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Functionalisable N-Heterocyclic Carbene–Triazole Palladium Complexes and Their Application in the Suzuki–Miyaura Reaction

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Dedicated to Dr. Bernard Meunier on the occasion of his official retirement from the CNRS

Keywords: Homogeneous catalysis / C–C coupling / Palladium / Carbene ligands / Nitrogen heterocycles

Seven functionalised N-heterocyclic carbene (NHC) ligands and their corresponding palladium(II) complexes have been synthesised with a triazole moiety as a modular and stable linkage between the catalytic centre and the secondary functional group. The complexes were prepared in good yields and fully characterised by NMR spectroscopy, mass spectrometry and X-ray crystallography. The complexes are active in the Suzuki–Miyaura cross-coupling reaction, with catalytic activities maintained whatever the triazolyl substituent. This opens the possibility for various functionalisations of NHC–palladium complexes.

Introduction

Palladium-catalysed C–C bond formations have undergone huge developments recently. These developments open the possibility for new synthetic strategies, by allowing retrosynthetic disconnections that were previously not achievable in a single step using conventional organic chemistry methods. These new strategies probably represent one of the most significant steps in the history of transition-metal-assisted reactions as they exhibit high tolerances towards a wide array of functional groups as well as excellent selectivities and efficiencies. Consequently Pd-catalysed C–C bond formations have been applied in numerous fields (organic synthesis, medicinal and materials chemistry, etc.) and they have also proved amenable to enantioselective synthesis, becoming one of the most powerful elements of the synthetic chemist's toolbox. These developments were recognised by the Nobel Prize jointly awarded to Heck, Neigishi and Suzuki in 2010. Among these reactions the Suzuki–Miyaura Reaction (SMR) has found numerous applications and has been recognised for its efficiency, especially providing easy access to unsymmetrical biaryl compounds.[1] Although widely used, the SMR remains an area of intense research efforts beyond activity and selectivity. Indeed mechanistic studies are still under investigation.[2] However, in the current era of sustainability there is a great need to imagine new tools that could allow efficient tethering of the metal complex to various substrates as this would enable the possibility of polyfunctional systems[3] or catalyst recovery.[4] This second approach has been exemplified with a range of supports (homogeneous or heterogeneous), to which ligands such as phosphines can be tethered.[5]

N-Heterocyclic carbenes (NHCs) are a class of appropriate ligands for palladium-catalysed transformations since NHC complexes show good activities and selectivities as well as high thermal, air and moisture stabilities.[6]

Immobilisation of homogeneous NHC-based catalysts on a support or in a phase (from which the reaction product can be easily extracted) combines homogeneous control (single-site molecularly-defined catalyst) and heterogeneous advantages (catalyst recovery and reuse). Towards this goal, a functionality is required on the NHC-ligand structure[7] either for grafting on to the support[8] or for immobilisation in the supporting phase.[9]

Finally, the challenge is to design NHC ligands that both meet the criteria imposed by the recovery approach and confer the required properties for catalytic activity, while retaining robustness (stability of the catalyst) and low cost (easy chemical synthesis of the ligand).

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Following our previous reports on user-friendly partners involved in the Suzuki–Miyaura reaction,[10] we report herein the design and modular synthesis of NHC-based palladium complexes in which the functional group required for catalyst recovery is linked to the catalytic centre by a triazole moiety, as well as a preliminary catalytic screening in the Suzuki–Miyaura cross-coupling reaction. Here again we have demonstrated ease of synthesis and handling to access diversely functionalised complexes and their catalytic efficiency has been investigated under simple and convenient conditions.

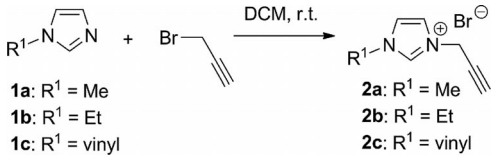
Results and Discussion

The association of two different moieties in a unique molecule requires a highly modular chemical tethering strategy exhibiting a wide tolerance towards a range of functional groups and providing the desired coupling product in high yield and regioselectivity. Among the various possible "click" strategies, the Huisgen coupling between azides and terminal alkynes to give 1,4-disubstituted 1,2,3-triazoles has attracted much attention.[11] Two examples of triazole-based NHC ligands have been reported in the literature[12,13] with the aim to build bidentate ligands, the triazole moiety acting as a potential N-donor ligand rather than as a neutral linkage.

