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Erstveröffentlichung in / First published in:

Dalton Transactions. 2015, 44(20), S. 9391–9399 [Zugriff am: 01.11.2019]. Royal Society of
Chemistry. ISSN 1477-9234.

DOI: <https://doi.org/10.1039/c5dt01067e>

Diese Version ist verfügbar / This version is available on:

<https://nbn-resolving.org/urn:nbn:de:bsz:14-qucosa2-361201>

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Cite this: *Dalton Trans.*, 2015, **44**, 9391

Palladium(II) complexes with electron-poor, 4,5-disubstituted diimidazol-2-ylidene ligands: synthesis, characterization and catalytic activity†

Piermaria Pinter,^a Andrea Biffis,^{*a} Cristina Tubaro,^a Mario Tenne,^b Maria Kaliner^b and Thomas Strassner^b

Diimidazolium salts featuring different bridges between the imidazolium groups, as well as electron-withdrawing groups (chloride, cyanide) at the 4- and 5-position of the heterocyclic rings, have been successfully prepared. The diimidazolium salts serve as convenient precursors of di(N-heterocyclic carbene) ligands, which coordinate in a chelating fashion to palladium(II) centres. The effect of the newly introduced electron-withdrawing groups on the spectroscopic and structural characteristics of the resulting complexes as well as on their reactivity as catalysts in a model alkyne hydroarylation reaction has been investigated and is discussed herein.

Received 17th March 2015,
Accepted 16th April 2015

DOI: 10.1039/c5dt01067e

www.rsc.org/dalton

Introduction

N-heterocyclic carbenes (NHCs) are compounds which have been continuously growing in number of reports and applications during the last two decades.^{1,2} Particularly numerous are investigations on their role as ligands towards metal centres, which have been considerably stimulated by the recognition of the unique properties of NHCs in this respect.^{1,3} Such molecules generally act as soft ligands with strongly σ -donating properties, thus resembling trialkylphosphanes. Their metal complexes are however more stable, since NHC ligands are less prone to dissociation than phosphane ligands.⁴ Furthermore, NHC ligands can provide more efficient steric shielding to metal centres, and their electronic properties can be varied to a remarkable extent while maintaining similar steric effects, a feature not attainable with phosphane ligands.⁵ In this connection, though, recent advances have mostly regarded the development of more strongly electron-donating NHC ligands, whereas less success has been obtained with the design of less electron donating NHCs.⁶ This is particularly true for poly-NHC ligands, for which the currently available spectrum of ligands with different steric

and electronic properties is much less broad than in the case of mono-NHC ligands.⁷

Modulation of the electronic properties of NHC ligands towards decreased electron donation can be in principle achieved in three ways, namely (a) through the N-heterocyclic backbone; (b) through the wingtip *N*-substituents; or (c) through functionalization of the heterocyclic carbons remote from the carbene carbon. The first alternative allows only a rather limited variation in the electronic properties of the carbene by employing more electron-withdrawing heterocyclic scaffolds, ranging from the more usual benzimidazole or 1,2,4-triazole to less commonly employed nitrogen-containing heterocycles such as xanthenes.⁸ A notable amount of work has been performed also on the second alternative, particularly employing *N*-aryl groups bearing strongly electron-withdrawing substituents.⁹ The last alternative is less explored,¹⁰ possibly because of synthetic difficulties in the preparation of backbone-substituted NHCs, which are particularly high in the case of poly-NHC with these characteristics. For example, in a previous report by Peris *et al.*¹¹ the synthesis of diimidazolium salts as NHC precursors with the heterocycle 4,5-dichloroimidazole was reported to be feasible using a propylene bridge between the two N-heterocyclic units, whereas it failed altogether with shorter bridges such as the methylene one.

We have ongoing research programs on the synthesis of mono- and polynuclear complexes of late transition metals with poly-NHC ligands, and we have extensively described their preparation and properties.^{12,13} In this contribution, we report on the successful preparation of a small library of dicarbene ligand precursors featuring electron withdrawing groups in the positions 4 and 5 of an imidazolium heterocycle

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† Electronic supplementary information (ESI) available: NMR spectra of the compounds, additional X-ray crystallographic details and cif files for complexes **3a**, **3b**, **3c** and **3e**. CCDC 1054314–1054317. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt01067e

Chart 1 Nature of the ligand precursors investigated.

