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Alkynyl-Functionalized Imidazolium for "Click" Dendrimer Functionalisation and Palladium Nanoparticle Stabilization

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Functionalization of imidazolium salts (IMSs) that allow easy derivation of molecular or solid supports are called for in various applications. Here, the synthesis of an alkyne-containing IMS can be achieved in three steps from 2,4,6-trimethylaniline, and this IMS can be further successfully functionalized by using either Sonogashira or a "click" CuAAC reaction that was applied to dendritic IMS synthesis giving high yields. Applications are illustrated for Pd nanoparticle stabilization by the IMS dendrimer for Suzuki–Miyaura catalysis.

Introduction

Imidazolium salts (IMSs) derived from imidazole through alkylation of both nitrogen atoms, leading to ion pairs, are widely used in chemical and biological fields, for instance as anticancer and antimicrobial drugs.[1] They are also well known for their ionic-liquid properties and are used as electrolytes or green solvents because of their low vapor pressure and high chemical stability.[2] Another key property is their deprotonation to *N*-heterocyclic carbenes (NHCs) such as **1** or bis(imidazolidines), which have many applications in organic synthesis.[3] NHCs have been widely used as strong σ donor ligands in metal complexes such as Ru metathesis catalysts,[4,5] for which functionalizable versions are useful for recycling purposes. Thus the synthesis of various NHCs is of interest, especially NHCs that are modified with "clickable" termini for easy functionalization of materials. Along this line, we targeted the synthesis of the new IMS **2** containing an alkyne terminus that is, for example, easily "clickable" by using a copper(I) alkyne-azide cycloaddition (CuAAC) reaction[6] or can participate in Sonogashira C–C cross coupling.[7] Molecular compounds and nanomaterials with azido termini, easily accessible from halogeno derivatives, are most often readily available. Consequently dendrimers, polymers, and nanoparticles (silica, iron oxide) terminated by azido groups are currently functionalized by using the CuAAC reaction (Figure 1).

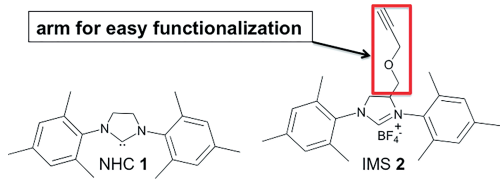

Figure 1. NHC **1** used in Ru metathesis catalysts and the targeted IMS **2**.

Dendrimers[8] that correspond to molecular micelles[9] occupy a privileged place among branched macromolecules because they are multifaceted monodisperse macromolecules, and their supramolecular properties have potential applications in medicinal chemistry[10] and nanoscience. In this latter area, they are often used as sensors,[11] green catalysts[12] or stabilizers of nanoparticles (NP).[13] We[11b,11c,14] and others[15] have explored the useful functionalization of azido-terminated dendrimers for various syntheses and applications including stabilization of PdNPs for catalysis,[16] and this method has now been applied here to functionalize dendrimers with IMS termini.

Results and Discussion

Synthesis of the Propargyl IMS 2

The synthesis of **2** was successfully achieved in only three steps from commercial products with an over yield of 35% (Scheme 1).

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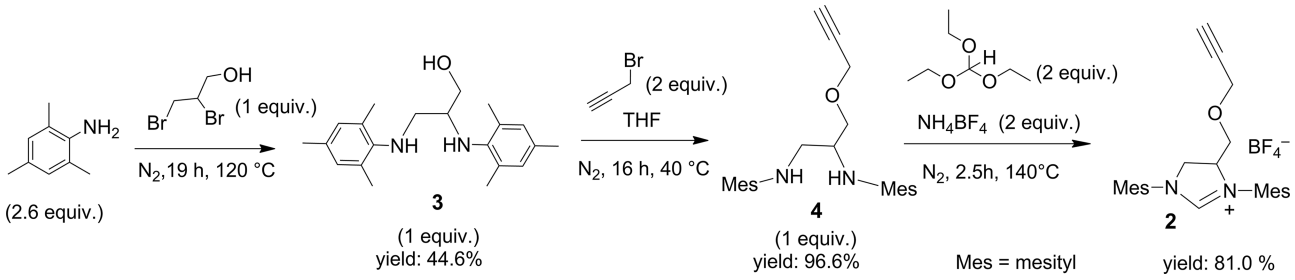

Scheme 1. Synthesis of the alkyne-containing imidazolium **2**.