In our case, we were attempting to design bifunctional ligands using the triazole moiety as a chemical linkage between the NHC functionality, required for the catalytic activity, and a second functionality introduced for another purpose (such as bioconjugation or introduction of a coordination site for a second metal). To allow for easy modulation of the ligand structure, a convergent synthesis of the NHC precursors was envisioned by means of the copper(I)-catalysed alkyne–azide cycloaddition of various imidazolium salts bearing terminal alkyne groups with a range of azides. Bellemin-Laponnaz et al. recently reported a similar approach featuring a ruthenium-catalysed cycloaddition directly on to alkyne-substituted Pd^{II} and Pt^{II} complexes.[14]

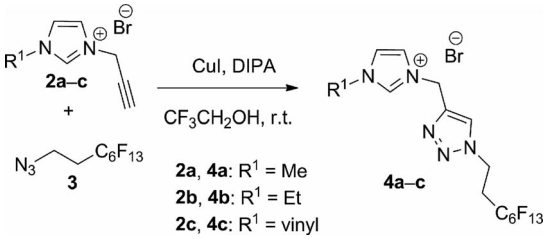
Complex Synthesis

Imidazolium salts 3-methyl-, 3-ethyl- and 3-vinyl-1-(prop-1-ynyl)-1*H*-imidazolium bromides **2a**–**c**, were obtained by direct reaction of 3-bromoprop-1-yne with the corresponding 1-methyl-, 1-ethyl- and or 1-vinylimidazoles **1a**–**c** (Scheme 1).[15]



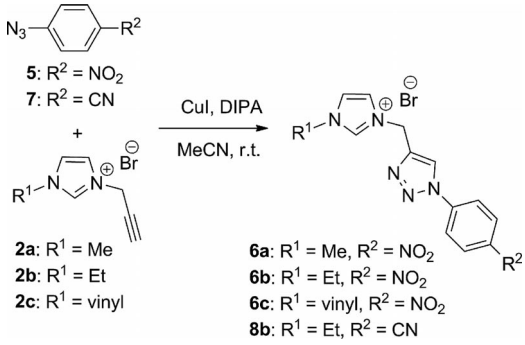
Scheme 1. Synthesis of imidazolium salts **2a**–**c**.

The triazole-based imidazolium salts **4a**–**c**, each bearing one fluorous ponytail, were prepared by the copper-catalysed Huisgen cycloaddition of the corresponding imidazolium salts **2a**–**c** with the fluorous azide **3**[16] in the presence of diisopropylamine (DIPA) in 2,2,2-trifluoroethanol (Scheme 2).[17]



Scheme 2. Synthesis of triazole-based imidazolium salts **4a**–**c**.

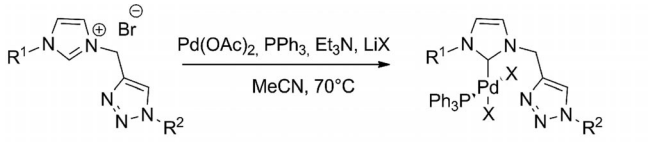
Analogously, the triazole-based imidazolium salts **6a**–**c**, each bearing an aryl–NO_2 moiety, were prepared by the copper-catalysed Huisgen cycloaddition of **2a**–**c** with the arylazide **5** in acetonitrile, whereas the triazole-based imidazolium salt **8b**, bearing an aryl–CN moiety, was prepared by the cycloaddition of **2b** with the arylazide **7** in acetonitrile (Scheme 3). All the triazole-based imidazolium salts **4a**–**c**, **6a**–**c** and **8b** were obtained as solids in good to excellent yields (70–99%). The formation of the triazole was confirmed in the ^1H NMR spectra by both the disappearance of the alkynyl proton (around 3 ppm) and the observation of a singlet assigned to the proton of the 1,2,3-triazole ring at 8.10–8.29 ppm for fluorous-tagged triazoles **4a**–**c** and at 9.13–9.21 ppm for aryl-substituted triazoles **6a**–**c** and **8b**.



Scheme 3. Synthesis of triazole-based imidazolium salts **6a**–**c** and **8b**.

Formation of the palladium complexes was first attempted by a transmetallation methodology,[18] but the synthesis of the required silver–NHC complex led to insoluble products that could never be properly characterised. Moving to a procedure described by Fukuyama,[9b] NHC–palladium complexes **9a**–**c**, **10a**–**c** and **11b** were prepared from the corresponding triazole-based imidazolium salts with $Pd(OAc)_2$ and PPh_3 in the presence of Et_3N and either LiCl or LiBr in acetonitrile. When using 5 mol-equiv. of Et_3N and 10 or 15 mol-equiv. of LiCl in the synthesis of the complexes, mixed chloro/bromo complexes were obtained as expected for **9a**–**b**, **10a**–**c** and **11b**. Surprisingly, **9c** was ob-

tained as the dichloro complex quantitatively. We then moved to the use of LiBr, for which 30 mol-equiv. was required to obtain **9a**–**b**, **10a**–**c** and **11b** as pure dibromo complexes. (Scheme 4). However, the dibromo complexes appeared less easy to handle (apparently highly hygroscopic) than the ones containing chlorides.



