Synthesis of New Dicationic Azolium Salts and Their Application as NHC Precursors in Suzuki–Miyaura Coupling

Sadaf Sadiq Khan, Jürgen Liebscher*

Institute of Chemistry, Humboldt-University Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany
Fax +49(30)20937552; E-mail: liebscher@chemie.hu-berlin.de

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Dedicated to Prof. Dr. Helmut Vorbrüggen on the occasion of his 80th birthday

Abstract: Novel dicationic azolium salts were developed as N-heterocyclic carbene (NHC) precursors wherein two 1,2,3-triazolium, one 1,2,3-triazolium and one imidazolium, or two imidazolium units, are tethered to each other through alkylene bridges. These dicationic systems were applied as precursors for ligands in palladium-catalyzed Suzuki–Miyaura couplings using different leaving groups. Interestingly, the combination of an imidazolium and a 1,2,3-triazolium unit performed better than either a single azolium salt or than dications where two imidazolium or two 1,2,3-triazolium units are found. Aryl chlorides, iodides and triflates turned out to be the best substrates for this new catalytic system.

Key words: cycloaddition, cross-coupling, catalysis, alkylation, heterocycles

Imidazolium salts are probably the most important class of ionic liquids (ILs). They are easy to synthesize and their properties can be tuned by adjusting the substituents attached to the imidazolium ring as well as by changing the anions within an extremely wide range.[1–3] They have been used as inert solvents in a variety of chemical reactions, palladium-catalyzed reactions included,[4–10] and often provide advantages over the use of traditional organic solvents. Their application in catalysis can improve the catalyst stability, the overall catalytic performance, and can allow convenient biphasic catalysis. As a special subclass of IL geminal or triple imidazolium[11] salts have attracted interest as di- and tricationic ionic liquids, respectively.[12,13] Although ILs are often considered as innocent solvents, there are also a number of cases wherein imidazolium-based ILs directly participate in the reactions, for example, under strongly basic conditions and/or in the presence of transition metals. Here, they are deprotonated at the 2-position to form N-heterocyclic carbenes (NHCs) or undergo oxidative addition to the metal, leading to complexes.[14–17] Palladium salts or palladium complexes can form NHC complexes even under non-basic conditions.[17–21] On the other hand, such strongly nucleophilic, imidazole-based NHCs were purposely synthesized and have turned out to be efficient ligands for heavy metals (Pd, Ru, etc.).[22] Their palladium complexes have advantageously been used in a number of palladium-catalyzed cross-coupling reactions, the Suzuki–Miyaura coupling included.[23–30] Here, they could also be applied to the – often reluctant – chloroarenes.[23,25,31] As a precondition for good coupling activity, bulky aryl substituents have to be present at both nitrogen atoms of the imidazolin-2-ylidene. The preparation of the NHC ligands in situ from the corresponding imidazolium salts by bases, in the presence of a suitable palladium species, provides a straightforward method for obtaining the catalysts.[23,25]

As a special type of imidazol-2-ylidene ligands for palladium complexes, compounds were used wherein more than one imidazole moiety were covalently connected to each other.[28,32,33] Amongst them, crown carbene complexes were found.[34] In such cases, the corresponding imidazolium salts were used and treated with an excess of base, thus implying that each imidazolium unit was transformed into the corresponding carbene. Other NHC ligands, such as pyrazolylidenes, pyridinylidenes, thiazolylidenes, or 1,2,4-triazolylidenes, are rare.[22,35]

We recently developed 1,2,3-triazolium salts as a new class of ionic liquid.[36] They can be synthesized in a straightforward, two-step procedure by copper(I)-catalyzed [3+2] cycloaddition of organic azides to alkynes in a click process developed by Meldal and Sharpless,[37,38] followed by N-alkylation. This methodology has also been used for the synthesis of so-called[39] IL-tagged organocatalysts by tethering organocatalytic moieties to triazolium salts.[40,41] 1,2,3-Triazolium salts are much less acidic than imidazolium salts and, thus, can be inert under basic conditions where imidazolium-based ILs are deprotonated. Nevertheless, 1,2,3-triazolium salts were recently shown to undergo complex formation with palladium acetate by deprotonation at a ring carbon atom.[42] This result prompted us to investigate whether mixtures of 1,2,3-triazolium salts and palladium species can act as catalysts in Suzuki–Miyaura reactions.

We chose the known 1,4-dibutyl-3-methyl-1,2,3-triazolium iodide (**4a**)[43] and, for comparison, commercial 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF_4) as precursors for the NHC. In addition, we synthesized a new 1,2,3-triazolium salt **4b** (Scheme 1), wherein the acidic 5-position is flanked by two voluminous mesityl groups. Such steric shielding was shown to be essential for good performance of imidazolium-based NHCs (see above). In order to investigate possible synergistic effects, we further synthesized NHC precursors wherein two azolium units, i.e., two 1,2,3-triazolium rings (**7**), one 1,2,3-triazolium