This rather modest yield is related to the known first step involving the reaction on a relatively large scale between 2,4,6-trimethylaniline and 2,3-dibromopropanol over 19 hours at 120 °C under nitrogen to form 2,3-bis(mesitylamino)-1-propanol (**3**) in only 44.6% yield.[17] The hydroxy group of **3** is then functionalized upon reaction with propargyl bromide in THF (16 h at 40 °C) in order to introduce the alkyne terminal group in the IMS, leading to the desired 2,3-bis(mesitylamino)-1-propoxypropargyl (**4**) in 96.6% yield. The appearance of two new signals at δ = 2.41 ppm (triplet) and at δ = 4.10 ppm (dd) in the ^{1}H NMR spectrum of the final product shows the success of the reaction and the presence of the alkyne moiety (Figure 2).

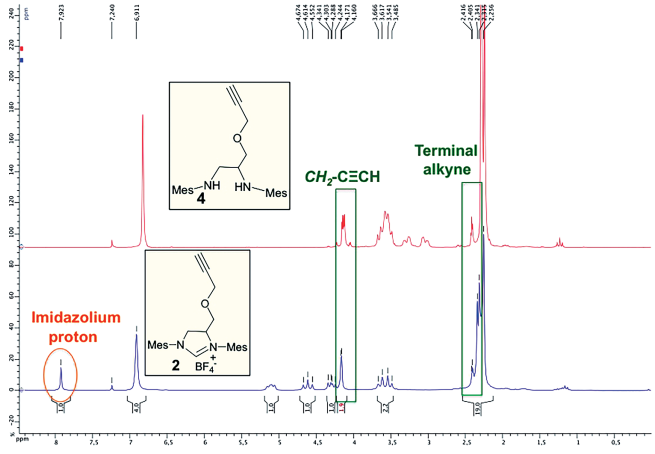

Figure 2. ^{1}H NMR spectra of **4** (up) and **2** (down).

The infrared spectrum reveals the presence of the alkyne with the absorption bands at $\nu_{C\equiv C}$ = 2113 cm^{-1} and $\nu_{C\equiv C}$ = 3268 cm^{-1} (Figure 3). The last step of the synthesis of the propargyl IMS **2** involves the reaction of **4** with triethyl orthoformate and $NaBF_4$ at 140 °C for 2.5 h yielding **2** in 81.0% yield (Scheme 1). Compound **2** was obtained as a brown solid and fully characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and infrared spectroscopy. The ^{1}H NMR spectrum of **2** indicates the presence of a new deshielded proton at δ = 7.92 ppm (Figure 2). This new signal corresponds to the imidazolium proton localized between the two nitrogen atoms. The signals of the protons of the mesityl and the terminal alkyne remain unchanged. Moreover, the infrared spectra of **4** and **2** are a little bit different. The appearance of two new intense peaks at 1631 cm^{-1} and 1059 cm^{-1} in the infrared spectrum of **2** are characteristic of C=N and BF_4^- groups, respectively (Figure 3).

After obtaining **2**, two different reactions were tested: the Sonogashira C–C cross coupling and the CuAAC "click" reaction. The Sonogashira reaction between **2** and iodobenzene was carried out in THF in the presence of DIPA as a base, and $[PdCl_2(PPH_3)_2]$ (8 mol.-%) and CuI (8 mol.-%) as cocatalysts at 40 °C for 1 day. The final product **5** was purified by precipitation from ether and recovered in only 71% yield, mainly due to the formation of side products (Scheme 2). Compound **2** also reacts with benzyl azide in THF in the presence of CuBr (60 mol.-%) as a catalyst at 40 °C over two days. The desired product **6** was recovered after precipitation from ether in 90.5% yield (Scheme 2). Since the CuAAC reaction leads to a better yield than the Sonogashira reaction and is more convenient, the "click" reaction was selected to functionalize the dendritic core.