4a: R^1 = Me, R^2 = CH_2CH_2-C_6F_{13}
4b: R^1 = Et, R^2 = CH_2CH_2-C_6F_{13}
4c: R^1 = vinyl, R^2 = CH_2CH_2-C_6F_{13}
6a: R^1 = Me, R^2 = 4-NO_2-C_6H_4
6b: R^1 = Et, R^2 = 4-NO_2-C_6H_4
6c: R^1 = vinyl, R^2 = 4-NO_2-C_6H_4
8b: R^1 = Et, R^2 = 4-CN-C_6H_4

9a: R^1 = Me, R^2 = CH_2CH_2-C_6F_{13}, X = Br
9b: R^1 = Et, R^2 = CH_2CH_2-C_6F_{13}, X = Br
9c: R^1 = vinyl, R^2 = CH_2CH_2-C_6F_{13}, X = Cl
10a: R^1 = Me, R^2 = 4-NO_2-C_6H_4, X = Br
10b: R^1 = Et, R^2 = 4-NO_2-C_6H_4, X = Br
10c: R^1 = vinyl, R^2 = 4-NO_2-C_6H_4, X = Br
11b: R^1 = Et, R^2 = 4-CN-C_6H_4, X = Br

Scheme 4. Synthesis of triazole-based NHC–palladium(II) complexes **9a**–**c**, **10a**–**c** and **11b**.

All the palladium(II) complexes were obtained as solids in good to excellent yields (73–99%). The formation of the NHC-based palladium complexes was confirmed by the disappearance of the acidic imidazolium proton at 8.92–9.29 ppm in **4a**–**c** and 9.28–9.69 ppm in **6a**–**c** in the ^{1}H NMR spectra, as well as the appearance of a resonance signal in the range of 155–176.5 ppm in the ^{13}C NMR spectra, ascribed to the carbenic carbon atom. This value is consistent with the values of around 160 ppm reported for mixed NHC and triphenylphosphine palladium(II) complexes.[9b,19] ^{31}P NMR spectroscopy of every complex ($\delta \approx$ 26 ppm) was also in full accordance with the ^{31}P chemical shifts reported for such carbene–phosphine complexes.

Notably, in the ^{1}H NMR spectra the methylene protons located between the imidazolium and the triazole rings of the ligand precursors appeared as singlets whereas an AX splitting pattern ($\Delta\nu$ between 180 and 300 Hz) with a coupling constant around 15 Hz was observed in the spectra of the complexes. Such a splitting pattern has also been observed by Elsevier and co-workers for NHC–triazole complexes and has been identified as evidence of the bidentate nature of the ligand, which prohibits rotation upon complexation.[13] Although from these data it could be suggested that under our reaction conditions a bidentate NHC–triazole complex might also be accessed, we were concerned by two facts: (1) no free triphenylphosphine is detected by ^{31}P NMR ($\delta \approx -5$ ppm); (2) the chemical shift difference between these two protons is larger than that observed by Elsevier and co workers. Indeed the chemical shift values were around 0.5 ppm for complexes **9a**–**c** bearing a perfluorinated chain and around 1.2 ppm for aryl-substituted complexes **10a**–**c** and **11b**. Moreover it must be pointed out that the solvent exhibited a significant effect on $\Delta\nu$, a decrease in its value being observed when switching from chloroform to acetonitrile. Considering this, we hypothesise that the chemical nonequivalence of the two methylene protons might arise from another interaction.

Single crystals of **10b** suitable for X-ray analysis were obtained by slow crystallisation from acetonitrile; the molecular structure of **10b** in the solid state is depicted in Figure 1.

