH_3$	$(CH_2)_3CF_3$	NTf_2	–21	335	1.68

[a] Melting point or glass transition temperature. [b] Thermal degradation. [c] 25 °C.

The ^{19}F NMR spectra helped to monitor the progress of the metathesis reactions while introducing fluorine-containing anions into salts with trifluorobutyl substituents. The relative areas of the resonance bands from the fluorine atoms of the anion (NTf_2) in **3e**, **5d**, and **5h** were readily compared with those of the fluorine atoms of the trifluorobutyl substituent on the cation.

Physical Properties of the Unsymmetric Salts. The physical properties of **3a**−**e** and **5a**−**h** are summarized in Schemes 1 and 2, respectively. The melting points or glass transition temperatures were determined by differential scanning calorimetry (DSC). As anticipated, the anion has a major influence on the melting point. With constant substituents on the dication and a change of the anion from PF_6 in **5c** and **f** to NTf_2 in **5b** and **e**, the melting points were greatly reduced. The melting points of the PF_6 salts are >100 °C; therefore, they are not classified as ionic liquids.[16] As seen in Scheme 1, for the NTf_2 salts with the same substituents on triazolium and imidazolium rings (**3a**−**d**), an increase of length and flexibility of alkyl groups resulted in a lower melting point: methyl (95 °C) > ethyl (52 °C) > propyl (43 °C) > butyl (−45 °C). Such a trend was also observed for analogously monocationic triazolium or imidazolium-based salts;[14a,17] moreover, these salts have a higher melting point than the bistriazolium and bisimidazolium analogues.[5b] With a constant methyl or butyl substituent on the imidazolium ring and variation of the alkyl groups on the triazolium ring from methyl to ethyl to butyl, the melting points decrease from 95 (**3a**) to 65 (**5a**) to −32 °C (**5b**) and from −37 (**5e**) to −41 (**5g**) to −45 (**3d**) °C, respectively, which is in keeping with salts containing the same substituent.[17a,17b] This suggests poorer packing in the crystal lattice as the alkyl group is elongated. However, when the positions of the alkyl groups are changed between the imidazolium and triazolium rings, no clear relationship between the structures of these salts and their melting points is observed. When the butyl group in **5b** and **3d** is replaced with a trifluorobutyl group in **5d** and **h**, the melting point increased, and not surprisingly, the bis-trifluorobutyl-substituted salt **3e** (65 °C) has a higher melting point than the mono-trifluorobutyl-substituted salt **5h** (−21 °C). Their decomposition temperatures were not essentially influenced. As determined by thermogravimetric analysis (TGA), the unsymmetric NTf_2 salts are thermally stable at >300 °C, which is higher than the decomposition temperature of the corresponding PF_6 salts.

The densities of these unsymmetric dicationic salts range from 1.62 to 1.76 g cm^{-3} with the density being inversely

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proportional to the bulkiness of the alkyl substituents. Not surprisingly, these values are higher than those of their monocationic analogues.[14a,17] This variation in density mimics the trend observed for monocationic analogues. Moreover, trifluorobutyl-quaternized salts have higher densities than those of their butyl analogues. Thus, it is likely that with slight structural changes in the cation, the densities of these salts can be fined tuned.

While all these diquaternary salts are soluble in ethyl acetate and acetone, they are immiscible with nonpolar solvents, such as diethyl ether and hexane. Their solubility is related to the length of the alkyl chains on the cationic rings. Not unexpectedly, with the elongation of the alkyl groups, the solubility of the salts in organic solvents increased, while they concomitantly decreased in H_2O (e. g., **3a** and **5a** are partially soluble in water). The influence of the anions on the solubility of the salts was demonstrated by the examples of different salts containing NTf_2 and PF_6 anions. PF_6 salts **5c** and **f** are partially soluble in water, but the corresponding NTf_2 salts **5b** and **e** form a biphasic mixture.

Synthesis and Structural Characterization of Palladium(II) Compound 6. The chelating palladium(II) dicarbene complexes from methylene-bridged bisimidazolium salts were usually prepared via the palladium(II) acetate route.[11] Generally, the syntheses of triazolium-based carbenes require milder reaction conditions than that of the imidazolium-based carbene compounds because of the higher acidity of the H5 proton. A recent study has demonstrated that a dynamic behavior was observed between mononuclear and binuclear palladium(II) carbene complexes from methylene-bridged bistriazolium salts.[13a] Thus, it is of great significance in organometallic chemistry to investigate palladium(II) dicarbene complexes from both triazolium and imidazolium-based unsymmetric salts. With a slightly modified synthetic procedure,[11] the reaction of **2d** with $Pd(OAc)_2$ in DMSO at 120 °C produced dinuclear complex **6.** The formation of **6** was partially confirmed by the absence of the ^{1}H NMR signals for the acidic protons of triazolium (H5) and imidazolium (H2) rings at 10.52 and 9.38 ppm, respectively, where the signals of its precursor, **2d**, were found. In the ^{13}C NMR spectra, the signals for the carbene carbon atoms of triazolium and imidazolium appear at 171.9 and 165.8 ppm, respectively, which are characteristic peaks for metal−carbene complexes.[11,12]

Yellow crystals of complex **6** were obtained through diffusion of ethyl ether into its CH_2Cl_2 solution. Single-crystal X-ray diffraction analysis showed that complex **6** is a binuclear structure in which two dicarbene ligands serve as a bridge between two palladium(II) centers (Table 1). As shown in Figure 1, the unsymmetric unit contains one-half of the centrosymmetric dimer. The palladium(II) center is in a slightly distorted square-planar geometry. It is coordinated by two *trans*-I and two *trans*-carbene carbon atoms from the imidazolium and triazolium rings of different ligands, respectively. The cis angles around Pd(II) are in the range of 87.99(19)−92.06(19)° (Table 2). The bond distances of Pd−C_{im} and Pd−C_{tz} are 2.013(7) and 2.041(7) Å,