The "click" reaction between **2** and the nona-azido core **7** was performed in THF at 45 °C (Scheme 3). An amount of 60% CuBr per branch is necessary to complete the "click" reaction between **2** and **7**, probably because of more or less stoichiometric coordination of the copper ions of the catalyst by the 1,2,3-triazole ligand and trapping inside the dendrimer. This inhibition effect has already been noted in "click" dendrimer construction when the CuAAC "click" reaction is conducted in the presence of a simple copper salt as a catalyst rather than a copper(I) catalyst[11b] containing a polydentate nitrogen ligand.[14,18] The end of the reaction was determined by infrared spectroscopy, the disappearance of the ν_{N3} band at 2097 cm^{-1} being observed after two days.

The imidazolium dendrimer **8** was obtained as a brown shiny powder in 85% yield, which indicates the easy use and high reactivity of **2** in CuAAC catalysis. The dendrimer **8** was characterized by ^{1}H and ^{13}C NMR and infrared spectroscopy and by mass spectrometry. The mass spectrum is difficult to analyse, as usual, when there are many counter anions (nine counter anions in this case). The weight M_w of **8** is 5685 + 23 (Na), and peaks around this molecular weight are observed in this area, especially the peak at m/z = 5710, which is close to the actual molecular weight. Surprisingly, **8** is neither soluble in water nor in alcoholic

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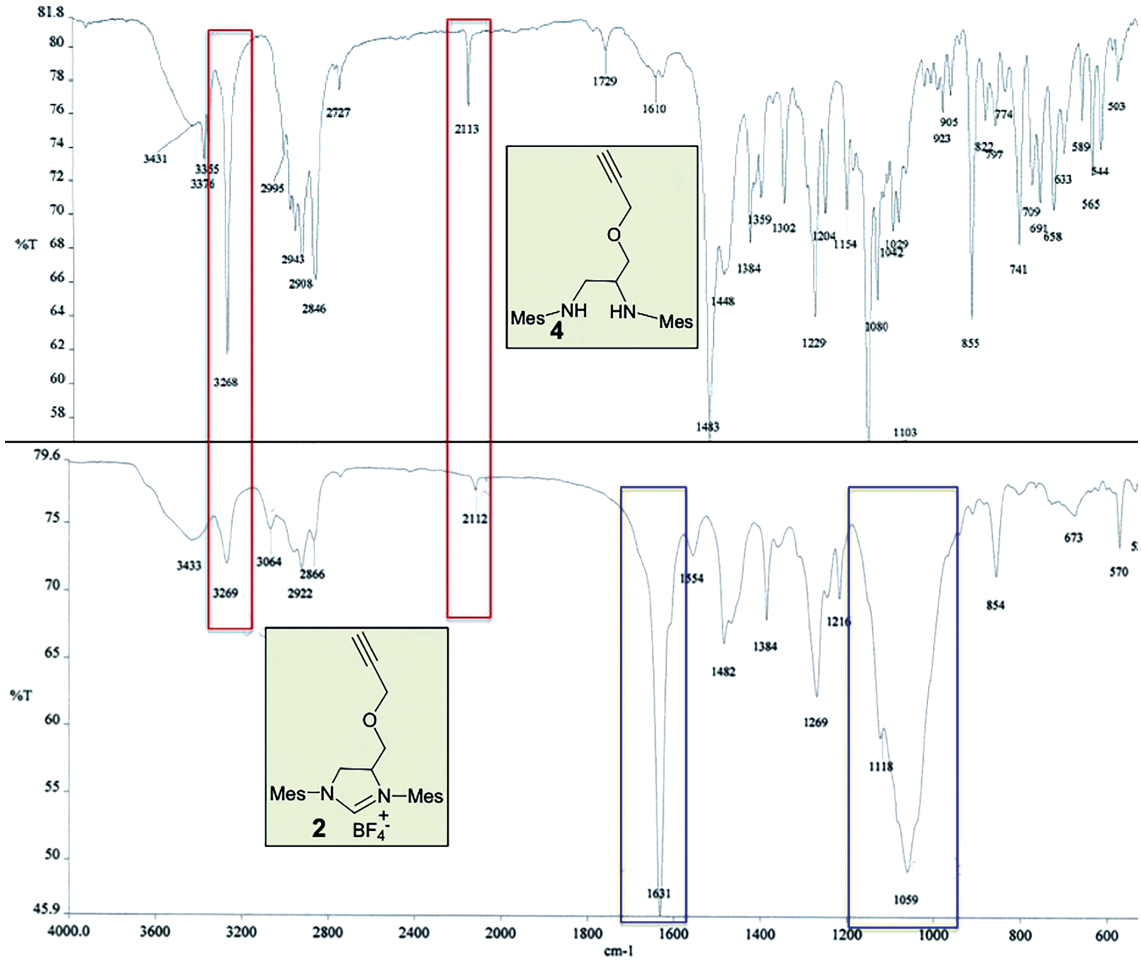
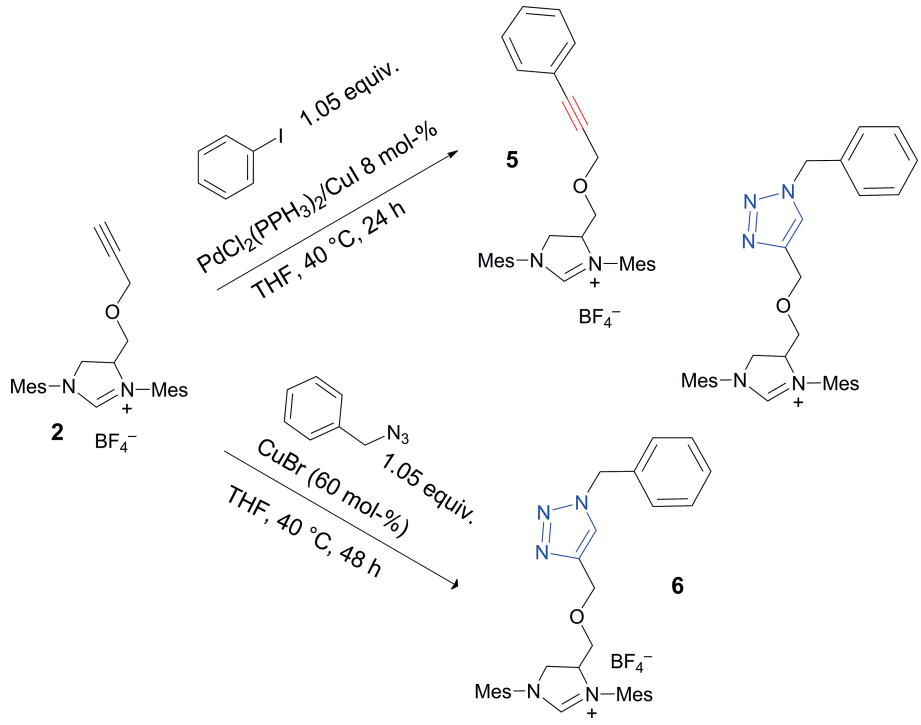