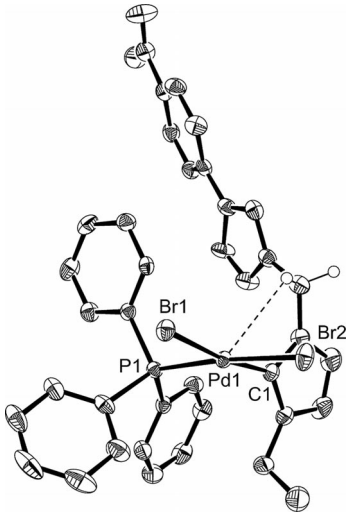


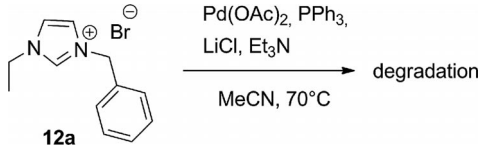
Figure 1. ORTEP plot of **10b** (50% probability; hydrogen atoms, except those on the methylene bridge and solvent molecule, omitted for clarity) showing the C–H···Pd interaction. Selected bond lengths [Å] and angles [°]: Pd(1)–C(1) 1.977(3), Pd(1)–P(1) 2.2656(8), Pd(1)–Br(1) 2.4797(4), Pd(1)–Br(2) 2.4836(4); C(1)–Pd(1)–P(1) 94.27(8), C(1)–Pd(1)–Br(2) 84.04(8), P(1)–Pd(1)–Br(2) 174.42(2), C(1)–Pd(1)–Br(1) 172.30(9), Br(1)–Pd(1)–Br(2) 92.892(13), P(1)–Pd(1)–Br(1) 89.43(2).

The palladium centre is coordinated by an NHC carbon atom, a triphenylphosphine phosphorus atom and two *cis* bromide ions, in a distorted square-planar geometry. The functionalised NHC ligand is thus coordinated to palladium in a monodentate fashion by the carbenic carbon with the imidazolylidene ring perpendicular to the coordination plane. The palladium–carbene distance Pd–C(1) [1.977(3) Å] and the palladium–phosphine distance Pd–P [2.2656(8) Å] are similar to the reported values for *cis* NHC–PPh_3–Pd^{II} complexes (Pd–C 1.97–1.99 Å and Pd–P 2.25–2.27 Å)[19,20] and shorter than those of analogous *trans* NHC–PPh_3–Pd^{II} complexes (Pd–C 2.03 Å and Pd–P 2.31–2.34 Å).[21]

The hypothesised monodentate nature of the NHC ligand is clearly confirmed by the crystallographic structure of **10b**, for which a triazole–palladium interaction is unambiguously excluded [d(N–Pd) = 4.479(3) Å; torsion angle (N1–N2–N3–Pd): 73.91(14)° when 180° would be expected in case of triazole coordination]. However, one can observe from the structure that the complex exhibits an anagostic interaction[22] between one proton of the methylene bridge and palladium [d(H–Pd) = 2.85 Å, angle (C–H–Pd): 112°, $\Delta\nu$ = 480 Hz], as already reported for NHC–palladium complexes.[23] This could explain the NMR splitting pattern observed for the two protons of the methylene bridge. A similar but smaller splitting ($\Delta\nu$ = 240 Hz) is also observed for the methylene protons of the ethyl moiety that also lay close to the metal centre [bond length (H–Pd): 2.98 Å, angle (C–H–Pd): 112°]. Of note, the values of these two splittings depend on both the nature of the NMR solvent used and

the temperature at which the NMR experiment is carried out, as expected for interactions mainly of an electrostatic nature. This splitting is also observed for the methylene protons of the ethyl moiety in complexes **9b** and **11b**.

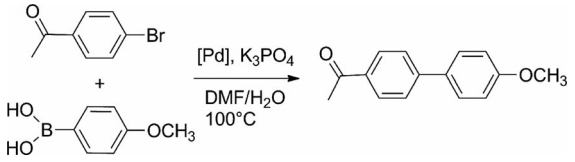
To further study the role of the triazole on the palladium coordination and on the properties of the complex, the synthesis of an analogous complex without the triazole ring was envisioned with 1-ethyl-3-benzyl-imidazolium bromide (**12a**) as the ligand precursor (Scheme 5). Unfortunately, the procedure used for all the triazole-based complexes failed in this case and the transmetallation procedure led to an insoluble product preventing analysis by NMR spectroscopy. This may be indicative of a polymeric structure. This result shows that the triazole ring plays a critical role in obtaining a stable monomeric palladium(II) complex, even if the triazole is not directly involved in the palladium coordination. Indeed, all the triazole-based NHC–palladium(II) complexes **9a**–**c**, **10a**–**c** and **11b** were obtained as air-stable solids despite a low steric bulk on the nitrogen atoms of the imidazolydene.



Scheme 5. Failure in the synthesis of a nontriazole-based NHC–palladium(II) complex from **12a**.

Catalytic Tests

The palladium-catalysed Suzuki–Miyaura cross-coupling reaction (Scheme 6) was chosen as a model reaction to evaluate the catalytic properties of these complexes. Initially, the complexes were tested for activity in the coupling of (4-methoxyphenyl)boronic acid with an easy substrate, 4-bromoacetophenone.