(Chart 1). Such ligand precursors can be readily employed as carbene sources for the preparation of novel palladium(II) complexes, where it is expected that the decreased electron-donating character of the ligands will affect their reactivity as catalysts in selected processes. The existence of such an effect will be tested in a model reaction in which the Pd catalytic centre typically acts as a soft Lewis acid, namely the hydroarylation of alkynes.

Results and discussion

Synthesis of the ligand precursors

We have chosen to employ two 4,5-disubstituted imidazoles as starting compounds, *i.e.* 4,5-dichloroimidazole and 4,5-dicyanoimidazole. The latter can be considered one of the most electron-poor N-heterocyclic scaffolds for the preparation of NHC ligands, due to the π -accepting properties of the cyano groups enforcing their inductive effect, as evidenced by the value of the Hammett parameter for the cyano group.¹⁴ The electron-withdrawing properties of mono-NHC ligands with this substitution pattern have been experimentally verified,^{10a} but to the best of our knowledge no preparation of poly-NHC ligands featuring cyano substituents at the heterocyclic rings has been reported up to now.

The synthesis of the ligand precursors **2a–2f** followed a well established route for the preparation of similar dicarbene precursors (Scheme 1). It consisted first in the preparation of the diimidazoles **1a–1f**, followed by their methylation at their

terminal nitrogen atoms. In both these reactions, though, the heterocyclic nitrogen atoms act as nucleophiles, and consequently their reactivity is expectedly decreased by the presence of electron-withdrawing substituents. Indeed, already the first step of the reaction turned out to be difficult in some instances, leading to spectroscopically but not analytically pure diimidazoles which could not be further purified. In particular, compound **1d** could be obtained spectroscopically pure in very low yield only after extensive purification. Furthermore, methylation of **1d** did not lead to the anticipated diimidazolium dication but instead to decomposition products. This is probably due to the reactivity of the methylene bridge, which is bound to two strongly electron-withdrawing heterocyclic rings.

On the other hand, all other diimidazoles could be successfully methylated using Meerwein's salt Me₃OBF₄, which proved to be a much more efficient methylation reagent compared to the previously employed methyl iodide.¹¹

The diimidazolium precursors were fully characterized by NMR showing the expected resonances for all compounds. In particular, the hydrogen atom and carbon atom in 2-position of the heterocyclic ring were found to be in all cases much more deshielded in the presence of –CN substituents than in the presence of –Cl substituents, thus confirming the stronger electron-withdrawing character of the former (see the Experimental section for details). However, the NMR resonances of the chloride-substituted precursors were only slightly different from those of the unsubstituted analogue,¹⁵ thus suggesting that the introduction of chloride substituents has only a marginal effect on the electron density at the 2-carbon.

Synthesis and characterization of the palladium complexes

The palladium complexes **3a–3c**, **3e** and **3f** were synthesized directly from the corresponding diimidazolium salts by reaction with palladium(II) acetate as the metal precursor (Scheme 2). The methodology followed previously published procedures¹⁶ and resulted in the clean preparation of the complexes in good yields. The colourless di-NHC complexes are air and water stable solids, and show remarkable stability under harsh conditions (concentrated acids as hydrochloric acid, nitric acid and aqua regia) and temperatures (up to 160 °C).

The elemental analyses of the Pd(II) complexes were consistent with their proposed composition, *i.e.* one dicarbene ligand

Scheme 1 Synthetic strategy for the preparation of the diimidazolium ligand precursors. Conditions: (i) CH₃CN, K₂CO₃, reflux 24 hours; (ii) Me₃OBF₄, CH₃CN, 85 °C, 24 hours.