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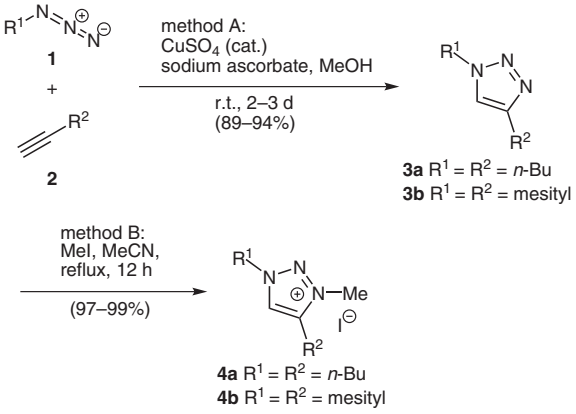
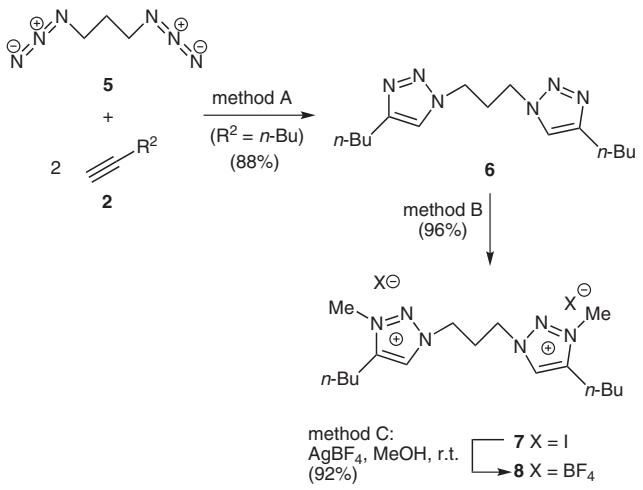
and one imidazolium moiety (**11**) and two imidazolium structures (**14**), are tethered to each other. The syntheses of the dicationic 1,2,3-triazolium compounds **7** and **11** were again based on our versatile two-step methodology based on copper-catalyzed [3+2] cycloaddition of azides and terminal alkynes to 1,4-disubstituted 1,2,3-triazoles and final N-alkylation (Scheme 2 and Scheme 3).



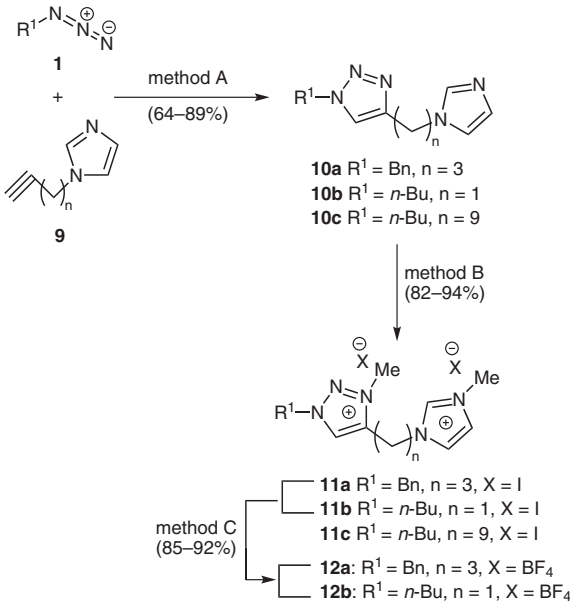
Scheme 1 Synthesis of 1,2,3-triazolium salts **4a** and **4b**



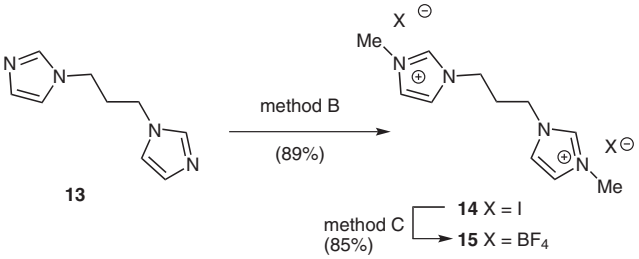
Scheme 2 Synthesis of di(1,2,3-triazolium) salts **7** and **8**

For the synthesis of the ditriazolium product **7**, 1,3-diazidopropane (**5**) and two equivalents of 1-hexyne were used as starting materials and both 1,2,3-triazole rings of the cycloaddition product **6** were finally methylated. When imidazolylalkynes **9** were applied in this sequence, the 1,2,3-triazoles **10** that were formed in the first step underwent methylation of both the triazole and the imidazole ring in the final step, thus giving the dicationic azolium products **11**. The corresponding 1,3-diimidazoliumpropane **14** was obtained by double methylation of the known 1,3-di(imidazol-1-yl)propane (**13**; Scheme 4).

All syntheses provided high yields of products. In order to investigate the effect of the anion in the NHC precursors, the iodides **7**, **11**, and **14** were transformed into the corresponding tetrafluoroborates **8**, **12**, and **15** by salt metathesis with silver tetrafluoroborate in quantitative yields. The



Scheme 3 Synthesis of mixed imidazolium triazolium salts **11a**–**12b**



Scheme 4 Synthesis of diimidazolium salts **14** and **15**

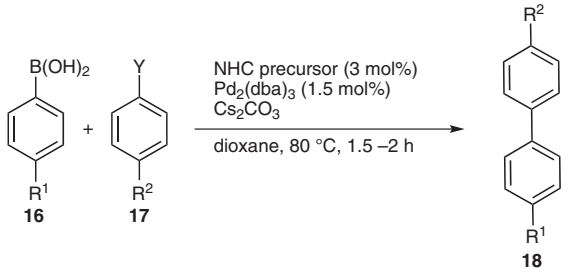
new azolium salts **4b**, **5b**, **7**, **8**, and **14** are solids, whereas **11**, **12**, and **15** appeared as oils. All structures were elucidated by NMR spectroscopy and by MS analysis.