Scheme 6. Suzuki–Miyaura coupling of (4-methoxyphenyl)boronic acid with 4-bromoacetophenone catalysed by triazole-based NHC–palladium(II) complexes.

The results were encouraging with all the catalysts **9a**–**c**, **10a**–**c** and **11b** showing good activities at 100 °C. When using 3 mol-equiv. of K_3PO_4 as a base and DMF/water (4:1) as a solvent (5 mL per mmol of substrate) full conversion of the bromide was obtained in 15 min with 1 mol-% catalyst loading [turnover frequency (TOF) > 400 h^{-1}]. When decreasing the base quantity to 1 mol-equiv., the solvent volume to 1 mL per mmol of substrate and the catalyst loading to 0.05 mol-%, reactions were completed within an hour for all the catalysts (TOF ≈ 2000 h^{-1}).

Although NHC–palladium complexes are well known for their robustness, we explored the heterogeneous or homogeneous nature of the catalytic species. We first noted that, under the conditions of the catalytic tests, the solutions remained yellow and clear with no induction period being observed and no black precipitate appearing in the reaction mixture. Moreover, upon mercury-poisoning experiments,[24] neither the efficiency nor the rates of the reactions were affected (see Supporting Information). These experiments tend to indicate the homogeneous nature of this catalysis and confirm the robustness of these NHC–metal complexes.

To further study the influence of the catalyst's substitution pattern on the reaction course, reactions carried out under the same conditions for all catalysts were stopped at the same time before full conversion and the relative activities of the complexes were evaluated by comparison of the 4-bromoacetophenone conversions, determined by HPLC, in each different assay (Table 1).

Table 1. Relative catalytic activity of the triazole-based NHC–palladium(II) complexes **9a**–**c**, **10a**–**c** and **11b** in the Suzuki–Miyaura coupling of (4-methoxyphenyl)boronic acid with 4-bromoacetophenone.

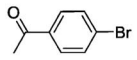
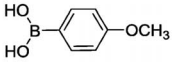
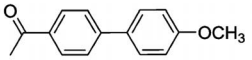
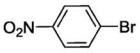
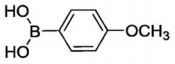
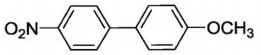
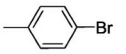
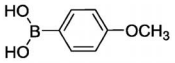
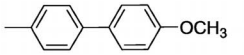
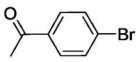
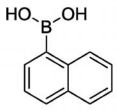
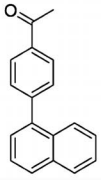
Entry	Catalyst[a]	Conversion[b]
1	**9a**	54%
2	**9b**	87%
3	**9c**	61%
4	**10a**	37%
5	**10b**	68%
6	**10c**	51%
7	**11b**	82%

[a] Reaction conditions: 4-bromoacetophenone 1.0 mmol, (4-methoxyphenyl)boronic acid 1.2 mmol, catalyst loading 0.05 mol-%, K_3PO_4 1.0 mmol, DMF/H_2O (4:1) 1 mL, 100 °C, in air, 15 min. [b] Determined by HPLC percentage area.

Several conclusions can be drawn from these results. Considering the substituent pattern of the NHC ring, the ethyl moiety appeared to be more active than its methyl or vinyl counterparts [**9b** (entry 2) more active than **9a** and **9c** (entries 1 and 3) and **10b** (entry 5) more active than **10a** and **10c** (entries 4 and 6)] and was thus kept for the rest of the study. Comparing the functionalities added by way of the triazole ring to these NHC-based complexes, catalysts **9a**–**c**, each bearing a fluorous ponytail, appeared more active than the corresponding **10a**–**10c** and **11b** catalysts, bearing aryl–NO_2 or –CN moieties (entry 1 vs. entry 4, entry 2 vs. entries 5 and 7, entry 3 vs. entry 6). Finally, the low influence of the structures of the complexes on their catalytic activities indicates that the triazole group is an adequate linkage between the NHC–Pd centre and the functionality required for any other purpose: whatever the triazolyl substituents, all complexes **9a**–**c**, **10a**–**c** and **11b** allowed for significant 4-bromoacetophenone conversion (37 to 87%) within only 15 min and at a 500 ppm catalyst loading.

Furthermore, as depicted in Table 2, complex **9b** has been evaluated in the Suzuki–Miyaura cross-coupling reaction of various substrates to illustrate the versatility of its

Table 2. Catalytic tests with **9b** in the Suzuki–Miyaura cross-coupling reaction of various substrates.