Scheme 2 Synthetic strategy for the preparation of Pd(II) complexes with dicarbene ligands.

and two bromides per metal centre (Scheme 2). The deprotonation of the diimidazolium salt was confirmed by the absence of the NMR signal assigned to the proton in 2-position of the imidazole heterocycles. Furthermore, loss of magnetic equivalence for the protons of methylene groups in the bridge indicates that the ligands adopt a rigid structure, which is an expected consequence of coordination to the metal in chelate fashion. The ^{13}C NMR spectra of the complexes were in some cases difficult to obtain due to poor solubility of the complexes, particularly in the case of the NHC ligands with propylene bridges. Nevertheless, the trend in the variation of the chemical shift of the carbon in 2-position with different substituents at the N-heterocyclic rings, which was previously observed in the ligand precursors, was maintained also in the corresponding Pd complexes. Thus, the carbene signal in CN-substituted complexes was found above 170 ppm, whereas with $-\text{Cl}$ substituents the resonance was shifted approximately 10 ppm to higher field; again, much smaller differences in this parameter were recorded between the Cl-substituted complexes and the corresponding unsubstituted complexes.¹⁵

Crystal structure determination of the complexes

The solid state structure of the complexes **3a**, **3b**, **3c** and **3e** was also confirmed by single-crystal X-ray analysis of samples grown in *N,N*-dimethylformamide solution upon slow diffusion of diethyl ether. A view of the crystal structures is reported in Fig. 1–4, together with the atomic labeling scheme. A list of the most important bond distances and angles is also reported in the figures' captions.

The structural parameters of complexes **3a** and **3b** do not differ substantially from those of the published analogues without the chloride substituents in the 4 and 5 positions.^{15b,17a} In particular, the Pd–C distances are very similar

Fig. 1 ORTEP drawing of complex **3a**. Ellipsoids are drawn at their 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–C1 1.980(10), Pd1–C6 1.995(10), Pd1–Br1 2.4761(14), Pd1–Br2 2.4659(14), C1–Pd1–C6 85.2(4), Br1–Pd1–Br2 91.02(5), Br1–Pd1–C1–N2 54.7(9), Pd1–C1–N1–C5 –4.2(12).

Fig. 2 ORTEP drawing of complex **3b**. Ellipsoids are drawn at their 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–C1 1.974(4), Pd1–C8 1.978(4), Pd1–Br1 2.4846(7), Pd1–Br2 2.4761(7), C1–Pd1–C8 84.36(17), Br1–Pd1–Br2 95.20(2), Br1–Pd1–C1–N2 –84.4(4), N2–C1–N1–C5 176.6(4).

Fig. 3 ORTEP drawing of complex **3c**. Ellipsoids are drawn at their 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–C1 1.984(4), Pd1–Br1 2.4734(8), C1–Pd1–C1' 93.4(2), Br1–Pd1–Br1' 93.00(4), Br1–Pd1–C1–N1 –95.7(3), N1–C5–C6–C7 86.4(6). Symmetry code $\bar{1}$: $x, 1/2y, z$.

in the examples with H and Cl substituents, which indicates a similar bond strength. This situation does not change significantly with the propylene bridged, cyano-substituted complex **3e**, which features averaged Pd–C bonds only slightly shorter than in the Cl substituted complex **3b** (1.968 vs. 1.976 Å). The structure of the xylene-bridged, chloride-substituted complex **3c** is remarkable, as the xylene bridge is bent towards the metal centre, instead of away from it. Such a conformation is unusual, although there is precedent in related dicarbene

Fig. 4 ORTEP drawing of complex **3e**. Ellipsoids are drawn at their 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–C1 1.964(6), Pd1–C8 1.971(6), Pd1–Br1 2.4521(8), Pd1–Br2 2.4557(8), C1–Pd1–C8 85.5(2), Br1–Pd1–Br2 95.25(3), Br1–Pd1–C1–N1 79.2(5), Pd1–C1–N2–C5 7.6(8).

complexes of palladium(II) as well as of ruthenium(II).^{18,19} π -coordination of the *o*-phenylene ring of the bridge with η^2 or η^6 hapticity has also been observed in the case of ruthenium.¹⁹

