Low-Melting Dialkyl- and Bis(polyfluoroalkyl)-Substituted 1,1′-Methylenebis(imidazolium) and 1,1′-Methylenebis(1,2,4-triazolium) Bis(trifluoromethanesulfonyl)amides: Ionic Liquids Leading to Bis(N-heterocyclic carbene) Complexes of Palladium

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Ionic liquids with pincer dicationic nuclei, **2a**−**6a** and **2b**−**6b**, were prepared from either 1,1′-methylenebis(imidazole) or 1,1′-methylenebis(1,2,4-triazole) via quaternization with alkyl or polyfluoroalkyl halides under classical or microwave irradiation conditions. Palladium-catalyzed Heck cross-coupling reactions were performed successfully in the ionic liquid **3a**. A single-crystal X-ray structure of a bis(N-heterocyclic carbene) complex of palladium (**7**) formed in the ionic liquid catalyst system supports its likelihood as the active catalyst.

Introduction

In recent years, ionic liquids as environmentally benign solvents for some organic reactions have attracted more and more interest in the field of synthetic chemistry.[1] Ionic liquids are normally defined as thermally stable salts with melting points <100 °C containing bulky organic cations and, most often, inorganic anions frequently with fluorine: e.g., hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), bis(trifluoromethanesulfonyl)amide (NTf_2^-), triflate (OTf^-), etc. These interesting liquids have unique physical−chemical properties: e.g., low melting point, very low vapor pressure, long liquid range, tunable miscibility, and good hydrolytic and thermal stability.[2] The ionic liquids commonly in use are those with alkylammonium, alkylphosphonium, *N*-alkylpyridinium, and especially *N*,*N*-dialkylimidazolium cations.[3] Imidazolium-based ionic liquids have been used extensively as reaction media that act as in situ imidazole carbene ligands with transition metals (N-heterocyclic carbene (NHC)). A series of Pd-catalyzed cross-coupling reactions have been successfully examined in this kind of ionic liquid system.[4]

Since the discovery of stable free N-heterocyclic carbene ligands in 1991,[5] many transition-metal carbene complexes have been prepared and their catalytic applications described.[6] Some chelate or pincer N-heterocyclic Pd−carbene complexes exhibit high catalytic reactivity for Heck and Suzuki reactions in organic solvents,[6k,7] while other NHC complexes perform more effectively in ionic liquid media.[8] However, while there are several reports that deal with ionic liquids with chelate or pincer dinuclear cations, there are not a large number of examples of catalyst applications of chelate

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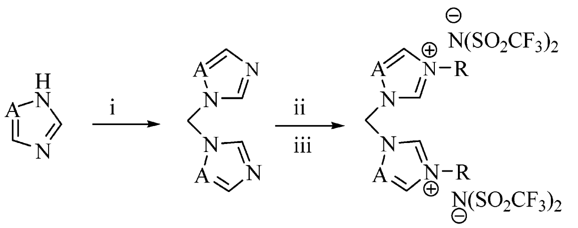
10.1021/om050210q CCC: $30.25

Scheme 1[a]



1a, A = C
1b, A = N

2a - **6a**, A = C
2b - **6b**, A = N

[a] Legend: (i) CH_2Cl_2 or CH_2Br_2, KOH, TBAB; (ii) RI or RBr, 110 or 130 °C, 20 h (R = CH_3 (**2a**, **2b**), C_4H_9 (**3a**, **3b**), C_6H_{13} (**4a**, **4b**), $(CH_2)_3CF_3$ (**5a**, **5b**), $CH_2CH_2C_4F_9$ (**6a**, **6b**)); (iii) $LiN(SO_2CF_3)_2$, 10/1 CH_3OH/H_2O, room temperature, 2 h.

or pincer N-heterocyclic Pd carbene complexes being utilized in ionic liquids. Ionic liquids comprised of different cations and anions influence organic reactions differently.[9] Recently, some ionic liquids have been prepared and their catalyst applications in cross-coupling reactions tested.[6k,10]

In this work, we report ionic liquids with pincer dications that can also be used in Pd-catalyzed cross-coupling reactions and, as is the case for $[BMIM]PF_6$ and $[BMIM]NTf_2$ as solvents (BMIM = butylmethylimidazole, NTf_2 = bis(trifluoromethanesulfonyl)amide), can form Pd carbene complexes in situ. On the basis of our previous work that deals with the synthesis of new quaternary salts containing alkyl and polyfluoroalkyl cations,[11] we have synthesized the new ionic liquids **2a**–**6a** and **2b**–**6b**, which contain the pincer dication 1,1′-methylene-3,3′-dialkylbis(imidazolium) or 1,1′-methylene-4,4′-dialkylbis(1,2,4-triazolium) with NTf_2^- as the anion. Applications in Heck cross-coupling reactions were tested using the ionic liquid **3a** as the reaction medium.