Entry	Aryl bromide	Boronic acid	Product	Catalyst loading	Time [min]	Yield	TON [TOF h^{-1}]
1				50 ppm	210	80%	16000 (4570)
2				500 ppm	150	89%	1780 (710)
3				500 ppm	100	75%	1500 (900)
4				500 ppm	100	96%	1920 (1150)

catalytic activity. It is noteworthy that catalyst loading could be easily decreased to 50 ppm [entry 1 turnover number (TON) 16000, TOF 4570 h^{-1}] while maintaining good activity in the coupling of 4-bromoacetophenone with (4-methoxyphenyl)boronic acid, achieving full conversion within 2 hours at 100 °C (isolated yield 80%). Similar activity was observed for 4-bromonitrobenzene (entry 2, TON 1780, TOF 710 h^{-1}). Switching to an electron-rich aryl bromide did not lower the reaction efficiency as exemplified by the results obtained with 4-bromotoluene (entry 3, TON 1500, TOF 900 h^{-1}). Interestingly, variation in the nature of the boronic acid partner was also well tolerated as naphthalene-1-boronic acid could also be coupled to 4-bromoacetophenone with a catalytic activity in the same range (entry 4, TON 1920, TOF 1150 h^{-1}). Although a partial coupling is also observed for aryl chlorides such as 4-chloroacetophenone and 4-chlorotoluene, with formation of the product being observed after 2 h, the conversion remains incomplete after 20 h at 100 °C with a 1% catalyst loading. Therefore these complexes have not been further considered for this application.

Conclusions

In summary, an easy to perform synthesis of new functionalised N-heterocyclic carbene precursors and their corresponding palladium(II) complexes has been established. This gave access to an array of organometallic complexes, which have been fully characterised. The introduction of a triazole moiety in the vicinity of the coordination sphere of the metal eases the isolation of air- and moisture-stable complexes despite the relatively nonbulky imidazolylidene substituents.

Moreover it has been shown that the triazole does not coordinate the metal. Nevertheless the complexes exhibited interesting structural features such as a Pd–HC anagostic interaction (involving a proton on the methylene bridge) evidenced through a crystallographic study. It must also be pointed out that the introduction of the triazole group did not preclude the catalytic activities of these complexes in the Suzuki–Miyaura cross-coupling reaction, irrespective of the identity of the substituent on the triazole group. This work represents a simple and straightforward strategy for various functionalisations of NHC–palladium complexes. Further structural studies of these new functionalised NHC-based ligands and their complexes are currently underway for various catalytic applications.

Experimental Section

General Methods: All commercially available reagents were used as received. Unless otherwise stated, all reactions were carried out under Argon with Schlenk techniques. Dichloromethane and pentane were dried under N_2 with a solvent purification system (SPS). Acetonitrile was distilled under Argon from CaH_2. NMR spectra were recorded at 25 °C with a Bruker Avance 300, 400 Ultrashield, DPX300 or Fourier 300 Ultrashield apparatus. ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are referenced to the solvent signal. $^{31}P\{^1H\}$ NMR chemical shifts are referenced to an external standard (85% aqueous H_3PO_4). $^{19}F\{^1H\}$ NMR chemical shifts are referenced to an external standard ($CFCl_3$). For atom number assignments for NMR spectroscopy, see Supporting Information. HRMS analyses were carried out with a Xevo G2 QTOF spectrometer (Waters). Hereafter the typical synthetic procedures, exemplified on the preparation of ligands **4b** and **6b** and the corresponding complexes **9b** and **10b,** are presented. Characterisation of all the triazole-based imidazolium salts **4a**–**c**, **6a**–**c** and **8b** and all the palladium complexes **9a**–**c**, **10a**–**c** and **11b** are detailed in Supporting Information.

Ligand Synthesis: A mixture of **2b** (1 mol-equiv.), fluorous azide **3** or aryl azide **5** (1.0 mol-equiv.), diisopropylamine (1.0 equiv.), CuI catalyst (5 mol-%) and trifluoroethanol (5 mL/mmol of imidazolium) was stirred overnight under an argon atmosphere at 25 °C. The reaction mixture was then filtered and concentrated. The resulting precipitate was washed with Et_2O and dried under vacuum to afford the corresponding fluorous ligand **4b** or nitro-substituted ligand **6b**.