With these NHC precursors in hand, we investigated their performance in the Suzuki–Miyaura reaction of arylboronic acids **16** with haloarenes, aryltriflates, and aryltosylates **17** (Scheme 5) by adopting a procedure reported for the application of imidazolium NHC precursors[25] involving $Pd_2(dba)_3$ as palladium source in the presence of cesium carbonate as base. First, we screened the NHC precursors in the reaction of phenylboronic acid with 4-chlorotoluene (Table 1, entry 1). As a reference, the reaction was first performed without the addition of an NHC precursor (31% yield). The addition of either $bmimBF_4$ or the trialkyl-1,2,3-triazolium iodide **4a** did not show a significant effect. This phenomenon corresponds with the known fact that bulky aryl substituents have to be present at both N-atoms of the imidazole ring. The sterically shielded 1,4-dimesityl-1,2,3-triazolium salt (**4b**) gave a somewhat higher yield (48%) but this was far from satisfactory and worse than those obtained in known cases where the corresponding imidazolium salts were used.[23,25] Whereas the application of the twin 1,2,3-triazolium NHC precursors **7** and **8** did not improve the yield, an increase

Table 1 Effect of the Addition of NHC Precursors on Yields of **18** in Suzuki–Miyaura Reaction of Phenylboronic Acid (Scheme 5)

				Yield (%) of products **18**												
Entry	R^1	R^2	Y	None	$bmimBF_4$	**4a**	**4b**	**7**	**8**	**11a**	**11b**	**11c**	**12a**	**12b**	**14**	**15**
1	H	Me	Cl	31	32	36	48	30	38	75	81	83	59	68	65	48
2	H	Me	Br	31	10	26	–[a]	–[a]	15	35	11		51		61	21
3	H	Me	I	74	65					70	90					
4	H	Me	OTf	83	69	–[a]	–[a]	–[a]	07	90	96		99	100	–[a]	21

[a] Only starting material was recovered.



Scheme 5 Suzuki–Miyaura cross-coupling reaction

was achieved with the twin imidazolium NHC precursors **14** (65%) and **15** (48%) (Table 1, entry 1).

Remarkably, a significant improvement was observed when the mixed NHC precursors **11a** (75%), **11b** (81%), or **11c** (83%) were used in the Suzuki–Miyaura reaction of 4-chlorotoluene with phenylboronic acid (Table 1, entry 1). Since their performance was much better than those of the symmetric di(1,2,3-triazolium) **7**, **8** and diimidazolium **14**, **15** compounds, there must exist a considerable synergistic effect caused by the presence of the two different heterocycles in the mixed system **11**. At this stage it was difficult to find a reason for this phenomenon. We assumed that the imidazole moiety of the mixed systems **11** is deprotonated by cesium carbonate, forming an imidazole-2-ylidene, which acts as a ligand for the palladium. The 1,2,3-triazolium moiety is much less acidic and thus less likely to be transformed into an NHC ligand. This is in line with the poor performance of the di-1,2,3-triazoliumpropanes **7** and **8**. But other reasons, such as formation of IL-stabilized nanoparticles in situ could also be responsible for the observed phenomena. In this context, it is worth mentioning that palladium nanoparticles prepared in situ can efficiently catalyze Suzuki–Miyaura reactions.[44]

Investigations into the use of leaving groups other than chloride revealed that bromide performed worse in all cases (Scheme 5, and Table 1, entry 2) and thus is not a good choice for our methodology. In the coupling of 4-bromotoluene, some cases were even observed wherein the addition of 1,2,3-triazolium NHC precursors prohibited the reaction (Table 1, entry 2; compounds **4b** and **7**). Some improvements could be achieved in the case of Suzuki–Miyaura coupling of 4-iodotoluene by using the triazolimidazolalkylenes **11** as NHC precursors (entry 3; increase in yield from 74% without an additive to 90% with addition of **11b**). However, the effect was not as marked as in the case of chlorotoluene (Table 1, entry 1; improvement from 31% to 81% with **11b**). Triflate turned out to be the best leaving group in this Suzuki–Miyaura reaction (Table 1, entry 4). Quantitative yields were obtained with the mixed NHC precursors **11** and **12**. Again for unknown reasons, the addition of the 1,2,3-triazolium salt **4** or the dicationic azolium salts **7** or **14** blocked the Suzuki–Miyaura coupling of 4-tolyltriflate.

We further tested our preferred NHC precursor **11b** with other substrates **17** (Table 2). As shown with 4-methylphenyltosylate (Table 2, entry 1), tosylate seems to be a disfavored leaving group in the Suzuki–Miyaura reaction (Scheme 5) since it failed to react in the presence of our otherwise optimal NHC precursor **11b**. Fluoride is also not suitable as a leaving group (5% yield; Table 2, entry 2). In reactant **17** (R^2 = Cl, Y = OTf), bearing two different potential leaving groups, the triflate was substituted (Table 2, entry 3; 55% yield), while the triflate group survived the coupling and bromide functioned as leaving group in 4-bromophenoxytriflate (Table 2, entry 4; yield 86%).

Table 2 Effect of Substituents and Leaving Groups on Yields of Products **18** of the Suzuki–Miyaura Reactions According to Scheme 5 Using **11b** as NHC Precursor

Entry	R^1	R^2	Y	Yield (%)
1	H	Me	OTs	–[a]
2	H	Me	F	5
3	H	Cl	OTf	55
4	H	OTf	Br	86
5	OMe	Me	Cl	100
6	OMe	Me	OTf	100
7	Ac	Me	OTf	24

[a] Only starting material was recovered.