Figure 3. Infrared spectra of **4** (top) and **2** (bottom).



Scheme 2. IMS **2** involved in both Sonogashira and CuAAC reactions.

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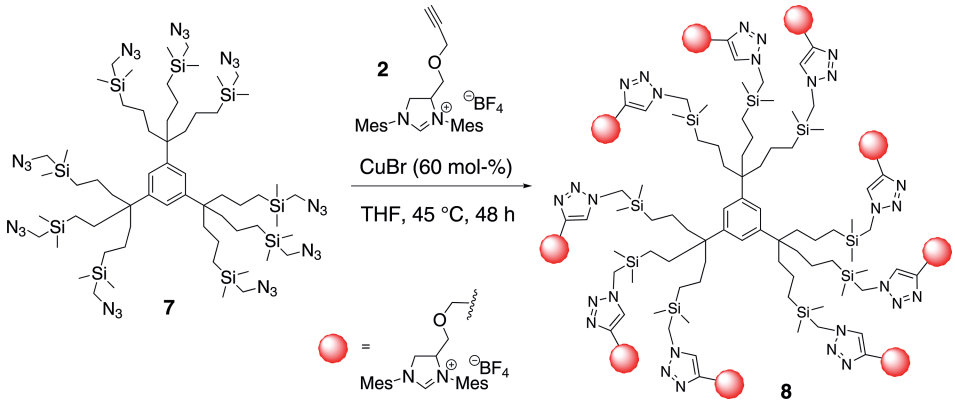


Scheme 3. Synthesis of the imidazolium dendrimer **8** by CuAAC "click" chemistry.

solvents. On the other hand, it is freely soluble in acetonitrile, acetone as well as dimethylformamide.