Table 1. Crystallographic Data for Compound **6**

empirical formula	$C_{28}H_{46}I_4N_{10}Pd_2$	fw	1243.15
cryst size (mm)	0.31× 0.09 × 0.04	cryst system	monoclinic
space group	$P2_1/c$	a (Å)	7.8006(5)
b (Å)	15.2620(9)	c (Å)	15.8084(10)
β (deg)	94.813(1)	V (Å^3)	1875.4(2)
Z	2	T (K)	87(2)
D_c (g cm^{-3})	2.201	μ (mm^{-1})	4.286
λ(Mo Kα) (Å)	0.71073	F(000)	1176
reflns collected	28 147	independent reflns	3403
obsd reflns	3115	R_{int}	0.0470
params	201	S on F^2	1.103
R_1 ($I > 2\sigma(I)$)[a]	0.0444	R_2 (all data)[b]	0.0976
largest diff. peak and hole [e·Å^{-3}]	1.675 and −1.076		

[a] $R_1 = \sum||F_o| - |F_c||)/\sum|F_o|$. [b] $R_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

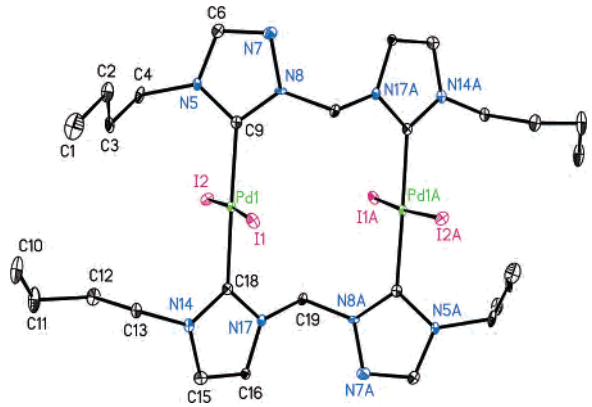


Figure 1. Molecular structure of **6** with thermal ellipsoids at 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **6**[a]

Pd(1)−C(9)	2.041(7)	Pd(1)−C(18)	2.013(7)
Pd(1)−I(1)	2.6124(7)	Pd(1)−I(2)	2.6105(7)
C(18)−Pd(1)−C(9)	179.0(3)	I(2)−Pd(1)−I(1)	175.78(3)
C(18)−Pd(1)−I(2)	87.99(19)	C(9)−Pd(1)−I(1)	90.82(19)
C(18)−Pd(1)−I(1)	89.18(19)	C(9)−Pd(1)−I(2)	92.06(19)
N(17)−C(19)−N(8A)	113.0(5)		

[a] Symmetry code: (A) $3 - x, -y + 1, -z + 1$.

respectively, which are similar to those of the palladium(II) carbene complexes.[11] The deviation of Pd(II) from the equatorial plane defined by two iodide anions and two carbene carbons is 0.0263 Å. The distortions of the triazolium and imidazolium rings from the PdC_2I_2 equatorial plane are 70.7 and 65.0°, respectively. Instead of formation of a chelating six-membered ring, the dicarbene ligands link two Pd(II) into a twelve-membered macrocycle. The Pd···Pd separation in the cycle is 4.442 Å. This can be regarded as being the result of the minimization of the geometric distortion and of the disturbing steric interactions introduced by the dicarbene ligands. Two dicarbene ligands were also bulged in the opposite direction to minimize the steric hindrance, and the butyl chains of the same ligand were pointed away from each other. The imidazolium ring is twisted with respect to the methylene-connnected triazolium ring with the dihedral angle between them being 44.1°. There are no other noteworthy weak interactions or short contacts between the adjacent macrocycles (Figure 2).

Palladium(II)-Catalyzed Heck Cross-Coupling Reaction in Ionic Liquid 3d. The palladium-catalyzed Heck

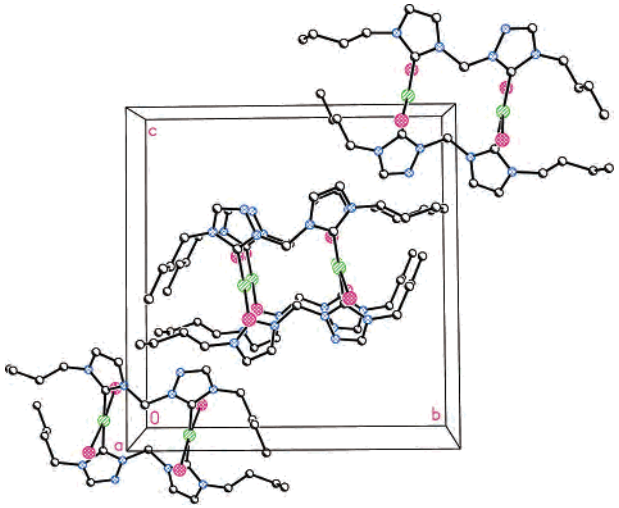
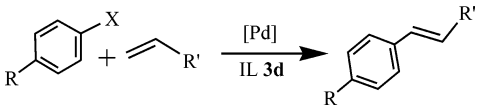


Figure 2. Packing diagram of **6** along the *a* axis.

Table 3. Heck Cross-Coupling Reactions of Aryl Halides with Vinyl Compounds in **3d**[a]



entry	X	R	R′	(cycle) yield[b]
1	I	H	$CO_2{}^n$Bu	(1) 86; (2) 91; (3) 89
2[c]	I	H	$CO_2{}^n$Bu	(1) 90; (2) 87; (3) 81
3	I	Me	$CO_2{}^n$Bu	92
4	I	MeO	$CO_2{}^n$Bu	87
5	I	F	$CO_2{}^n$Bu	90
6	I	NO_2	$CO_2{}^n$Bu	88
7	I	H	$CO_2{}^n$Me	85
8	I	H	ph	88
9	I	Me	ph	87
10	I	MeO	ph	89
11	I	NO_2	ph	91
12	I	F	ph	86
13	Br	H	$CO_2{}^n$Bu	35[d]
14	Cl	H	$CO_2{}^n$Bu	<1[d]

[a] All reactions were carried out using 1 mmol of aryl halide, 1.25 mmol of olefin, 1.5 mmol of Et_3N, 2 mol % catalyst, and 2 mL of ionic liquid at 120 °C for 12 h. [b] Isolated yield (%). [c] $PdCl_2$ as a catalyst precursor. [d] GC yield.

cross-coupling reaction of olefins with aryl halides is one of the most important and reliable reactions for carbon−carbon bond formation in organic synthesis. Various ionic liquids have been employed as solvents in Heck reactions.[5,7,19] In this work, the Heck reaction was evaluated using the palladium(II) dicarbene complex **6** and $PdCl_2$ as precatalysts immobilized in ionic liquid **3d**. According to procedures reported previously,[19] the coupling reaction of iodobenzene and *n*-butyl acrylate was performed with the catalyst loading of 2 mol % in the presence of Et_3N at 120 °C. *n*-Butyl (*E*)-cinnamate was formed in an excellent isolated yield. Moreover, the ionic liquids containing the catalysts can be recovered and recycled three times without loss in catalytic activity (Table 3, entries 1−2).