In complex **3e**, though, the *o*-phenylene ring remains more than 3 Å away from the palladium centre, hence too far to postulate an interaction between the two, so that the observed *syn* conformation is most likely the result of steric effects caused by the presence of the chloride substituents in 4- and 5-position. The large phenylene bridge leads to a wider C–Pd–C angle when compared to the other complexes **3a**, **3b** and **3e**, as well as to a similar complex without chloro substituents and with the phenyl ring bent toward the carbene backbone.^{17b}

Catalytic efficiency of the complexes in alkyne hydroarylation

The hydroarylation of alkynes (Scheme 3) is an intensively studied reaction leading to aromatic C–H bond functionalization.²⁰ In this reaction, the C–H bond of an arene adds formally *trans* to the triple bond of an alkyne, generally forming the thermodynamically less favoured *cis*-arylalkene (**a**) as the major product. The study of this reaction was pioneered by the group of Fujiwara (hence the alternative name “Fujiwara

reaction” for the intermolecular hydroarylation of alkynes) using mainly palladium(II) or platinum(II) salts as catalyst;²¹ more recently, palladium complexes with unsubstituted dicarbene ligands have been showcased as highly efficient catalysts for this reaction.²²

The currently accepted mechanistic view of the Pd-catalyzed Fujiwara reaction involves activation of the alkyne by the catalyst upon π -coordination to the Pd centre and subsequent electrophilic attack of the coordinated alkyne to the arene.²³ We reasoned that use of dicarbene ligands featuring electron-withdrawing substituents on the NHC moieties could decrease the electron density on the metal centre, consequently enhance its Lewis acidity and therefore eventually promote catalytic activity. Such a positive effect of an increased positive charge on the metal centre was already recognized by Fujiwara²⁴ and has been observed in several other mechanistically related reactions involving unsaturated hydrocarbons.²⁵ Therefore, we set out to evaluate the reactivity of the palladium complexes in a standard hydroarylation reaction, namely the reaction between ethyl propiolate and pentamethylbenzene, under reaction conditions previously optimized by our group for unsubstituted dicarbene–Pd complex catalysts.^{22b} The results are reported in Table 1. For comparison, results previously obtained under the same reaction conditions with the unsubstituted complexes **3g** and **3h** (Chart 2), as well as with palladium(II) acetate have been included in the Table.

The thermodynamically less favoured *cis*-arylalkene (**a**) was indeed obtained as the virtually exclusive product in the majority of cases, with a catalytic efficiency which proved

Table 1 Catalytic hydroarylation with different Pd complex catalysts

Catalyst	% Yield ^a at 5 h	TOF _{t=5 h} (h ^{−1})	% Yield ^a at 24 h
3a	29(a)	58	45(a)
3b	0	—	0
3c	45(a)	90	82(a)
3e	0	—	0
3f	12(b), 1(a)	26	34(b), 4(a)
3g ^{22b}	60(a)	120	84(a)
3h ^{22b}	42(a)	84	61(a)
Pd(OAc) ₂	16(a)	32	42(a)

^a Yield determined with respect to the limiting reagent by ¹H NMR analysis of the reaction mixture (CDCl₃); yield of product (**b**) determined with respect to the limiting reagent (the alkyne).

Scheme 3 The investigated hydroarylation reaction.

Chart 2 Structures of the two unsubstituted Pd dicarbene complex catalysts used as reference.

higher than that of simple $\text{Pd}(\text{OAc})_2$, thus confirming the usefulness of dicarbene palladium(II) complexes as catalysts for this reaction. However, no reaction was recorded with the propylene-bridged catalysts **3b** and **3e**; this is probably the consequence of the very poor solubility of these complexes (see above). Indeed, the employed palladium–dicarbene complexes are expected to sustain the employed reaction conditions, given that they have been previously found able to resist to even more aggressive reaction environments (pure HTFA, presence of strong oxidants, higher temperature).^{13a,b,16} Whereas the catalytic activity of the complexes with a methylene bridge (**3a** and **3g**) was found to be significantly higher for the unsubstituted complex **3g** ($\text{TOF}_{t=5\text{ h}} 58$ vs. 120 h^{-1}), in the case of the complexes with the *o*-xylylene bridge **3c** and **3h** the catalytic activities were similar ($\text{TOF}_{t=5\text{ h}} 90$ vs. 84 h^{-1}) and the productivity after 24 hours higher for the Cl-substituted complex **3c** (82% yield) compared to the unsubstituted one (61% yield). Such small differences are coherent, given the corresponding small difference in the electron-richness of unsubstituted and Cl-substituted carbene ligands which resulted from the characterization data presented herein.