As an application, the stabilization of palladium nanoparticles (PdNPs) with **8** using its intradendritic triazolyl rings was probed. In previous examples, PdNPs stabilized by dendrimers were synthesized in aqueous solution when the dendrimer is water soluble, and this solution was directly used as a catalytic medium for C–C coupling.[13c] Given the insolubility of **8** in water, the stabilization of PdNPs with **8** was probed, in this case, in acetonitrile for further isolation of the dendrimer-stabilized PdNPs in the solid state. Indeed, an acetonitrile solution of a stoichiometric amount of 9 equiv. of $[Pd(OAc)_2]$ per dendrimer was added to the acetonitrile solution of **8**, provoking an instantaneous color change from brown/orange to intense green. Then, reduction of triazole-coordinated Pd^{II} to Pd^0 was carried out by addition of $NaBH_4$ as a solid (6 equiv. per Pd atom) to the **8**/$Pd(OAc)_2$ solution leading to a direct change of color from green to brown/black that is characteristic of PdNPs. This was followed by isolation of the solid after solvent removal. TEM microscopy of the PdNPs revealed a size between 2.0 nm and 6.0 nm (average size: 4 ± 1.2 nm), but another small population with sizes around 16 nm was also observed (Figure 4).

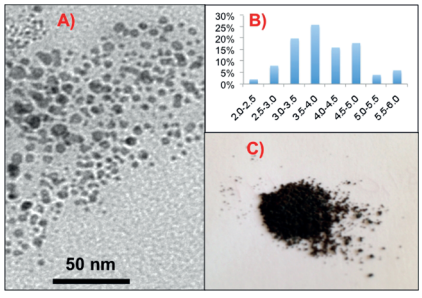
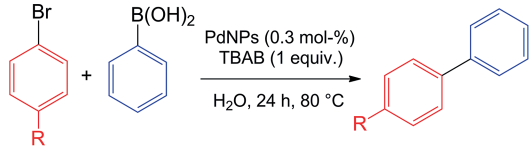


Figure 4. PdNPs stabilized by dendrimer **8** and analyzed by TEM (A), their distribution histogram (B) and isolation at the solid state (C).

The formation of these bigger PdNPs is due to the evaporation of the solvent, leading to nanoscale aggregations. X-ray diffraction (XRD) analysis reveals the presence of Pd^0 in the catalyst, indicating that the excess of $NaBH_4$ probably reduced most of the Pd^{II} species. The new catalyst was tested for the Suzuki–Miyaura C–C cross-coupling reaction that has become one of the most known and powerful Pd^0 reactions allowing the synthesis of biaryl compounds, such as natural products, pharmaceuticals, polymers, etc.[19]

Thus coupling between bromobenzene and phenylboronic acid was carried out in water at 80 °C over 24 h with 0.3 mol.-% of the Pd catalyst. The presence of TBAB as a phase transfer agent is mandatory for total conversion (isolated yield: 94%). The reaction was performed on four others substrates leading to quantitative yields; see Equation (1). The catalyst loses half of its activity after the first run. The mechanism of such homogeneous Suzuki–Miyaura reactions catalyzed by PdNPs usually involves Pd leaching from the PdNP catalyst subsequent to oxidative addition of the aryl halide followed by active catalysis by solvent-coordinated Pd atoms, and no catalyst recycling is efficient without support.[13c–13e,16c]



R = H (94%), NO_2 (98%), $COCH_3$ (100%), CHO (96%), OCH_3 (91%) (1)

Conclusion and Outlook

The successful synthesis of a new alkyne-containing IMS **2** has been achieved, and this IMS could be easily functionalized using both the Sonogashira and the "click" CuAAC reactions. Easy functionalization by the CuAAC reaction has been conducted with a nona-branched dendritic core **7** in high yield, showing that the functional IMS allows easy derivatization of supports. This dendrimer **8** is potentially usable as a ionic liquid and, moreover, **2**, **5**, **6** or **8** should be sources of carbenic species for metal coordination when they are in the presence of a base such as *t*BuOK or

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KHMDS.[20] Finally, the IMS **2** has been shown to be a good precursor of catalytically active PdNPs.