These attractive results encouraged us to further investigate the reactions of *n*-butyl acrylate with aryl iodides containing electron-withdrawing or electron-donating groups in the presence of **6** under identical conditions. As shown in Table 3, the corresponding *n*-butyl (*E*)-cinnamates were obtained in high yields with complete regioselectivity for the *β*-position (Table 3, entries 3−6). No appreciable difference in yields between the activated and deactivated aryl iodides was found.

Because of the success of above reactions, we continued our investigation by exploring Heck reactions of aryl iodides with other olefins, such as methyl acrylate and styrene, under the same conditions (Table 3, entries 7−12). High isolated yields were also obtained. In all cases, the crude product was easily separated from the reaction mixture by simple extraction and decantation with ethyl ether. Further purification by flash chromatography on silica gel was performed to give the desired pure products. The resulting solution was washed with water to remove inorganic salts and dried under vacuum before use. We also examined the scope of this reaction by coupling *n*-butyl acrylate with bromobenzene and chlorobenzene using the same reaction conditions. However, only 35% conversion and a trace of target product could be detected from GC-MS (Table 3, entries 13−14).

Conclusions

In summary, we have developed an efficient approach to the rational design and synthesis of a new family of both imidazolium and triazolium-based unsymmetric dicationic salts with alkyl and polyfluoroalkyl substituents. The relationship between their structures and melting point, thermal stability, and density, as well as solubility in common solvents, was determined. These properties are comparable with correspondingly symmetric bisimidazolium or bistriazolium-based salts and monocationic imidazolium or triazolium-based salts. A dinuclear palladium(II) dicarbene complex from an unsymmetric salt was used as a catalyst precursor in an ionic liquid possessing an analogous framework structure. The preliminary results of palladium-catalyzed Heck cross-coupling reactions show that the unsymmetric dicationic ionic liquids are a suitable solvent for cross-coupling reactions.

Experimental Section

1-(Chloromethyl)-1H-1,2,4-triazole was prepared as reported previously.[20] Tetrahydrofuran (THF) was dried with sodium and distilled over a purple solution of benzophenone. The other chemicals were obtained commercially and were used as received. A standard Schlenk line system was used for handling the air- and moisture-sensitive reactions under nitrogen. IR spectra were recorded using KBr plates for neat liquids and KBr pellets for solids. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on spectrometers at 300, 75, and 282 MHz, respectively, using acetone-d_6 as a locking solvent, except where otherwise indicated. Chemical shifts were reported in parts per million relative to the appropriate standard: $CFCl_3$ for the ^{19}F NMR spectra and TMS for the ^{1}H and ^{13}C NMR spectra. GC/MS spectra were determined using an appropriate instrument. The densities of the solid salts and ionic liquids were

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measured at 25 °C using a Micromeritics Accupyc 1330 gas pycnometer and a pycnometer, respectively. Differential scanning calorimetry (DSC) measurements were performed using a calorimeter equipped with an auto-cool accessory and calibrated using indium. The following procedure was used in experiments for each sample: cooled from 40 to −80 °C and heated to 400 or 500 °C at 10 °C/min. The transition temperature, T_m, was taken as peak maximum. Thermogravimetric analysis (TGA) measurements were carried out by heating samples at 10 °C/min from 25 to 500 °C in a dynamic nitrogen atmosphere (flow rate = 70 mL/min). Thin-layer chromatography (TLC) analysis was performed with Al backed plates precoated with silica gel and examined under UV (254 nm). Flash column chromatography was executed on silica gel (60−200 μm, 60 A). Elemental analyses were performed on a CE-440 elemental analyzer.

X-ray Crystallography. Crystals of **6** were removed from the flask and 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.[21] Data for **6** were collected at 87(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 30 s, and a full sphere of data was collected. A total of 2450 frames were collected with a final resolution of 0.83 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[22] software and refined using SAINTPlus[23] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[24] The structure was solved by direct methods and refined by least-squares method on F^2 using the SHELXTL program package.[25] The structure of **6** was solved in the space group $P2_1/c$ (No. 14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. Soft restraints were imposed on both ipso carbons (C9, C18) to maintain anisotropy. No decomposition was observed during data collection. Details of the data collection and refinement for **6** are given in Table 1. The selected bond lengths and angles for **6** are listed in the Table 2. Further details are provided in the Supporting Information.

1-(1*H*-Imidazole-1-yl)methylene-1*H*-1,2,4-triazole 1. A solution of imidazole (6.81 g, 100 mmol) in dry THF (20 mL) was added slowly to a stirred solution of sodium hydride (4.2 g, 105 mmol) in THF (100 mL). The mixture was stirred at reflux under nitrogen for 1 h and then cooled to room temperature. 1-(Chloromethyl)-1H-1,2,4-triazole (11.75 g, 100 mmol) in THF (10 mL) was added dropwise to the reaction mixture which was stirred at 60 °C for 24 h. After the mixture was cooled to 25 °C, the inorganic salt was removed by filtration through Celite and washed with THF several times. The combined solution was evaporated under reduced pressure. The residue was purified by chromatography on silica gel to give a colorless solid. Yield: 11.5 g (77%). ^{1}H NMR ($CDCl_3$): δ 8.20 (s, 1H), 7.96 (s, 1H), 7.71 (s, 1H), 7.09 (s, 2H), 6.19 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 153.1, 142.9, 137.0, 131.1, 118.6, 58.1. GC-MS (EI): *m*/*z* (%) 149 (M^+, 21). Anal. Calcd for $C_6H_7N_5$ (149.15): C, 48.32; H, 4.73; N 46.95. Found: C, 47.85; H, 4.62; N, 46.69.