Results and Discussion

1,1′-Dialkyl-3,3′-methylenebis(imidazolium) dihalides form metal carbene complexes and are often prepared from a 1-alkyl-substituted imidazole and methylene bromide or iodide under similar conditions.[12] Here we report an alternate route to obtain these quaternary salts (Scheme 1). Compounds **1a** and **1b** were prepared from imidazole and 1,2,4-triazole with little modification of literature methods.[13] They were then quaternized with alkyl or polyfluoroalkyl halides under neat reaction conditions or in DMF (**6a**, **6b**) when 1*H*,1*H*,2*H*,2*H*-perfluoro-1-iodohexane was used. The resulting halide was metathesized with $LiN(SO_2CF_3)_2$ in CH_3OH/H_2O (10/1, v/v). Compounds **2a**–**6a** and **2b**–**6b** were obtained in high yields (86–94%). Generally, 1,1′-methylenebis(imidazole) (**1a**) can be readily quaternized at 110 °C, while 1,1′-methylenebis(1,2,4-triazole) (**1b**) requires heating to 130 °C. In both systems, a rather long reaction time (20 h) was required for complete quaternization to occur. However, when microwave conditions were employed, complete reaction with the alkyl halide occurred in ~30 min (see Experimental Section).[14]

Table 1. Phase Transition and Thermal Decomposition Temperatures of 2a–6a and 2b–6b

compd	R	T_g (°C)[a]	T_d (°C)[b]
2a	CH_3	−45	408
3a	C_4H_9	−51	412
4a	C_6H_{13}	−49	404
5a	$(CH_2)_3CF_3$	−47	442
6a	$(CH_2)_2C_4F_9$	−19	420
2b	CH_3	−26	325
3b	C_4H_9	−39	321
4b	C_6H_{13}	94	342
5b	$(CH_2)_3CF_3$	−45	362
6b	$(CH_2)_2C_4F_9$	−53	349

[a] Phase transition temperature. [b] Thermal degradation temperature.

All of the new compounds, **2a**–**6a** and **2b**–**6b**, were characterized by their ^1H, ^{13}C, and ^{19}F NMR spectra and elemental analyses. With the exception of **6b**, each compound, **2a**–**6a** and **2b**–**5b**, showed only one set of signals in their ^1H and ^{13}C NMR spectra for the substituted alkylimidazolium ring, 1,2,4-triazolium ring, and the methylene-bridged rings. These results indicate the equivalence of the substituted alkyl groups and aromatic ring, which supports a symmetric structure. However, in the ^1H NMR spectrum of **6b**, one broad singlet at 7.73 ppm and two sets of triplets at 5.04 and 4.98 ppm (J = 7.2 and 7.4 Hz) were observed for the two protons of the methylene-bridged triazole rings and $N4-CH_2$, respectively. In the ^{13}C NMR spectrum, two sets of triplets were found at 44.5 and 40.5 ppm with J = 4.8 and 4.9 Hz (carbon and fluorine coupling) for the carbon in $N4-CH_2$. This shows the nonequivalence of the two protons and carbon in $N4-CH_2$. For **2a**–**6a**, the chemical shifts of the protons of the methylene-bridged imidazolium rings ($-NCH_2N-$) and the acidic proton H2 ($-NCHN-$) in the imidazole ring are at 6.97–7.10 and 9.30–9.70 ppm, respectively. The chemical shifts of the corresponding **2b**–**6b** are found at 7.27–7.73 and 10.28–10.63 ppm. This clearly supports the acidity of the H5 proton (chemical shifts are downfield) of the 1,2,4-triazole ring being higher than that of the H2 of the imidazole ring in these ionic liquids.

Phase transition temperatures (midpoints of glass transitions or melting points) and thermal decomposition points for **2a**–**6a** and **2b**–**6b** as determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are given in Table 1.At 25 °C, with the exception of **4b**, which melts at 94 °C, all of the quaternary salts with NTf_2^- as the anion are liquids and, therefore, fall into the ionic liquid class.