Experimental Section

Purification Procedures

Biphenyl: Bromobenzene and phenylboronic acid: simple flash chromatography with petroleum ether as the mobile phase and silica as the stationary phase.

4-Nitrobiphenyl: Reaction between 1,4-bromonitrobenzene and phenylboronic acid: flash chromatography with 95% petroleum ether/5% dichloromethane as mobile phase and silica as stationary phase.

4-Biphenylcarbaldehyde: Reaction between bromobenzaldehyde and phenylboronic acid: flash chromatography with 95% petroleum ether/5% dichloromethane as the mobile phase and silica as the stationary phase.

4-Acetylbiphenyl: Reaction between 4-bromoacetophenone and phenylboronic acid: flash chromatography with 95% petroleum ether / 5% diethyl ether as the mobile phase and silica as the stationary phase.

***N*,*N*′-Dimesityl-2,3-diamino-1-propanol (3):** 2,3-dibromopropanol (10 g, 45.9 mmol, 1 equiv.) and 2,4,6-trimethylaniline (16 g, 118 mmol, 2.6 equiv.) were introduced into a Schlenk tube. The reaction medium was stirred at 120 °C for 20 h. The temperature was then decreased to room temperature and an aqueous solution of NaOH (50 mL of a 15 mol.-% solution) was added. Then CH_2Cl_2 (50 mL) was added, the organic phase was collected, and the aqueous phase was extracted twice with CH_2Cl_2 (2× 50 mL). The organic phases were combined, dried with Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was purified by silica chromatography column with Et_2O/pentane (1:1), and 6.7 g **of 3** was obtained (44.6% yield).

***N*¹,*N*²-Dimesityl-3-(prop-2-yn-1-yloxy)propane-1,2-diamine (4):** Compound **3** (3.1 g, 9.48 mmol, 1 equiv.), propargyl bromide (2.1 mL, 19 mmol, 2 equiv.) and distilled THF (40 mL) were placed in a Schlenk tube and NaH (28.5 mmol, 3 equiv.) was slowly added. The reaction was stirred at 40 °C for 16 h. At the end of the reaction and when the temperature had decreased to room temperature, water (20 mL) was added. The THF solvent was evaporated under reduced pressure, and the water phase was extracted 3 times with CH_2Cl_2 (50 mL). The organic phases were combined, dried with Na_2SO_4, the solvent was evaporated under reduced pressure, and 3.3 g of the desired product **4** was obtained as a brown solid (96.6% yield). ^{1}H NMR (200 MHz. $CDCl_3$): δ = Ar-C*H*$_3$ 2.24–2.37 (m, 18 H), C≡C*H* 2.41 (t, 1 H, ^2J = 2.4 Hz), C*H*$_2$ 3.08 (dd, 1 H, ^2J = 12, ^3J = 5.7 Hz), C*H*$_2$ 3.33 (dd, 1 H, ^2J = 12, ^3J = 5.6 Hz), C*H* + C*H*$_2$ + 2× N*H* 3.5–3.75 (m, 5 H), C*H*$_2$ 4.18 (dd, 1 H, ^2J = 15.7, ^3J = 2.5 Hz), C*H*$_2$ 4.23 (dd, 1 H, ^2J = 15.7, ^3J = 2.5 Hz), *H* aromatic 6.87 (s, 4 H) ppm. ^{13}C NMR (50.33 MHz. $CDCl_3$): δ = 18.52, 19.00, 20.74 (CH_3 Ar), 50.75, 56.68, 58.66, 70.50 (3× CH_2 + 1× CH), 74.91, 79.62 (C ethylenic), 129.45, 129.60, 129.79, 130.09, 131.02, 131.46, 141.75, 143.77 (C Aromatic) ppm.