General Procedures for Preparation of 2a−e. Compound **1** (0.15 g, 1 mmol) and alkyl halide (3 mmol) in DMF (0.5 mL) were placed in a Pyrex glass tube. After the samples were cooled to −195 °C, the tube was evacuated and sealed. The reaction mixture was heated at 110 °C for 48 h. After the tube was cooled and carefully opened, the volatile materials and DMF were removed under reduced pressure. The orange residue was washed several times with cold acetone (10 mL) to give a colorless solid.

1-(3-Methylimidazolium-1-yl)methylene-(4-methyl-1,2,4-triazolium) Diiodide 2a. Yield: 92%. ^{1}H NMR (DMSO-d_6): δ 10.25 (s, 1H), 9.39 (s, 1H), 9.26 (s, 1H), 7.90 (s, 1H), 7.80 (s, 1H), 6.88 (s, 2H), 3.96 (s, 3H), 3.93 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 146.3, 145.0, 138.2, 124.2, 122.6, 60.2, 36.3, 34.5.

1-(3-Ethylimidazolium-1-yl)methylene-(4-ethyl-1,2,4-triazolium) Dibromide 2b. Yield: 90%. ^{1}H NMR (DMSO-d_6): δ 10.52 (s, 1H), 9.59 (s, 1H), 9.42 (s, 1H), 8.01 (s, 1H), 7.94 (s, 1H), 6.92 (s, 2H), 4.37 (q, 2H, $J = 7.5$ Hz), 4.29 (q, 2H, $J = 7.5$ Hz), 1.52−1.42 (m, 6H). ^{13}C NMR (DMSO-d_6): δ 145.2, 144.4, 137.5, 122.8, 122.6, 60.1, 44.7, 43.4, 14.8, 14.2.

1-(3-Propylimidazolium-1-yl)methylene-(4-propyl-1,2,4-triazolium) Diiodide 2c. Yield: 84%. ^{1}H NMR (DMSO-d_6): δ 10.47 (s, 1H), 9.54 (s, 1H), 9.31 (s, 1H), 8.07 (s, 1H), 7.95 (s, 1H), 7.23 (s, 2H), 4.53 (t, 2H, $J = 7.4$ Hz), 4.44 (t, 2H, $J = 7.2$ Hz), 2.15−1.93 (m, 4H), 1.07−0.95 (m, 6H). ^{13}C NMR (DMSO-d_6): δ 146.7, 145.2, 138.6, 124.5, 124.3, 62.5, 52.6, 51.4, 23.8, 23.6, 10.5, 10.7.

1-(3-Butylimidazolium-1-yl)methylene-(4-butyl-1,2,4-triazolium) Diiodide 2d. Yield: 87%. ^{1}H NMR (DMSO-d_6): δ 10.36 (s, 1H), 9.50 (s, 1H), 9.38 (s, 1H), 7.95 (s, 1H), 7.91 (s, 1H), 6.84 (s, 2H), 4.32 (t, 2H, $J = 7.5$ Hz), 4.26 (t, 2H, $J = 7.5$ Hz), 1.86−1.75 (m, 4H), 1.37−1.23 (m, 4H), 0.94−0.88 (m, 6H). ^{13}C NMR (DMSO-d_6): δ 145.4, 144.5, 137.8, 123.1, 122.9, 60.4; 49.0, 47.6, 31.1, 30.6, 18.6, 13.2;

1-((3-Trifluorobutyl-imidazolium-1-yl)methylene-(4-trifluorobutyl-1,2,4-tria- zolium) Diiodide 2e. Yield: 89%. ^{1}H NMR (CD_3CN): δ 10.75 (s, 1H), 9.57 (s, 1H), 8.89 (s, 1H), 7.96 (s, 1H), 7.56 (s, 1H), 6.98 (s, 2H), 4.46 (t, 2H, $J = 7.5$ Hz), 4.31 (t, 2H, $J = 7.5$ Hz), 2.32−2.23 (m, 8H). ^{13}C NMR (CD_3CN): δ 145.9, 145.2, 138.7, 129.6 (q, $J = 275.0$ Hz), 124.1, 123.8, 61.3, 49.5, 48.2, 30.8 (q, $J = 29.0$ Hz), 30.7 (q, $J = 29.0$ Hz), 23.1 (q, $J = 3.3$ Hz), 22.9 (q, $J = 3.3$ Hz). ^{19}F NMR (CD_3CN): δ −66.8 (t, $J = 9.6$, 6F).

General Procedures for Preparation of 3a−e. Three equivalents of lithium bis(trifluoromethanesulfonyl)amide or potassium hexafluorophosphate was added to a stirring solution of **2a−e** in a mixture of water (5 mL) and acetone (5 mL). The reaction mixture was stirred at 25 °C for 5 h. The acetone was evaporated under reduced pressure, and the water layer was extracted three times with ethyl acetate (3 × 10 mL). The combined organic layer was washed three times with water (3 × 10 mL) and once with saturated $Na_2S_2O_3$ solution (5 mL), and then it was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum to give **3a−e**.

1-(3-Methylimidazolium-1-yl)methylene-(4-methyl-1,2,4-triazolium) Bi[bis(trifluoromethanesulfonyl)amide] 3a. Colorless solid. Yield: 82%. IR (KBr pellet): 3163 (w), 2951 (vw), 2857 (vw), 1583 (m), 1562 (m), 1512 (w), 1496 (m), 1465 (m), 1354 (s), 1195 (br, s), 1139 (s), 1051 (s), 968 (w), 889 (vw), 855 (w), 790 (m), 742 (w), 649 (vw), 595 (m), 571 (s), 509 (w), 495 (vw) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 10.21 (s, 1H), 9.36 (s, 1H), 9.23 (s, 1H), 7.87 (s, 1H), 7.78 (s, 1H), 6.86 (s, 2H), 3.94 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 146.4, 145.1, 138.2, 124.2, 122.6, 120.9 (q, $J = 319.3$ Hz), 60.2, 36.2, 34.4. ^{19}F NMR (DMSO-d_6): δ −78.7(s, 12F). Anal. Calcd for $C_{12}H_{13}F_{12}N_7O_8S_4$ (738.95): C, 19.49; H, 1.77; N 13.26. Found: C, 19.64; H, 1.61; N, 13.19.