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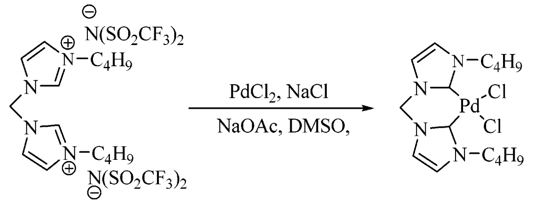
Scheme 2



3a **7**

When the characteristics of the bis(imidazolium) salts (**2a**−**6a)** are compared with their bis(triazolium) analogues (**2b**−**6b**), it is seen that the former have lower glass transition temperatures and higher decomposition temperatures (T_d at 404−442 °C) than the latter with the corresponding alkyl or polyfluoroalkyl substituents (T_d at 321−362 °C). When polyfluoroalkyl groups are present in the quaternary salts, the decomposition temperatures (T_d) are slightly higher than for the corresponding alkyl-substituted compounds: i.e., **5a** > **3a** (butyl), **6a** > **4a** (hexyl), **5b** > **3b** (butyl), and **6b** > **4b** (hexyl). However, their glass transition temperatures do not vary in a regular manner, with **6b** exhibiting the lowest T_g at −53.1 °C and, surprisingly, **4b** the highest. This low melting point for **6b** probably arises from the poor packing characteristics in the solid due to the nonsymmetric structure (as was noted above in discussing its NMR spectra). The polyfluoroalkyl compounds tend to be more viscous than their hydrocarbon analogues. All of the ionic liquids have good solubilities in acetone, ethyl acetate, ethanol, and methanol, but they are immiscible in hexane, ether, and water.

Some pincer Pd carbene complexes with a Pd−Br or a Pd−I bond have been prepared from the reaction of 1,1′-dialkyl-3,3′-methylenebis(imidazolium) bromide or iodide with $Pd(OAc)_2$ in a DMSO solution.[15] There are few corresponding reports concerning chelating Pd carbene complexes with a Pd−Cl bond.[6i] When we reacted **3a** with $PdCl_2$ in the presence of NaOAc in DMSO, we obtained the pincer Pd carbene complex **7**, with retention of the Pd−Cl bonds (Scheme 2). In the ^1H NMR spectrum, the signal for the acidic proton (−NCHN−, 9.48 ppm) at the 2-position in the imidazolium ring of **3a** has disappeared and the protons of the methylene group bonded to N3 in the ring are split into two signals at 4.90 and 4.02 ppm. A carbene carbon is seen at 156.8 ppm in the ^{13}C NMR spectrum. This is in agreement with its solid-state structure, as determined by single-crystal X-ray diffraction (Figure 1). Complex **7** exists in the cis form with the palladacycle (six-membered ring, Pd1−C9−N8−C10−N11−C15) fixed in a boat conformation (see the Supporting Information). The coordination geometry around the palladium atom is square planar, with angles of ~90° between the four substituents (C9−Pd1−C15, 85.1°; C9−Pd1−Cl1, 92.4°; Cl1−Pd1−Cl2, 89.4°; Cl2−Pd1−C15, 92.9°). The narrow angle for C9−Pd1−C15 is due to the chelation of the bis(imidazolium), which is constrained by the methylene bridge. There are two independent molecules in the asymmetric unit, and only one is shown in Figure 1. Both molecules are nearly identical. An overlay fit of the [methylenebis(imidazolium)]$PdCl_2$ units, omitting the alkyl side chains, indicates a weighted RMS deviation of 0.0547 Å. The main difference between both molecules is in the orientation of the butyl groups.

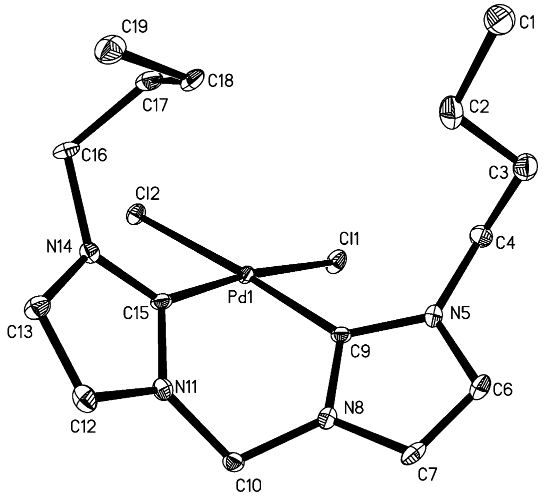
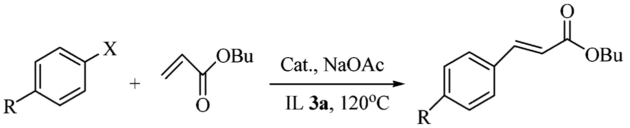