Although this leaving group tendency corresponds to reported cases using phosphanes as ligands,[45] it was difficult to explain why **11b** performed so badly in the reaction

of 4-bromotoluene (Table 1, entry 2) while 4-bromophenyltriflate gave high yields (Table 2, entry 4, 86%). It is possible that this effect is due to the more electron-deficient nature of 4-bromophenyltriflate leading to a more rapid oxidative addition to the palladium than the 4-bromotoluene. Electron-donating substituents in the arene ring of the arene boronic acid **16** seem to be favorable, since 4-methoxyphenylboronic acid gave quantitative yields with 4-chlorotoluene as well as with 4-methylphenyltriflate (Table 2, entries 5 and 6). On the other hand, 4-acetylphenylboronic acid gave only 24% coupling product, indicating that electron-withdrawing substituents in the boronic acid are disfavored (Table 2, entry 7).

In summary, a number of new 1,2,3-triazolium salts were synthesized wherein an additional 1,2,3-triazolium or imidazolium moiety was tethered to the triazole ring via alkylene bridges. The novel compounds were synthesized by copper-catalyzed [3+2] cycloaddition of alkynes with azides and final N-alkylation. An investigation into the suitability of several 1,2,3-triazolium salts to act as precursors for NHC ligands in palladium-catalyzed Suzuki–Miyaura reactions revealed that the combination of a 1,2,3-triazolium and imidazolium moiety tethered to each other by alkylene bridges (compounds **11** and **12**) represents a new and effective catalyst system in particular for coupling of chloro arenes or aryl triflates. The application of 1,2,3-triazolium salts lacking an additional imidazolium salt either do not, or only marginally improve the performance of the Suzuki–Miyaura reactions even if two bulky mesityl groups flank the potentially acidic 5-position of the triazolium ring. We are presently designing other 1,2,3-triazolium-based dicationic NHC precursors to highlight the function of the triazolium moiety and to extend the scope of this methodology.

Chemicals were purchased from Aldrich and Acros. Silica gel 60 (0.04–0.063 mm, Acros) was used for preparative column chromatography. Melting points were determined with a Boetius hotstage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz, respectively, on a Bruker AC-300 with TMS as an internal standard. Elemental analyses were ascertained with a Euro EA analyser. High-resolution mass spectra (ESI) were measured with a Thermo Finnigan LTQ-FT-ICR-MS with MeOH as a solvent. The structures of the Suzuki coupling products **18** were confirmed by comparison of the NMR spectra with reported data.[45,46]

Synthesis of 1,2,3-Triazoles 4, 6, and 10; General Procedure (Method A)

To a solution of azide **1** or **5** (20 mmol) in MeOH (100 mL), sodium ascorbate (800 mg, 20 mol%), $CuSO_4$ (480 mg, 15 mol%) and the alkyne **2** or **9** (20 mmol) were added (for triazole **6** the amounts of alkyne **2**, copper sulfate and sodium ascorbate were doubled). The solution was stirred at r.t. for 2–3 d (reaction monitored by TLC). After completion of the reaction, H_2O (500 mL) was added and the mixture was extracted with EtOAc (3 × 500 mL). The combined organic layers were washed with brine (500 mL) and then dried over Na_2SO_4. Evaporation of the solvent in vacuo gave the product, which was pure according to TLC and NMR analyses and thus was used in subsequent alkylation without prior purification.

1,4-Dimesityl-1*H*-1,2,3-triazole (3b)

Yield: 94%; colorless crystals; mp 155 °C.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.50 (s, 1 H, CH_{triaz}), 7.06 (s, 2 H, ArH-C_{triaz}), 7.01 (s, 2 H, ArH-N_{triaz}), 2.44 (s, 3 H, *p*-CH_3Ar-N_{triaz}), 2.41 (s, 3 H, *p*-CH_3Ar-C_{triaz}), 2.22 (s, 3 H, *o*-CH_3ArH-N_{triaz}), 2.08 (s, 3 H, *o*-CH_3Ar-C_{triaz}).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 145.4 (C_{triaz}), 140.8 (C_{Ar}), 138.3 (C_{Ar}), 137.8 (C_{Ar}), 135.1 (C_{Ar}), 133.6 (C_{Ar}), 131.8 (C_{Ar}), 129.1 (CH_{Ar}), 128.4 (CH_{Ar}), 127.6 (CH_{Ar}), 124.5 (CH_{triaz}), 21.2 (*p*-CH_3Ar-C_{triaz}), 20.9 (*o*-CH_3Ar-C_{triaz}), 20.7 (*p*-CH_3Ar-N_{triaz}), 17.3 (*o*-CH_3Ar-N_{triaz}).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{23}N_3$: 306.1970; found: 306.1956.

Anal. Calcd for $C_{20}H_{23}N_3$: C, 78.65; H, 7.59; N, 13.76. Found: C, 78.44; H, 7.90; N, 13.57.

1,3-Di(4-butyl-1*H*-1,2,3-triazol-1-yl)propane (6)

Recrystallized from EtOAc.

Yield: 88%; white solid; mp 145 °C.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.31 (s, 2 H, CH_{triaz}), 4.27 (t, *J* = 6.14 Hz, 4 H, CH_2N), 2.61–2.65 (m, 4 H, CH_2C_{triaz}), 2.42–2.46 (m, 2 H, NCH_2CH_2), 1.56–1.60 (m, 4 H, $CH_3CH_2CH_2$), 1.25–1.37 (m, 4 H, CH_3CH_2), 0.86 (t, *J* = 7.29 Hz, 6 H, CH_3CH_2).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 121.7 (CH_{triaz}), 46.5 (NCH_2), 31.4 ($CH_3CH_2CH_2$), 30.6 (CH_2C), 25.2 (CH_3CH_2), 22.2 (NCH_2CH_2), 13.7 (CH_3CH_2).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{26}N_6$: 291.2297; found: 291.2282.