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1-(3-Ethylimidazolium-1-yl)methylene-(4-ethyl-1,2,4-triazolium) Bi[bis(trifluoromethanesulfonyl)amide] 3b. Colorless solid. Yield: 89%. IR (KBr pellet): 3132 (w), 2971 (vw), 2857 (vw), 1589 (m), 1562 (m), 1521 (w), 1450 (m), 1355 (s), 1196 (br, s), 1137 (s), 1054 (s), 974 (vw), 907 (w), 781 (m), 741 (m), 649 (vw), 615 (m), 571 (s), 513 (w) cm^{-1}. ^1H NMR: δ 10.48 (s, 1H), 9.55 (s, 1H), 9.34 (s, 1H), 8.08 (s, 1H), 7.96 (s, 1H), 7.25 (s, 2H), 4.61 (q, 2H, $J = 7.5$ Hz), 4.50 (q, 2H, $J = 7.5$ Hz), 1.66−1.56 (m, 6H). ^{13}C NMR: δ 146.7, 145.3, 138.5, 124.4, 124.2, 121.8 (q, $J = 319.3$ Hz), 62.3, 46.7, 45.5, 15.3, 14.9. ^{19}F NMR: δ −79.9 (s, 12F). Anal. Calcd for $C_{14}H_{17}F_{12}N_7O_8S_4$ (766.98): C, 21.90; H, 2.23; N 12.78. Found: C, 21.55; H, 2.19; N, 12.41.

1-(3-Propylimidazolium-1-yl)methylene-(4-propyl-1,2,4-triazolium) Bi[bis(trifluoromethanesulfonyl)amide] 3c. Colorless solid. Yield: 85%. IR (KBr pellet): 3167 (w), 2953 (vw), 2851 (vw), 1578 (m), 1559 (m), 1519 (w), 1491 (m), 1467 (m), 1353 (s), 1197 (br, s), 1139 (s), 1061 (s), 974 (vw), 778 (w), 745 (w), 649 (vw), 619 (m), 553 (m), 513 (w) cm^{-1}. ^1H NMR: δ 10.40 (s, 1H), 9.49 (s, 1H), 9.26 (s, 1H), 8.03 (s, 1H), 7.88 (s, 1H), 7.18 (s, 2H), 4.48 (t, 2H, $J = 7.4$ Hz), 4.39 (t, $J = 7.2$ Hz, 2H), 2.08−1.93 (m, 4H), 1.01−0.92 (m, 6H). ^{13}C NMR: δ 146.6, 145.2, 138.6, 124.4, 124.2, 120.8 (q, $J = 319.1$ Hz), 62.2, 52.6, 51.2, 23.8, 23.5, 10.5, 10.6. ^{19}F NMR: δ −79.9 (s, 12F). Anal. Calcd for $C_{16}H_{21}F_{12}N_7O_8S_4$ (795.01): C, 24.15; H, 2.66; N 12.32. Found: C, 24.22; H, 2.58; N, 12.11.

1-(3-Butylimidazolium-1-yl)methylene-(4-butyl-1,2,4-triazolium) Bi[bis(trifluoromethanesulfonyl)amide] 3d. Pale-yellow liquid. Yield: 95%. IR (KBr plate): 3167 (w), 2962 (vw), 2857 (vw), 1580 (m), 1561 (m), 1523 (w), 1446 (m), 1354 (s), 1195 (br, s), 1133 (s), 1057 (s), 974 (vw), 835 (br, s), 778 (w), 652 (vw), 617 (m), 557 (s), 513 (w) cm^{-1}. ^1H NMR: δ 10.52 (s, 1H), 9.60 (s, 1H), 9.38 (s, 1H), 8.11 (s, 1H), 7.98 (s, 1H), 7.29 (s, 2H), 4.59 (t, 2H, $J = 7.5$ Hz), 4.92 (t, 2H, $J = 7.5$ Hz), 2.08−2.03 (m, 4H), 1.48−1.39 (m, 4H), 1.0−0.93 (m, 6H). ^{13}C NMR: δ 146.8, 145.4, 138.8, 124.5, 124.3, 120.9 (q, $J = 319.3$ Hz), 62.3, 51.0, 49.7, 32.5, 32.1, 19.9, 13.5. ^{19}F NMR: δ −79.8 (s, 12F). Anal. Calcd for $C_{18}H_{25}F_{12}N_7O_8S_4$ (823.05): C, 26.24; H, 3.06; N 11.91. Found: C, 26.22; H, 3.04; N, 11.77.

1-(3-Trifluorobutylimidazolium-1-yl)methylene-(4-trifluorobutyl-1,2,4-triazolium) Bi[bis(trifluoromethanesulfonyl)amide] 3e. Colorless solid. Yield: 86%. IR (KBr pellet): 3163 (w), 2967 (vw), 2859 (vw), 1578 (m), 1558 (m), 1491 (m), 1467 (m), 1353 (s), 1139 (s), 1037 (s), 968 (w), 920 (vw), 851 (m), 791 (m), 744 (w), 646 (vw), 568 (s), 513 (w) cm^{-1}. ^1H NMR: δ 10.54 (s, 1H), 9.62 (s, 1H), 9.38 (s, 1H), 8.10 (s, 1H), 8.00 (s, 1H), 7.25 (s, 2H), 4.72 (t, 2H, $J = 7.5$ Hz), 4.61 (t, 2H, $J = 7.5$ Hz), 2.48−2.30 (m, 8H). ^{13}C NMR: δ 146.8, 145.6, 139.1, 127.9 (q, $J = 275.0$ Hz), 124.6, 124.5, 120.8 (q, $J = 319.1$ Hz), 62.3, 49.9, 48.5 30.9 (q, $J = 29.5$ Hz), 30.8 (q, $J = 29.5$ Hz), 23.6 (q, $J = 3.3$ Hz), 23.3 (q, $J = 3.3$ Hz). ^{19}F NMR: δ −66.92 (t, 6F, $J = 10.7$), −79.89 (s, 12F). Anal. Calcd for $C_{18}H_{19}F_{18}N_7O_8S_4$ (930.99): C, 23.20; H, 2.06; N 10.53. Found: C, 22.86; H, 1.88; N, 10.20.