1-Ethyl-3-[4-methyl-1-(1*H*,1*H*,2*H*,2*H*-perfluororoctyl)-1*H*-1,2,3-triazole]imidazolium Bromide (4b): Beige solid (1.45 g, 87%). ^1H NMR (400 MHz, CD_3CN): δ = 9.21 (br. s, 1 H, H^2), 8.29 (s, 1 H, H^{10}), 7.59 (d, $J_{4,5}$ = 1.8 Hz, 1 H, H^4), 7.49 (d, $J_{5,4}$ = 1.8 Hz, 1 H, H^5), 5.58 (s, 2 H, H^8), 4.80–4.76 (t, $J_{11,12}$ = 7 Hz, 2 H, H^{11}), 4.27–

4.21 (q, $J_{6,7}$ = 7.3 Hz, 2 H, H^6), 3.00–2.89 (tt, $J_{11,12}$ = 7 Hz, J = 19 Hz, 2 H, H^{12}), δ = 1.50–1.47 (t, $J_{6,7}$ = 7.3 Hz, 3 H, H^7) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, [D$_6$]DMSO): δ = 141.0 (C^9), 136.4 (C^2), 125.6 (C^{10}), 122.9 (C^4), 122.8 (C^5), 119.2, 118.0, 111.9, 111.7, 111.2, 109.3 (C^{13-18}), 44.8 (C^8), 44.30 (C^{11}), 42.4 (C^6), 30.7 (C^{12}), 15.5 (C^7) ppm. $^{19}F\{^1H\}$ NMR (376 MHz, CD_3CN): δ = –81.6 (3 F), –114.7 (2 F), –122.4 (2 F), –123.4 (2 F), –124.0 (2 F), –126.7 (2 F) ppm. ESI-MS: m/z = 524 [M$^+$].

1-Ethyl-3-[4-methyl-1-(4-nitrophenyl)-1*H*-1,2,3-triazole]imidazolium Bromide (6b): Brown solid (0.712 g, 99%). ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 9.38 (s, 1 H, H^2), 9.18 (s, 1 H, H^{10}), 8.50 (d, $J_{13,12}$ = 9.2 Hz, 2 H, H^{13}), 8.24 (d, $J_{12,13}$ = 9.2 Hz, 2 H, H^{12}), 7.89–7.87 (m, 2 H, H^4, H^5), 5.70 (s, 2 H, H^8), 4.25 (q, $J_{6,7}$ = 7.3 Hz, 2 H, H^6), 1.44 (t, $J_{7,6}$ = 7.3 Hz, 3 H, H^7) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, [D$_6$]DMSO): δ = 147.4 (C^{14}), 142.6 (C^9), 141.0 (C^{11}), 136.6 (C^2), 126.1 (C^{13}), 124.2 (C^5), 123.2 (C^{10}), 122.9 (C^4), 121.4 (C^{12}), 44.9 (C^8), 44.0 (C^6), 15.5 (C^7) ppm. ESI-MS: m/z = 299.0 [M$^+$].

Complex Synthesis: The imidazolium-based ligand **4b** or **6b** (1 mol-equiv.), PPh_3 (1 mol-equiv.), triethylamine (5 mol-equiv.) and lithium bromide (30 mol-equiv.) were added sequentially to a stirred solution of $Pd(OAc)_2$ (1 mol-equiv.) in acetonitrile (10 mL/mmol of ligand) under argon. The resulting mixture was heated at 70 °C for 12 h under argon. The reaction mixture was then filtered and the resulting precipitate was washed with water and dried under vacuum to afford the corresponding palladium complex **9b** or **10b**.

Dibromo-{1-ethyl-3-[4-methyl-1-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1*H*-1,2,3-triazole]imidazol-2-ylidene}triphenylphosphinepalladium(II) (9b): Yellow solid (0.14 g, 75%). ^1H NMR (300 MHz, CD_3CN): δ = 8.10 (s, 1 H, H^{10}), 7.59–7.45 (m, 15 H, PPh_3), 6.86 (d, $J_{4,5}$ = 2.0 Hz, 1 H, H^4), 6.79 (d, $J_{5,4}$ = 2.0 Hz, 1 H, H^5), 5.51 (d, $J_{8,8'}$ = 15.3 Hz, 1 H, H^8), 5.08 (d, $J_{8',8}$ = 15.3 Hz, 1 H, $H^{8'}$), 4.86 (t, $J_{11,12}$ = 7.0 Hz, 2 H, H^{11}), 4.21–4.14 (dq, $J_{6,7}$ = 7.3 Hz, $J_{6,6'}$ = 13.4 Hz, 1 H, H^6), 3.62–3.54 (dq, $J_{6',7}$ = 7.3, $J_{6',6}$ = 13.4 Hz, 1 H, $H^{6'}$), 3.0–2.83 (tt, $J_{12,11}$ = 7.0, J = 18.9 Hz, 2 H, H^{12}), 1.22 (dd, $J_{7,6}$ = $J_{7,6'}$ = 7.3 Hz, 3 H, H^7) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, [D$_6$]DMSO): δ = 158.8 (C^2), 140.8 (C^9), 133.9 (d, J = 10.9 Hz, PPh_3), 131.1 (PPh_3), 130.1 (d, J = 52.0 Hz, PPh_3), 128.5 (d, J = 10.9 Hz, PPh_3), 125.0 (C^{10}), 122.1 (C^5), 121.9 (C^4), 45.2 (C^6), 45.0 (C^8), 41.8 (C^{11}), 30.3 (t, J = 20.0 Hz, C^{12}), 14.7 (C^7) ppm. $^{19}F\{^1H\}$ NMR (376 MHz, CD_3CN): δ = –81 (3 F), –114.5 (2 F), –122.4 (2 F), –123.3 (2 F), –124.0 (2 F), –126.7 (2 F) ppm. $^{31}P\{^1H\}$ NMR (122 MHz, [D$_6$]DMSO): δ = 26.6 ppm. HRMS: calcd. [M – Br]$^+$ 972.0171; found 972.0189.