4-[3-(1*H*-Imidazol-1-yl)propyl]-1-benzyl-1*H*-1,2,3-triazole (10a)

Yield: 89%; light-yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.30–7.40 (m, 9 H, CH_{Ar} + CH_{triaz} + CH_{imidaz}), 5.49 (s, 2 H, Ph-CH_2), 4.06 (m, 2 H, CH_2NCH), 2.61 (m, 2 H, CH_2CN), 2.22 (m, 2 H, $CH_2CH_2CH_2$).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 146.5 (C_{triaz}), 135.3 (NCHN), 134.7 (C_{Ar}), 129.1 (CH_{Ar}), 128.8 (CH_{Ar}), 128.3 (CH_{Ar}), 128.2 (CH_{triaz}), 128.0 (CH_2NCHCH), 121.6 (CH_2NCHCH), 54.7 (PhCH_2), 42.0 (CH_2NCHN), 30.1 (CH_2CN), 22.4 ($CH_2CH_2CH_2$).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{17}N_5$: 268.1562; found: 268.1551.

4-[(1*H*-Imidazol-1-yl)methyl]-1-butyl-1*H*-1,2,3-triazole (10b)

Yield: 64%; yellow oil.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{15}N_5$: 206.1406; found: 206.1417.

4-[9-(1*H*-Imidazol-1-yl)nonyl]-1-butyl-1*H*-1,2,3-triazole (10c)

Yield: 97%; light-yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.50 (s, 1 H, NCHN), 7.28 (s, 1 H, $CH_2NCHCHN$), 7.24 (s, 1 H, $CH_2NCHCHN$), 6.99 (s, 1 H, CH_{triaz}), 4.30 (t, *J* = 7.23 Hz, 2 H, CH_2NN), 3.93 (t, *J* = 7.09 Hz, 2 H, CH_2NCHN), 2.56–2.63 (m, 2 H, CH_2C_{triaz}), 1.81–1.91 (m, 2 H, $CH_3CH_2CH_2$), 1.74–1.78 (m, 2 H, $CH_2CH_2C_{triaz}$), 1.60–1.70 (m, 2 H, CH_3CH_2), 1.28–1.38 (m, 12 H, 6 × CH_2), 0.94 (t, *J* = 7.35 Hz, 3 H, CH_3CH_2).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 148.2 (C_{triaz}), 133.3 (NCHN), 129.4 (CH_{triaz}), 127.5 ($CH_2NCHCHN$), 120.3 ($CH_2NCHCHN$), 49.8 (CH_2NN), 47.2 (CH_2NCHN), 32.3 ($CH_2CH_2CH_2C_{triaz}$), 31.0 ($CH_3CH_2CH_2$), 29.4 (alkyl-CH_2), 29.2 (alkyl-CH_2), 29.1 (alkyl-CH_2), 29.1 (alkyl-CH_2), 28.9 ($CH_2CH_2CH_2NCHN$), 26.4 ($CH_2CH_2C_{triaz}$), 25.6 (CH_2C_{triaz}), 19.7 (CH_3CH_2), 13.4 (CH_3CH_2).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{31}N_5$: 318.2658; found: 318.2607.

Synthesis of 1,2,3-Triazolium and Imidazolium Salts 4, 7, 11, and 14; General Procedure (Method B)

A solution of the 1,2,3-triazole **3a**, **3b**, **6**, **10a**, **10b**, **10c**, or imidazole **13** (20 mmol) and MeI (5 equiv for **3a** and **3b** and 10 equiv for the other 1,2,3-triazoles and imidazoles) in anhydrous MeCN (30 mL) was heated at reflux for 12 h. All volatile compounds were removed under vacuum with a rotary evaporator to give iodides **4a**, **4b**, **7**, **11a**, **11b**, **11c**, and **14** as solids or clear sticky oils, which were then washed with Et_2O (3 × 50 mL) to afford the pure product after removing traces of solvents under vacuum.

3,5-Dimesityl-1-methyl-3*H*-1,2,3-triazol-1-ium Iodide (4b)

Yield: 97%; white solid; mp 185 °C.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.30 (s, 1 H, CH_{triaz}), 6.99–7.01 (m, 4 H, CH_{Ar}), 4.21 (s, 3 H, CH_3N), 2.31–2.33 (m, 6 H, *o*-CH_3ArN_{triaz}), 2.12 (m, 12 H, *o*,*p*-CH_3ArC_{triaz} + *p*-CH_3ArN_{triaz}).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 142.5 (C_{triaz}), 137.8 (C_{Ar}), 134.0 (C_{Ar}), 132.4 (C_{Ar}), 131.0 (C_{Ar}), 129.8 (CH_{Ar}), 129.3 (CH_{Ar}), 116.9 (CH_{triaz}), 39.4 (CH_3N), 21.2 (*p*-CH_3ArC_{triaz} + *p*-CH_3ArN_{triaz}), 20.6 (*o*-CH_3ArC_{triaz}), 17.8 (*o*-CH_3ArN_{triaz}).