Figure 1. Molecular structure of the Pd carbene complex **7**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Heck Cross-Coupling Reactions in the Ionic Liquid 3a with Different Aryl Halides and Butyl Acrylate



entry	Pd source	R	X	time (h)	yield[a] (%)
1	$PdCl_2$	H	I	6	92
2	$PdCl_2$	H	Br	18	71 (67, 70)[b]
3	$PdCl_2$	H	Cl	24	3[b]
4	$PdCl_2$	NO_2	Br	18	73
5	$PdCl_2$	CF_3	Br	18	69
6	$PdCl_2$	CH_3	Br	18	57
7	**7**	H	Br	12	76 (70, 65)[b]

[a] Isolated yield. [b] GC-MS yield for recycling second and third times.

Heck cross-coupling reactions of aromatic halides with the electron-poor olefin butyl acrylate were evaluated using both $PdCl_2$ and the Pd carbene complex **7** as preformed catalysts immobilized in the ionic liquid **3a**. The conditions employed were similar to those described in the literature.[4] Not unexpectedly, iodobenzene was found to have the highest reactivity, giving *trans*-cinnamic acid *n*-butyl ester in 92% yield, while bromobenzene, with mild reactivity, resulted in 71% yield. However, chlorobenzene only resulted in a low 3% yield (GC-MS). The results are given in Table 2. We have also carried out some reactions of bromobenzene derivatives with electron-donating and electron-withdrawing groups, with satisfactory results being obtained. Catalyst recycle is an important factor in ionic liquid-assisted reactions. Some new ionic liquids with excellent immobilized character can be reused over 10 times.[10] We also performed the catalyst recycling reactions in the ionic liquid **3a**, using bromobenzene with butyl acrylate in the presence of $PdCl_2$ or **7**. Although our system does not allow such extensive recycling, the recovered ionic liquid **3a** can be reused three times without significant loss of activity, and the yield increased slightly when **7**

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[15] Herrmann, W. A.; Schwarz, J.; Gardiner, M. G.; Spiegler, M. *J. Organomet. Chem.* **1999**, *575*, 80−86.

was used. However, **3a** (with $PdCl_2$ or **7**) is not as effective for cross-coupling as, for example, a Pd carbene catalyst in [BMIM]NTf_2[16] or in [1,1′,3-tributyl-2,2′-biimidazolium]$PdCl_2$ hexafluorophosphate,[10b] where the yields are consistently higher and the recyclability greater.

In summary, in this paper we report the synthesis of a family of new ionic liquids that contain pincer dications substituted with different dialkyl or dipolyfluoroalkyl moieties. Their thermal properties were determined using DSC and TGA. The ionic liquid **3a** was used as a solvent in successful Pd-catalyzed Heck cross-coupling reactions. The X-ray structure for the Pd carbene complex **7**, which is the likely form of the catalyst in this ionic liquid system, was obtained.

Experimental Section

The chemicals were obtained commercially. Silica gel (0.060−0.200 mm, pore diameter ~4 nm) was used for column chromatography, and a standard Schlenk line system was used for some reactions. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on spectrometers at 300, 75, and 282 MHz, respectively, in acetone-d_6 unless otherwise stated. Chemical shifts were reported in ppm relative to the appropriate standard: $CFCl_3$ for ^{19}F and TMS for ^1H and ^{13}C NMR spectra. DSC data were recorded by heating from −80 to +200 °C at 10 °C/min. Thermogravimetric analysis (TGA) measurements were made by heating samples from 20 to 500 °C at 10 °C/min under a dynamic nitrogen atmosphere. Microwave-assisted reactions were carried out in a self-tuning single-mode CEM Discover$^\beta$ focused synthesizer operated at 250 W. Elemental analyses were performed at the Shanghai Institute of Organic Chemistry.

Crystallography. Data for complex **7** were collected at 86(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, $\lambda = 0.710\,73$ Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using ω scans of 0.3° per frame for 5 s, and a full sphere of data was collected. A total of 2450 frames were collected with a final resolution of 0.77 Å. The first 50 frames were re-collected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[17] software and refined using SAINTPlus[18] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[19] The structure was solved by direct methods and refined by least-squares method on F^2 using the SHELXTL program package.[20] The structure was solved in the space group *Pn* (No. 7, chiral) by analysis of systematic absences. All atoms were refined anisotropically. The structure was refined as a racemic twin. There is a possibility of a pseudosymmetry center which converts the space group to $P2_1/c$. This was investigated, but no reasonable solution could be obtained. The high residuals are close to the metal centers. No decomposition was observed during data collection. Details of the data collection and refinement are provided in the Supporting Information.