1,3-Dimesityl-4-[(prop-2-yn-1-yloxy)methyl]-4,5-dihydro-1*H*-imidazol-3-ium Tetrafluoroborate (2): Compound **4** (2.7 g, 7.4 mmol, 1 equiv.), triethyl orthoformate (2.5 mL, 15 mmol, 2 equiv.) and NH_4BF_4 (770 mg, 7.4 mmol, 1 equiv.) were placed in a Schlenk tube. The reaction was stirred at 140 °C for 2.5 h under N_2. At the end of the reaction the temperature was decreased to 50 °C, and the liquid was evaporated under reduced pressure. The resultant brown solid was washed several times with pentane and Et_2O and then was dried under reduced pressure for a few hours, and 2.77 g of **2** was obtained (81% yield). ^{1}H NMR (200 MHz. $CDCl_3$): δ = Ar-C*H*$_3$ 2.24–2.39 (m, 18 H), C≡C*H* 2.43 (m, 1 H), C*H*$_2$ 3.5–3.7 (m, 2 H), C*H*$_2$ 4.19 (d, 2 H), C*H*$_2$ 4.25–4.38 (m, 1 H), C*H*$_2$ 4.63 (m, 1 H), C*H* 5.12 (m, 1 H), *H* aromatic 6.93 (s, 4 H), *H* imidazolium 7.92 (s, 1 H) ppm. ^{13}C NMR (50.33 MHz. $CDCl_3$): δ = 17.70, 18.28, 21.14 (CH_3 Ar), 52.82, 58.62, 63.83, 66.28 (3× CH_2, 1× CH), 76.02, 78.2 (C ethylenic), 128.39, 130.15, 130.35, 130.64, 135.46, 135.59, 136.10, 140.50, 140.76 (C aromatic), 158.53 (C imidazolium) ppm.

4-{[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methoxy]methyl}-1,3-dimesityl-4,5-dihydro-1*H*-imidazol-3-ium Tetrafluoroborate (Test for the CuAAC "Click" Reaction): Benzyl azide (0.75 mmol, 1 equiv.) and **2** (470 mg, 0.78 mmol, 1.05 equiv.) were dissolved in distilled THF (5 mL) in a Schlenk tube, CuBr (48 mg, 60 mol.-%) was added, and the reaction was maintained at 40 °C for 36 h. At the end of the reaction, water (20 mL) and ammonia solution (1 mL, 37%) were added, and the medium was stirred for 10 min. The aqueous phase was extracted 3 times with CH_2Cl_2 (20 mL). The organic phases were combined and washed 3 times with water (20 mL) dried with Na_2SO_4, the solvent was evaporated, and 230 mg of the desired "click" product was obtained (90.5% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ = Ar-C*H*$_3$ 2.18–2.32 (m, 18 H), C*H*$_2$ 3.52 (d, 1 H), C*H*$_2$ 3.73 (dd, 1 H, ^2J = 11.4, ^3J = 2 Hz), C*H*$_2$ 4.34 (dd, 1 H, ^2J = 12 Hz ^3J = 7.3 Hz), C*H*$_2$ 4.46–4.66 (m, 3 H), C*H* 5.04 (m, 1 H), C*H*$_2$-triazole 5.48 (s, 2 H), *H* benzyl 6.7–7 (m, 5 H), *H* aromatic 7.32 (s, 4 H); *H*-triazole 7.71 (s,1 H), *H* imidazolium 7.85 (s, 1 H) ppm. ^{13}C NMR (50.33 MHz, $CDCl_3$): δ = 17.62, 18.40, 21.21 (CH_3 Ar), 52.93, 54.35, 64.25, 66.49 (3× CH_2, 1× CH), 123.95, 128.38, 128.60, 128.90, 129.29, 130.19, 130.52, 135.02, 135.43, 136.18, 140.80, 140.93 (C Aromatic + 2 C triazole), 158.01 (C imidazolium) ppm.