General Procedures for Preparation of 4a and 4b. 1-Methylimidazole (0.90 g, 11 mmol) or 1-butylimidazole (1.37 g, 11 mmol) and sodium iodide (1.65 g, 11.0 mmol) were added to a solution of 1-(chloromethyl)-1H-1,2,4-triazole (1.18 g, 10.0 mmol) in acetone (30 mL). After the mixture was stirred for 2 days at 25 °C, the solution was filtered through Celite, and the solvent was removed under vacuum to yield a brown solid. The solid was washed three times with Et_2O (20 mL) and then was recrystallized from acetone to yield colorless solid.

1-(Methylimidazolium-1-yl)methylene-(1,2,4-triazole)) Iodide 4a. Yield: 79%. ^1H NMR (CD_3CN): δ 9.02 (s, 1H), 8.77 (s, 1H), 7.99 (s, 1H), 7.67 (d, 1H, $J = 1.8$ Hz), 7.38 (d, 1H, $J = 1.8$ Hz), 6.58 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (CD_3CN): δ 153.8, 146.3, 137.9, 124.9, 123.0, 59.9, 37.3.

1-(Butyimidazolium-1-yl)methylene-(1,2,4-triazole)] Iodide 4b. Yield: 66%. ^1H NMR (CD_3CN): δ 9.49 (s, 1H), 9.00 (s, 1H), 7.97 (s, 1H), 7.84 (s, 1H), 7.56 (s, 1H), 6.76 (s, 2H), 4.20 (t, 2H, $J = 7.3$ Hz), 1.85−1.75 (m, 2H), 1.34−1.24 (m, 2H), 0.87 (t, 2H, $J = 7.5$ Hz). ^{13}C NMR (CD_3CN): δ 153.6, 146.1, 137.1, 123.5, 122.9, 59.7, 50.3, 31.9, 19.5, 13.3.

General Procedures for Preparation of 5a−h. A solution of **4a** or **b** (1 mmol) and alkyl halide (2 mmol) in DMF (0.5 mL) was placed in a Pyrex glass tube. After it was cooled to −195 °C, the tube was evacuated and sealed. The reaction mixture was heated at 110 °C for 24 h. After the tube was cooled and carefully opened, the volatile materials and DMF were removed under reduced pressure. The residue was dissolved in a mixture of water (5 mL) and acetone (5 mL), and then lithium bis(trifluoromethanesulfonyl)-amide or potassium hexafluorophosphate (3.0 mmol) was added. The reaction mixture was stirred at 25 °C for 5 h. The acetone was evaporated under reduced pressure, and the water layer was extracted three times with ethyl acetate (3 × 10 mL). The combined organic layer was washed three times with water (3 × 10 mL) and once with saturated $Na_2S_2O_3$ solution (5 mL), and then it was dried over anhydrous Na_2SO_4. The solvent was removed in vacuo to give **5a−h**.

1-(3-Methylimidazolium-1-yl)methylene-(4-ethyl-1,2,4-triazolium) bi[Bis(trifluoromethanesulfonyl)amide] 5a. Colorless solid. Yield: 78%. IR (KBr pellet): 3163 (w), 2992 (vw), 2857 (vw), 1615 (m), 1561 (m), 1528 (m), 1491 (w), 1454 (m), 1352 (s), 1233 (br, s), 1054 (s), 974 (vw), 885 (w), 861 (w), 839 (w), 780 (m), 742 (s), 649 (vw), 617 (m), 569 (s), 513 (w), 405 (vw) cm^{-1}. ^1H NMR: δ 10.43 (s, 1H), 9.46 (s, 1H), 9.30 (s, 1H), 8.03 (s, 1H), 7.83 (s, 1H), 7.22 (s, 2H), 4.58 (q, 2H, $J = 7.3$ Hz), 4.11 (s, 3H), 1.62 (t, 3H, $J = 7.3$ Hz). ^{13}C NMR: δ 146.5, 145.1, 139.2, 125.7, 124.0, 120.8 (q, $J = 319.2$ Hz), 62.0, 45.3, 37.2, 14.7. ^{19}F NMR: δ −79.9 (s, 12F). Anal. Calcd for $C_{13}H_{15}F_{12}N_7O_8S_4$ (752.97): C, 20.72; H, 2.01; N 13.01. Found: C, 20.82; H, 1.92; N, 12.80.

1-(3-Methylimidazolium-1-yl)methylene-(4-butyl-1,2,4-triazolium) Bi[bis(trifluoromethanesulfonyl)amide] 5b. Pale-yellow liquid. Yield: 87%. IR (KBr plate): 3163 (w), 2976 (vw), 2857 (vw), 1586 (m), 1561 (m), 1519 (w), 1492 (m), 1467 (m), 1357 (s), 1192 (br, s), 1139 (s), 1059 (s), 974 (vw), 969 (w), 901 (vw), 789 (m), 741 (m), 647 (vw), 558 (s), 510 (w) cm^{-1}. ^1H NMR: δ 10.47 (s, 1H), 9.48 (s, 1H), 9.32 (s, 1H), 8.06 (s, 1H), 7.85 (s, 1H), 7.24 (s, 2H), 4.56 (t, 2H, $J = 7.5$ Hz), 4.14 (s, 3H), 2.02−1.96 (m, 2H), 1.51−1.41 (m, 2H), 0.95 (t, 3H, $J = 7.3$ Hz). ^{13}C NMR: δ 146.7, 145.3, 139.3, 125.7, 124.0, 120.8 (q, $J = 319.0$ Hz), 62.1, 49.5, 37.2, 32.0, 19.8, 13.5. ^{19}F NMR: δ −79.9 (s, 12F); Anal. Calcd for $C_{15}H_{19}F_{12}N_7O_8S_4$ (781.59): C, 23.05; H, 2.45; N 12.54. Found: C, 23.04; H, 2.49; N, 12.41.