Anal. Calcd for $C_{21}H_{26}IN_3$: C, 56.38; H, 5.86; I, 28.37; N, 9.39. Found: C, 56.33; H, 5.79; I, 28.79; N, 9.41.

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{21}H_{26}N_3^+$: 320.2127; found: 320.2099.

1,1′-(Propane-1,3-diyl)bis(4-butyl-2-methyl-1*H*-1,2,3-triazol-2-ium) Diiodide (7)

Yield: 96%; yellow solid; mp 131 °C.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.31 (s, 2 H, 2 × CH_{triaz}), 4.27 (t, *J* = 6.23 Hz, 4 H, 2 × CH_2N), 4.21 (s, 6 H, 2 × CH_3N), 2.74–2.79 (m, 6 H, NCH_2CH_2 and 2 × CH_2C_{triaz}), 1.62–1.72 (m, 4 H, 2 × $CH_3CH_2CH_2$), 1.31–1.43 (m, 4 H, 2 × CH_3CH_2), 0.86 (t, *J* = 7.29 Hz, 6 H, 2 × CH_3CH_2).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 144.9 (C_{triaz}), 129.4 (2 × CH_{triaz}), 49.7 (2 × NCH_2), 39.0 (2 × CH_3N), 28.4 (2 × $CH_3CH_2CH_2$), 28.3 (2 × CH_2C_{triaz}), 23.6 (2 × CH_3CH_2), 22.0 (NCH_2CH_2), 13.4 (2 × CH_3CH_2).

Anal. Calcd for $C_{17}H_{32}I_2N_6$: C, 35.55; H, 5.62; I, 44.20; N, 14.63. Found: C, 35.37; H, 5.61; I, 44.66; N, 14.41.

HRMS (ESI): *m*/*z* [M]$^{2+}$ calcd for $C_{17}H_{32}N_6^{2+}$: 160.1344; found: 160.1300.

3-Benzyl-1-methyl-5-[3-(3-methyl-1*H*-imidazol-3-ium-1-yl)propyl]-3*H*-1,2,3-triazol-1-ium Diiodide (11a)

Yield: 94%; brownish yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.45 (s, 1 H, NCHN), 8.97 (s, 1 H, CH_2NCHCH), 7.87 (s, 1 H, CH_2NCHCH), 7.30–7.45 (m, 6 H, CH_{Ar} + CH_{triaz}), 5.66 (s, 2 H, $PhCH_2$), 4.52 (t, *J* = 7.34 Hz, 2 H, CH_2NCHN), 4.27 (s, 3 H, CH_3NN), 3.88 (s, 3 H, CH_3NCHN), 3.12 (t, *J* = 7.51 Hz, 2 H, CH_2CN), 2.44 (m, 2 H, $CH_2CH_2CH_2$).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 143.2 (C_{triaz}), 136.4 (NCHN), 130.9 (C_{Ar}), 129.9 (CH_{Ar}), 129.4 (CH_{Ar}), 129.2 (CH_{Ar}), 128.7 (CH_{triaz}), 128.1 (CH_2NCHCH), 123.2 (CH_2NCHCH), 57.4 ($PhCH_2$), 48.2 (CH_2NCHN), 39.1 (CH_3NCHN), 36.6 (CH_3NN), 27.7 (CH_2CN), 20.7 ($CH_2CH_2CH_2$).

HRMS (ESI): *m*/*z* [M]$^{2+}$ calcd for $C_{17}H_{23}N_5^{2+}$: 148.5971; found: 148.5971.

3-Butyl-1-methyl-5-[(3-Methyl-1*H*-imidazol-3-ium-1-yl)methyl]-3*H*-1,2,3-triazol-1-ium Diiodide (11b)

Yield: 82%; brownish yellow oil.

^{1}H NMR (CD_3OD, 300 MHz): δ = 9.11 (s, 1 H, NCHN), 8.29 (s, 1 H, CH_2NCHCH), 7.70 (s, 1 H, CH_2NCHCH), 7.62 (s, 1 H, CH_{triaz}), 4.46 (m, 2 H, CH_2NN), 4.03 (m, 2 H, CH_2NCHN), 3.96–4.00 (m, 6 H, CH_3NCHN + CH_3NN), 1.89–1.94 (m, 2 H, $CH_3CH_2CH_2$), 1.32–1.37 (m, 2 H, CH_3CH_2), 0.97 (t, *J* = 7.36 Hz, 3 H, CH_3CH_2).

^{13}C NMR (CD_3OD, 75 MHz): δ = 141.5 (C_{triaz}), 138.1 (NCHN), 132.3 (CH_2NCHCH), 125.2 (CH_2NCHCH), 123.7 (CH_{triaz}), 50.0 (CH_2NN), 43.9 (CH_2NCHN), 38.7 (CH_3NCHN), 35.5 (CH_3NN), 31.8 ($CH_3CH_2CH_2$), 19.2 (CH_3CH_2), 12.4 (CH_3CH_2).

HRMS (ESI): *m*/*z* [M]$^{2+}$ calcd for $C_{12}H_{21}N_5^{2+}$: 117.5893; found: 117.5892.

3-Butyl-1-methyl-5-[9-(3-methyl-1*H*-imidazol-3-ium-1-yl)nonyl]-3*H*-1,2,3-triazol-1-ium Iodide (11c)

Yield: 98%; yellow oil.