General Procedure for the Preparation of 2a−6a and 2b−6b. An alkyl or polyfluoroalkyl halide (3.0 mmol) and **1a** or **1b** (1.0 mmol) were placed in a Pyrex glass tube, which was sealed and heated at 110 or 130 °C for 20 h, respectively. When 1*H*,1*H*,2*H*,2*H*-perfluoro-1-iodohexane was used, 2 mL of DMF was added to the reaction mixture. After the mixture was cooled, the solvent was removed in vacuo and the residue was washed three times (3 × 10 mL) with ethyl acetate and acetone and dried under vacuum. The residue was taken up in methanol (20 mL), a solution (2 mL) of lithium bis(trifluoromethanesulfonyl)amide (2.2 mmol) was added, and the solution was stirred at 25 °C for 2 h. The solvent was removed and extracted with ethyl acetate (3 × 20 mL), and the extract was washed with water and dried with anhydrous magnesium sulfate. The solvent was removed under vacuum at 45 °C for 12 h to leave products **2a**−**6a** and **2b**−**6b**.

General Procedure for Microwave Reactions. Into a septum-sealed microwave tube, the alkyl or polyfluoroalkyl halide (3.0 mmol) and **1a** or **1b** (1.0 mmol) were charged. The resulting mixture was irradiated in the microwave cavity at 110 or 130 °C at 250 W (by modulation of power) for 30 min. The solution was cooled rapidly to 25 °C by passing compressed air through the microwave cavity. The purification procedure was the same as above.

Preparation of [1,1′-Methylene-3,3′-dibutylbis(imidazolin-2,2′-diylidene)]palladium(II) Dichloride (7). 1,1′-Methylenebis(3-*n*-butylimidazolium) bis[bis(trifluoromethanesulfonyl)amide] (**3a**; 1.0 mmol), palladium chloride (1.0 mmol), sodium acetate (2.2 mmol), and sodium chloride (2.2 mmol) were dissolved in 10 mL of DMSO, and the mixture was stirred for 5 h at 90 °C. After the mixture was cooled, the solvent was removed under vacuum and the residue was washed with water (10 mL) and extracted with chloroform (20 mL). The chloroform was removed to obtain the product (234 mg; yield 52.6%) The single crystal for X-ray study was obtained by slowly evaporating the solvent from an acetonitrile solution of the compound. ^1H NMR (DMSO-d_6): δ 7.57 (s, 2H, −NCHCHN−), 7.38 (s, 2H, −NCHCHN−), 6.26 (s, 2H, $-NCH_2N-$), 4.90(m, 2H, NCH_2), 4.02 (m, 2H, NCH_2), 1.74 (m, 4H, CH_2CH_2), 1.22 (m, 4H, CH_2CH_3), 0.89 (t, $J = 7.4$ Hz, 6H, CH_3). ^{13}C NMR: δ 156.8, 122.1, 121.2, 62.5, 49.5, 32.9, 19.2, 13.6. Anal. Calcd for $C_{15}H_{24}Cl_2N_4Pd$: C, 41.16; H, 5.53; N, 12.80. Found: C, 41.21; H, 5.86; N, 12.58.

Typical Procedure for the Heck Cross-Coupling Reaction. Into a 50 mL two-necked round-bottomed flask were placed the ionic liquid **3a** (2 mL), aryl halide (1.0 mmol), anhydrous sodium acetate (1.2 mmol), $PdCl_2$ or complex **7** (1.0 mol % of the aryl halide), and butyl acrylate (1.5 mmol). The resulting mixture was heated to 120 °C for different times (from 6 to 24 h). After the mixture was cooled, the product was extracted from the ionic liquid with ether (5 × 10 mL). The solvent was removed from the organic layer, and column chromatography was performed to obtain the desired products (see the Supporting Information). Successively the ionic liquid was washed with water (3 × 15 mL), extracted with ethyl acetate (10 mL), and dried under vacuum for use in the next reaction.

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Supporting Information Available: X-ray data as a CIF file for [1,1′-methylene-3,3′-dibutylbis(imidazolin-2,2′-diylidene)]palladium(II) dichloride (**7**) and text, tables, and figures giving analytical data for **2a**−**6a** and **2b**−**6b** and structural data for **7**. This information is available free of charge via the Internet at http://pubs.acs.org.

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