Imidazolium Dendrimer 8: The azido-core **7** (100 mg, 0.066 mmol, 1 equiv.) and **2** (305 mg, 0.66 mmol, 1.1 equiv.) were dissolved in distilled THF (5 mL) in a Schlenk flask, CuBr (60 mg, 60 mol.-%) was added, and the reaction was maintained at 40 °C for 48 h. At the end of the reaction, a precipitate on the wall of the Schlenk flask was observed. The product was filtered and washed with THF several times. Acetone or acetonitrile was used to dissolve the product and filtration through Celite was performed. The solvent was evaporated and 320 mg of the desired "click" product was obtained (85% yield). ^{1}H NMR of **8** in CD_3CN (200 MHz, ppm): 8.70 (9 H imidazolium), 8.20 (9 H, trz), 7.07–6.94 (37 H, Ar + 3 H core), 5.24–3.58 (81 H), 2.43–2.23 (162 H, CH_3 mesityl), 1.81–0.68 (54 H, $CH_2CH_2CH_2Si$); 0.05 [54 H, $Si(CH_3)_2$] ppm. ^{13}C NMR of **8** in CD_3CN (50 MHz): 160.45 (CH, imidazolim), 147.94 (Cq trz), 141.65–129.82 (aromatics + CH trz), 67.72–53.82 (3CH_2, CH), 45.02 (*C*H_2CH$_2$CH$_2$Si), 42.54 (Si*C*H_2trz), 21.39–15.83 (CH_3 mesityl + *C*H_2Si + *C*H_2CH$_2$Si) ppm.

Correct elemental analysis could not be obtained because of the insolubility of **8** in weakly polar solvents and the presence of inorganic salts.

Synthesis of the PdNPs: Dendrimer **8** (63.3 mg, n = 0.0111 mmol, M_w = 5685 g mol^{-1}) was dissolved in CH_3CN (3 mL) in a Schlenk tube under nitrogen. $Pd(OAc)_2$ (22.5 mg, 9 equiv.) was then added to the CH_3CN solution. The reaction was stirred for 1 h under nitrogen at 20 °C and $NaBH_4$ (22.6 mg, 54 equiv.) was then added quickly. The reaction medium was stirred for 2 min, and all the solvent was evaporated in vacuo, leading to black PdNPs in the solid state. Correct elemental analysis could not be obtained be-

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cause of the insolubility of the PdNPs in weakly-polar solvents and the presence of inorganic salts.

General Procedure for the Suzuki–Miyaura Coupling: The bromoarene (1 mmol), phenylboronic acid (1.5 mmol), K_3PO_4 (2 mmol), the catalyst (0.3 mol-% i.e. 1.4 mg) and TBAB (1 mmol) were placed in a Schlenk tube together with H_2O (3 mL). The reaction was stirred at 80 °C for 24 h after which the reaction mixture was extracted twice with diethyl ether (Et_2O, all the reactants and final products were soluble in Et_2O), the organic phase was dried with Na_2SO_4, and the solvent was removed under vacuum. In parallel, the reaction was checked by using TLC with petroleum ether as eluent in nearly all the cases, and ^1H NMR spectroscopy. Purification by flash chromatography column was conducted with silica gel as the stationary phase and petroleum ether as the mobile phase. After each reaction, the Schlenk flask was washed with a solution of aqua regia (3 volumes of hydrochloric acid for 1 volume of nitric acid) in order to remove traces of Pd.

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Dendrimer-Stabilized Nanoparticles

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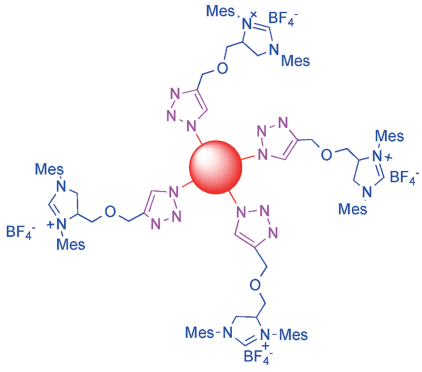
Alkynyl-Functionalized Imidazolium for "Click" Dendrimer Functionalisation and Palladium Nanoparticle Stabilization

Keywords: Dendrimers / Nanostructures / Click chemistry / Homogeneous catalysis / Palladium



An imidazolium salt containing an alkynyl group was synthesized in three steps in order to functionalize nanomaterials by means of CuAAC and Sonogashira reactions. For instance, a nona-azido dendritic core could be "clicked" with the alkynyl-containing imidazolium salt. The resulting dendrimer allows the stabilization of palladium nanoparticles that are active in the Suzuki–Miyaura cross-coupling reaction.

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