^{1}H NMR (CD_3OD, 300 MHz): δ = 9.08 (s, 1 H, NCHN), 8.70 (s, 1 H, $CH_2NCHCHN$), 7.71 (s, 1 H, $CH_2NCHCHN$), 7.61 (s, 1 H, CH_{triaz}), 4.63 (t, *J* = 7.26 Hz, 2 H, CH_2NN), 4.28 (t, *J* = 7.23 Hz, 2 H, CH_2NCHN), 4.27 (s, 3 H, CH_3NN), 3.98 (s, 3 H, CH_3NCH), 2.93 (t, *J* = 7.82 Hz, 2 H, CH_2C_{triaz}), 2.00–2.05 (m, 2 H, $CH_3CH_2CH_2$), 1.94 (m, 2 H, $CH_2CH_2C_{triaz}$), 1.82 (m, 2 H, CH_3CH_2), 1.38–1.48 (m, 12 H, 6 × alkyl-CH_2), 1.01 (t, *J* = 7.37 Hz, 3 H, CH_3CH_2).

^{13}C NMR (CD_3OD, 75 MHz): δ = 144.8 (C_{triaz}), 136.4 (NCHN), 128.0 (CH_{triaz}), 123.5 ($CH_2NCHCHN$), 122.3 ($CH_2NCHCHN$), 53.3 (CH_2NN), 49.5 (CH_2NCHN), 37.0 (CH_3NCH), 35.5 (CH_3NN), 30.9 ($CH_2CH_2CH_2C_{triaz}$), 29.7 ($CH_3CH_2CH_2$), 28.7 (alkyl-CH_2), 28.6 (alkyl-CH_2), 28.6 (alkyl-CH_2), 28.5 (alkyl-CH_2), 26.4 ($CH_2CH_2CH_2NCHN$), 25.7 ($CH_2CH_2C_{triaz}$), 23.0 (CH_2C_{triaz}), 19.0 (CH_3CH_2), 12.4 (CH_3CH_2).

HRMS (ESI): *m*/*z* [M]$^{2+}$ calcd for $C_{20}H_{37}N_5^{2+}$: 173.6519; found: 173.6518.

1,1′-(Propane-1,3-diyl)bis(3-methyl-1*H*-imidazol-3-ium) Diiodide (14)

Yield: 89%; yellow solid; mp 137 °C.

^{1}H NMR (CD_3CN, 300 MHz): δ = 9.12 (s, 2 H, 2 × NCHN), 7.65 (m, 2 H, 2 × CH_2NCHCH), 7.43 (m, 2 H, 2 × CH_2NCHCH), 4.36 (t, *J* = 7.18 Hz, 4 H, 2 × CH_2N), 3.88 (s, 6 H, 2 × CH_3N), 2.46–2.55 (m, 2 H, $CH_2CH_2CH_2$).

^{13}C NMR (CD_3CN, 75 MHz): δ = 137.3 (2 × NCHN), 124.4 (2 × CH_2NCHCH), 123.1 (2 × CH_2NCHCH), 46.8 (2 × CH_2N), 37.0 (2 × CH_3N), 30.8 ($CH_2CH_2CH_2$).

Anal. Calcd for $C_{11}H_{18}I_2N_4$: C, 28.72; H, 3.94; I, 55.16; N, 12.18. Found: C, 28.71; H, 3.89; I, 55.32; N, 11.90.

HRMS (ESI): *m*/*z* [M]$^{2+}$ calcd for $C_{11}H_{18}N_4^{2+}$: 103.076; found: 103.0758.

Synthesis of 1,2,3-Triazolium Salts and Imidazolium Salts 8, 12, and 15; General Procedure (Method C)

A solution of $AgBF_4$ (10 mmol) in anhydrous MeOH (30 mL) was added portion-wise to a stirred solution of triazolium salts **7**, **11a**, **11b** or imidazolium salt **14** (10 mmol) in MeOH (30 mL) until no more precipitate of AgI was formed. The supernatant was decanted, evaporated and washed with Et_2O (2 × 10 mL) to afford pure products **8**, **12a**, **12b**, and **15** after removing traces of solvents under vacuum.

1,1′-(Propane-1,3-diyl)bis(4-butyl-2-methyl-1*H*-1,2,3-triazol-2-ium) Ditetrafluoroborate (8)
Yield: 92%; colourless solid; mp 72 °C.

^{1}H NMR (CD_3OD, 300 MHz): δ = 8.43 (s, 2 H, 2 × CH_{triaz}), 4.69 (t, *J* = 6.88 Hz, 4 H, 2 × CH_2N), 4.21 (s, 6 H, 2 × CH_3N), 2.85 (t, *J* = 7.30 Hz, 4 H, 2 × CH_2C_{triaz}), 2.66–2.75 (pent, *J* = 6.92 Hz, 2 H, NCH_2CH_2), 1.70–1.80 (m, 4 H, 2 × $CH_3CH_2CH_2$), 1.49 (sext, *J* = 7.31 Hz, 4 H, 2 × CH_3CH_2), 0.99 (t, *J* = 7.33 Hz, 6 H, 2 × CH_3CH_2).

^{13}C NMR (CD_3OD, 75 MHz): δ = 146.5 (C_{triaz}), 129.3 (2 × CH_{triaz}), 50.9 (2 × NCH_2), 37.8 (2 × CH_3N), 29.5 (2 × $CH_3CH_2CH_2$), 29.4 (2 × CH_2C_{triaz}), 23.7 (2 × CH_3CH_2), 23.0 (NCH_2CH_2), 13.8 (2 × CH_3CH_2).

HRMS (ESI): *m*/*z* $[M]^{2+}$ calcd for $C_{17}H_{32}N_6^{2+}$: 160.1344; found: 160.1300.