Dibromo-{1-ethyl-3-[4-methyl-1-(4-nitrophenyl)-1*H*-1,2,3-triazole]-imidazol-2-ylidene}triphenylphosphinepalladium(II) (10b): Grey-green solid (0.344 g, 78%). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.07 (s, 1 H, H^{10}), 8.36 (d, $J_{13,12}$ = 9.2 Hz, 2 H, H^{13}), 7.96 (d, $J_{12,13}$ = 9.2 Hz, 2 H, H^{12}), 7.67–7.35 (m, 15 H, PPh_3), 6.79 (d, $J_{4,5}$ = 2.1 Hz, 1 H, H^4), 6.67 (d, $J_{5,4}$ = 2.1 Hz, 1 H, H^5), 5.94 (d, $J_{8,8'}$ = 14.8 Hz, 1 H, H^8), 4.60 (d, $J_{8',8}$ = 14.8 Hz, 1 H, $H^{8'}$), 4.45–4.40 (m, 1 H, H^6), 3.79–3.73 (m, 1 H, $H^{6'}$), 1.6 (m, 3 H, H^7) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 162.4 (C^2), 147.4 (C^{14}), 143.2 (C^9), 140.8 (C^{11}), 134.2 (d, J = 11.0 Hz, PPh_3), 131.3 (PPh_3), 130.1 (d, J = 53.5 Hz, PPh_3), 128.6 (d, J = 11.0 Hz, PPh_3), 125.5 (C^{13}), 124.3 (C^5), 121.8 (C^{10}), 121.4 (C^4), 120.7 (C^{12}), 46.0 (C^6), 45.5 (C^8), 14.8 (C^7) ppm. $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$): δ = 27.3 ppm. HRMS: calcd. [M – Br]$^+$ 747.0307; found 747.0330.

Typical Suzuki–Miyaura Cross-coupling Reaction: A mixture of boronic acid (1.2 mol-equiv.), arylbromide (1.0 mol-equiv.), K_3PO_4 (1.0–3.0 mol-equiv.), NHC-based palladium catalyst (0.005–1 mol-%) in DMF/water (4:1) (1–5 mL/mmol of substrate) was stirred at 100 °C until full conversion of the arylbromide. The reaction mixture was cooled to room temperature, after which water was added. The mixture was then extracted with diethyl ether and the organic extracts dried with $MgSO_4$, filtered and concentrated in vacuo. Purification by flash chromatography gave the pure cross-coupled product. The spectroscopic data were in agreement with those previously reported for 4-methoxy-4′-acetyl-biphenyl,[25] 4-methoxy-4′-nitrobiphenyl,[26] 4-methoxy-4′-methylbiphenyl[25,27] and 4′-(1-naphthyl)-acetophenone.[28]

Crystal Structure Determination: Diffraction data for **10b** were collected at low temperature (180 K) with an Agilent Technologies GEMINI EOS diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The diffractometer was equipped with an Oxford Instrument Cryojet cooler device. The structure was solved by direct methods with SIR92.[29] All non-hydrogen atoms were refined anisotropically by means of least-squares procedures on F^2 with the aid of the program SHELXL-97.[30] The H atoms were refined isotropically at calculated positions by a riding model with their isotropic displacement parameters constrained to 1.5× the equivalent isotropic displacement parameters of their pivot atoms for terminal sp^3 carbon and 1.2× for all other carbon atoms.

CCDC-939074 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Text detailing the preparation and characterisation of all ligand precursors and palladium complexes, catalysis protocols and X-ray crystallographic data.

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