1-(3-Methylimidazolium-1-yl)methylene-(4-butyl-1,2,4-triazolium) Bis(hexafluorophosphate) 5c. Colorless solid. Yield: 84%. IR (KBr pellet): 3165 (w), 2961 (vw), 2862 (vw), 1580 (m), 1561 (m), 1519 (w), 1462 (m), 1351 (s), 1198 (br, s), 1134 (s), 1058 (s), 974 (vw), 837 (br, s), 778 (w), 741 (w), 652 (vw), 617 (m), 557 (s), 513 (w) cm^{-1}. ^1H NMR: δ 10.26 (s, 1H), 9.32 (s, 1H), 9.22 (s, 1H), 8.00 (s, 1H), 7.77 (s, 1H), 7.13 (s, 2H), 4.49 (t, 2H, $J = 7.5$ Hz), 4.08 (s, 3H), 2.01−1.91 (m, 2H), 1.48−1.36 (m, 2H), 0.93 (t, 3H, $J = 7.4$ Hz). ^{13}C NMR: δ 146.5, 145.2, 139.3, 125.5, 124.0, 62.0, 49.4, 37.1, 31.8, 19.8, 13.5. ^{19}F NMR: δ −71.2, −73.7 (d, 12F, $J = 707.3$ Hz). Anal. Calcd for $C_{11}H_{19}F_{12}N_5P_2$ (511.09): C, 25.84; H, 3.75; N 13.70. Found: C, 25.63; H, 3.73; N, 13.43.

1-(3-Methylimidazolium-1-yl)methylene-(4-trifluorobutyl-1,2,4-triazolium) Bi[bis(trifluoromethanesulfonyl)amide] 5d. Colorless solid. Yield: 86%. IR (KBr pellet): 3163 (w), 2957 (vw), 2857 (vw), 1584 (m), 1561 (m), 1519 (w), 1491 (m), 1464 (m), 1353 (s), 1195 (br, s), 1136 (s), 1056 (s), 964 (vw), 912 (vw), 852 (w), 788 (m), 741 (w), 650 (vw), 616 (m), 572 (s), 513 (m), 411 (vw) cm^{-1}. ^1H NMR: δ 10.40 (s, 1H), 9.33 (s, 1H), 9.22 (s, 1H), 7.95 (s, 1H), 7.72 (s, 1H), 7.10 (s, 2H), 4.61 (t, 2H, J = 7.5 Hz), 4.06 (s, 3H), 2.44−2.27 (m, 4H). ^{13}C NMR: δ 146.6, 145.4, 139.2, 128.4 (q, J = 273.6 Hz), 125.6, 124.0, 120.8 (q, J = 319.0 Hz, NTf_2), 62.1, 48.4, 37.2, 30.8 (q, J = 29.5 Hz), 23.1 (q, J = 3.3 Hz). ^{19}F NMR: δ −66.9 (t, 3F, J = 10.3 Hz), −79.9 (s, 12F). Anal. Calcd for $C_{15}H_{16}F_{15}N_7O_8S_4$ (834.97): C, 21.56; H, 1.93; N 11.73. Found: C, 21.32; H, 1.95; N, 11.53.

1-(3-Butylimidazolium-1-yl)methylene-(4-methyl-1,2,4-triazolium) Bi[bis(trifluoromethanesulfonyl)amide] 5e. Pale-yellow liquid. Yield: 87%. IR (KBr plate): 3144 (w), 2959 (vw), 2857 (vw), 1585 (m), 1559 (m), 1519 (w), 1491 (m), 1460 (m), 1352 (s), 1197 (br, s), 1135 (s), 1059 (s), 974 (vw), 867 (w), 849 (w), 784 (w), 742 (m), 647 (w), 615 (m), 569 (s), 511 (w), 411 (vw) cm^{-1}. ^1H NMR: δ 10.43 (s, 1H), 9.57 (s, 1H), 9.21 (s, 1H), 8.07 (s, 1H), 7.93 (s, 1H), 7.25 (s, 2H), 4.45 (t, 2H, J = 7.4 Hz), 4.20 (s, 3H), 2.00−1.90 (m, 2H), 1.45−1.35 (m, 2H), 0.93 (t, 3H, J = 7.3 Hz). ^{13}C NMR: δ 147.7, 146.1, 138.7, 124.5, 124.2, 120.9 (q, J = 318.8 Hz), 62.2, 51.0, 35.6, 32.4, 19.9, 13.5. ^{19}F NMR: δ −79.9 (s, 12F). Anal. Calcd for $C_{15}H_{19}F_{12}N_7O_8S_4$ (781.59): C, 23.05; H, 2.45; N 12.54. Found: C, 22.76; H, 2.41; N, 12.24.

1-(3-Butylimidazolium-1-yl)methylene-(4-methyl-1,2,4-triazolium) Bis(hexafluorophosphate) 5f. Colorless solid. Yield: 80%. IR (KBr pellet): 3163 (w), 2951 (vw), 2857 (vw), 1582 (m), 1561 (m), 1519 (w), 1491 (m), 1464 (m), 1353 (s), 1195 (br, s), 1139 (s), 1059 (s), 974 (vw), 839 (br, s), 778 (w), 741 (w), 649 (vw), 617 (m), 558 (s), 513 (w) cm^{-1}. ^1H NMR: δ 10.22 (s, 1H), 9.42 (s, 1H), 9.15 (s, 1H), 8.03 (s, 1H), 7.89 (s, 1H), 7.16 (s, 2H), 4.42 (t, 2H, J = 7.4 Hz), 4.16 (s, 3H), 1.99−1.89 (m, 2H), 1.44−1.32 (m, 2H), 0.93 (t, 3H, J = 7.3 Hz). ^{13}C NMR: δ 147.5, 146.0, 138.6, 124.3, 124.2, 62.0, 50.9, 35.4, 32.3, 19.9, 13.6. ^{19}F NMR: δ −71.3, −73.8 (d, 12F, J = 707.3 Hz). Anal. Calcd for $C_{11}H_{19}F_{12}N_5P_2$ (511.09): C, 25.84; H, 3.75; N 13.70. Found: C, 25.89; H, 3.76; N, 13.17.