3-Benzyl-1-methyl-5-[3-(3-methyl-1*H*-imidazol-3-ium-1-yl)propyl]-3*H*-1,2,3-triazol-1-ium Ditetrafluoroborate (12a)
Yield: 92%; yellow oil.

^{1}H NMR (CD_3OD, 300 MHz): δ = 8.80 (s, 1 H, NCHN), 8.53 (s, 1 H, CH_2NCHCH), 7.62 (s, 1 H, CH_2NCHCH), 7.41–7.53 (m, 6 H, CH_{Ar} + CH_{triaz}), 5.76 (s, 2 H, $PhCH_2$), 4.34 (t, *J* = 7.24 Hz, 2 H, CH_2NCHN), 4.20 (s, 3 H, CH_3NN), 3.90 (s, 3 H, CH_3NCHN), 2.94 (m, 2 H, CH_2CN), 2.28–2.38 (m, 2 H, $CH_2CH_2CH_2$).

^{13}C NMR (CD_3OD, 75 MHz): δ = 143.5 (C_{triaz}), 136.7 (NCHN), 130.2 (C_{Ar}), 129.2 (CH_{Ar}), 128.9 (CH_{Ar}), 128.8 (CH_{Ar}), 127.8 (CH_{triaz}), 123.6 (CH_2NCHCH), 122.1 (CH_2NCHCH), 56.7 ($PhCH_2$), 48.0 (CH_2NCHN), 36.6 (CH_3NCHN), 35.1 (CH_3NN), 26.6 (CH_2CN), 19.5 ($CH_2CH_2CH_2$).

HRMS (ESI): *m*/*z* $[M]^{2+}$ calcd for $C_{17}H_{23}N_5^{2+}$: 148.5971; found: 148.5971.

3-Butyl-1-methyl-5-[(3-methyl-1*H*-imidazol-3-ium-1-yl)methyl]-3*H*-1,2,3-triazol-1-ium Ditetrafluoroborate (12b)
Yield: 85%; light-yellow oil.

^{1}H NMR (CD_3OD, 300 MHz): δ = 8.81 (s, 1 H, NCHN), 8.35 (s, 1 H, CH_2NCHCH), 7.59 (s, 1 H, CH_2NCHCH), 7.52 (s, 1 H, CH_{triaz}), 4.46 (t, *J* = 7.17 Hz, 2 H, CH_2NN), 3.92 (m, 2 H, CH_2NCHN), 3.87 (s, 3 H, CH_3N^+-CHN), 3.36 (s, 3 H, CH_3N^+-N), 1.86–1.94 (m, 2 H, $CH_3CH_2CH_2$), 1.28–1.36 (m, 2 H, CH_3CH_2), 0.92 (t, *J* = 6.69 Hz, 3 H, CH_3CH_2).

^{13}C NMR (CD_3OD, 75 MHz): δ = 137.8 (C_{triaz}), 136.8 (NCHN), 129.9 (CH_2NCHCH), 123.9 (CH_2NCHCH), 122.0 (CH_{triaz}), 50.8 (CH_2NN), 43.6 (CH_2NCHN), 37.3 (CH_3N^+-CHN), 35.2 (CH_3N^+-N), 31.4 ($CH_3CH_2CH_2$), 19.1 (CH_3CH_2), 12.3 (CH_3CH_2).

HRMS (ESI): *m*/*z* $[M]^{2+}$ calcd for $C_{12}H_{21}N_5^{2+}$: 117.5893; found: 117.5892.

1,1′-(Propane-1,3-diyl)bis(3-methyl-1*H*-imidazol-3-ium) Ditetrafluoroborate (15)
Yield: 85%; colourless oil.

^{1}H NMR (CD_3OD, 300 MHz): δ = 8.75 (s, 2 H, 2 × NCHN), 7.58 (m, 2 H, 2 × CH_2NCHCH), 7.51 (m, 2 H, 2 × CH_2NCHCH), 4.29 (m, 4 H, 2 × CH_2N), 3.90 (s, 6 H, 2 × CH_3N), 2.44–2.53 (m, 2 H, $CH_2CH_2CH_2$).

^{13}C NMR (CD_3OD, 75 MHz): δ = 137.9 (2 × NCHN), 124.9 (2 × CH_2NCHCH), 123.3 (2 × CH_2NCHCH), 47.2 (2 × CH_2N), 36.3 (2 × CH_3N), 31.1 ($CH_2CH_2CH_2$).

HRMS (ESI): *m*/*z* $[M]^{2+}$ calcd for $C_{11}H_{18}N_4^{2+}$: 103.076; found: 103.0758.

Suzuki Cross-Coupling Reaction; General Procedure[25]
Under an argon atmosphere, 1,4-dioxane (3 mL), aryl chloride, iodide, bromide, triflate or tosylate **17** (1.0 mmol), and arylboronic acid **16** (1.5 mmol) were added in turn to a Schlenk tube charged with $Pd_2(dba)_3$ (14 mg, 0.015 mmol), the NHC precursor (0.03 mmol), Cs_2CO_3 (652 mg, 2.00 mmol) and a magnetic stirring bar. The Schlenk tube was placed in an 80 °C oil bath and the reaction mixture was stirred for 1.5–2.0 h. The mixture was then allowed to cool to r.t. and the mixture was purified either by flash chromatography, or filtered through a pad of Celite, concentrated and then purified by flash chromatography. The structure of the coupling product **18** was confirmed by comparison of the NMR data to those reported in the literature.[25]

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