1-(3-Butylimidazolium-1-yl)methylene-(4-ethyl-1,2,4-triazolium) Bi[bis(trifluoromethanesulfonyl)amide] 5g. Pale-yellow liquid. Yield: 88%. IR (KBr plate): 3143 (w), 2973 (vw), 2892 (vw), 1582 (m), 1561 (m), 1527 (w), 1458 (m), 1351 (s), 1199 (br, s), 1134 (s), 1054 (s), 974 (vw), 847 (m), 785 (w), 643 (w), 617 (s), 567 (m), 514 (m) cm^{-1}. ^1H NMR: δ 10.49 (s, 1H), 9.57 (s, 1H), 9.32 (s, 1H), 8.07 (s, 1H), 7.93 (s, 1H), 7.23 (s, 2H), 4.59 (q, 2H, J = 7.3 Hz), 4.45 (t, 2H, J = 7.3 Hz), 4.14 (s, 3H), 2.00−1.90 (m, 2H), 1.63 (t, 3H, J = 7.3 Hz), 1.45−1.35 (m, 2H), 0.93 (t, 3H, J = 7.3 Hz). ^{13}C NMR: δ 146.6, 145.3, 138.7, 124.5, 124.3, 120.9 (q, J = 319.3 Hz), 62.2, 51.0, 45.4, 32.5, 19.9, 14.8, 13.5. ^{19}F NMR: δ −79.8 (s, 12F). Anal. Calcd for $C_{16}H_{21}F_{12}N_7O_8S_4$ (795.01): C, 24.15; H, 2.66; N 12.32. Found: C, 24.39; H, 2.77; N, 12.14.

1-(3-Butylimidazolium-1-yl)methylene-(4-trifluorobutyl-1,2,4-triazolium) Bi[bis(trifluoromethanesulfonyl)amide] 5h. Pale-yellow liquid. Yield: 91%. IR (KBr plate): 3163 (w), 2973 (vw), 2857 (vw), 1578 (m), 1559 (m), 1517 (w), 1492 (w), 1464 (m), 1351 (s), 1194 (br, s), 1139 (s), 1055 (s), 968 (vw), 920 (vw), 851 (vw), 789 (m), 742 (m), 650 (m), 616 (s), 571 (s), 511 (m), 405 (vw) cm^{-1}. ^1H NMR: δ 10.55 (s, 1H), 9.55 (s, 1H), 9.37 (s, 1H), 8.05 (s, 1H), 7.93 (s, 1H), 7.24 (s, 2H), 4.70 (t, 2H, J = 7.5 Hz), 4.45 (t, 2H, J = 7.5 Hz), 2.49−2.19 (m, 4H), 1.96−1.88 (m, 2H), 0.93 (t, 3H, J = 7.4 Hz). ^{13}C NMR: δ 146.8, 145.6, 138.7, 127.8 (q, J = 273.8 Hz), 124.4, 124.3, 120.8 (q, J = 319.0 Hz), 62.2, 50.9, 48.4, 32.4, 30.9 (q, J = 29.1 Hz), 23.3 (q, J = 3.3 Hz), 19.8, 13.5. ^{19}F NMR: δ −66.9 (t, 3F, J = 10.4 Hz), −79.9 (s, 12F). Anal. Calcd for $C_{18}H_{22}F_{15}N_7O_8S_4$ (877.02): C, 24.63; H, 2.53; N 11.17. Found: C, 24.52; H, 2.56; N, 10.97.

Synthesis of Dipalladium Bis[1-(3-butylimidazolium-1-yl)-methylene-(4-butyl-1,2,4-triazolium)] 6. A mixture of **2d** (0.24 g, 0.5 mmol) and $Pd(OAc)_2$ (0.11 g, 0.5 mmol) in DMSO (20 mL) was stirred at 25 °C for 3 h. After the reaction mixture was heated at 120 °C for 12 h, the solvent was removed under vacuum at this temperature. The residue was washed three times with hexane (10 mL) and ethyl ether (10 mL), respectively. Yellow crystals of **6** were obtained through diffusion of ethyl ether into its CH_2Cl_2 solution. Yield: 0.27 g, 87%. IR (KBr pellet): 3165 (w), 2962 (vw), 2851 (vw), 1578 (m), 1561 (m), 1517 (w), 1464 (m), 1354 (s), 1192 (br, s), 1133 (s), 1057 (s), 974 (vw), 921 (vw), 835 (br, s), 789 (w), 742 (m), 652 (vw), 617 (m), 557 (s), 513 (w). ^1H NMR ($CDCl_3$): δ 8.38 (s, 2H), 7.85 (s, 2H), 7.35 (s, 2H), 7.15 (s, 4H), 4.43 (t, 4H, J = 7.5 Hz), 4.26 (t, 4H, J = 7.5 Hz), 2.11−2.02 (m, 4H), 1.97−1.87 (m, 4H), 1.44−1.37 (m, 8H), 0.99−0.91 (m, 12H). ^{13}C NMR (DMSO-d_6): δ 171.9, 165.8, 144.8, 123.3, 122.7, 64.8, 50.0, 47.8, 32.4, 31.9, 19.1, 18.9, 13.3, 13.2. Anal. Calcd for $C_{28}H_{46}I_4N_{10}Pd_2$ (1243.18): C, 27.05; H, 3.73; N 11.27. Found: C, 26.94; H, 3.70; N, 11.52.

General Procedures for the Heck Reaction in Ionic Liquid. Palladium(II) catalyst **6** (25 mg, 0.02 mmol) was dissolved in ionic liquid **3d** (2 mL), and the solution was degassed under reduced pressure for 1 h. The aryl halide (1.0 mmol), the olefin (1.25 mmol), and Et_3N (1.5 mmol) were added subsequently under nitrogen. The resulting mixture was stirred for 12 h at 120 °C. After the mixture ws cooled to 25 °C, the product was extracted from the reaction mixture by addition of ethyl ether (3 mL), followed by decanting of the ethyl ether solution. This process was repeated three additional times (3 × 3 mL). The combined organic layer was concentrated by rotary evaporation. The residue was purified by flash chromatography on silica gel to give the desired product. The ionic liquid-containing palladium(II) catalyst was washed three times with water (3 × 3 mL) to remove the excess of base and its salt and dried under reduced pressure at 60 °C for 4 h to remove traces of ethyl ether and water. It was ready for the next cycle.

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Supporting Information Available: Crystallographic data of complex **6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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