Finally, the behaviour of the CN-substituted complex with the *o*-xylylene bridge **3f** was peculiar, in that the catalytic activity ($\text{TOF}_{t=5\text{ h}} 26\text{ h}^{-1}$) was lower than in the case of the other complexes with the same bridge; furthermore, the selectivity of the reaction was completely changed, as the diene (**b**) (Scheme 3), resulting from the formal insertion of two alkyne molecules into the arene C–H bond, was predominantly formed. Such a product was occasionally obtained in very low amount with unsubstituted dicarbene–Pd complexes under the reaction conditions reported in Scheme 3, whereas it was the major product when more strongly acidic conditions were employed for the process.^{22b}

We can provide an explanation for this observation by considering the proposed catalytic cycle of the hydroarylation reaction leading to the standard product (**a**) (Scheme 4, catalytic cycle on the right).²³ On the basis of this cycle, it can be expected that the electrophilic character of the catalyst will

actually influence several steps of the catalytic cycle. A stronger electrophilic character of the complex will activate more strongly the coordinated alkyne for electrophilic attack, but it would also make the final protonolysis more difficult. If the vinylpalladium intermediate is more slowly protonolyzed, it will have more time to further react with another alkyne molecule, forming upon coordination, insertion and subsequent protonolysis the double insertion product (**b**) (Scheme 4, catalytic cycle on the left). Further support can be obtained from previously published studies on the related hydroarylation of alkenes, in which an increased electrophilicity of the metal centre indeed enhanced the reactivity of the coordinated alkene but also slowed down the subsequent, rate determining protonolysis step and consequently the reaction rate.²⁶

Conclusions

In conclusion, we have shown that contrary to common expectations, diimidazolium salts bearing electron-withdrawing substituents at the positions 4 and 5 of the heterocyclic ring can indeed be prepared with relative ease *via* general synthetic methods. Such salts readily form palladium(II)–dicarbene complexes upon reaction with $\text{Pd}(\text{OAc})_2$. The resulting complexes display structural and spectroscopic properties which depend on the electron-withdrawing character of the substituents, particularly in the case of π -accepting cyano groups. In this latter case, the presence of the electron-withdrawing substituents appears to significantly influence the electron density at the metal centre, and consequently results in an important modification of the reactivity of the complex as catalyst in a model hydroarylation reaction. We are currently extending the investigations on this poorly represented class of dicarbene ligands and their metal complexes, as well as on potential applications thereof.

Experimental

General

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry argon or dinitrogen. The reagents were purchased as high-purity products and generally used as received. Solvents were technical grade and generally used as received. Dry CH_3CN was obtained from a solvent purification system under an inert atmosphere of dinitrogen. CH_2Cl_2 was distilled prior to use. DMSO and DMSO- d_6 were dried and stored over molecular sieves (4 Å). NMR spectra were recorded at 300 MHz (300.1 MHz for ^1H , 282 MHz for ^{19}F and 75.5 for ^{13}C), at 600 MHz (600.01 MHz for ^1H and 150.07 for ^{13}C) or at 500 MHz (500 MHz for ^1H and 126 MHz for ^{13}C); chemical shifts (δ) are reported in units of ppm relative to TMS and are referenced to the residual solvent signals for both ^1H and ^{13}C ; ^{19}F -NMR signals are referred to CCl_3F . Details concerning the determination of the solid-state structures are given in the ESI.†

Scheme 4 The currently accepted mechanism for the Fujiwara hydroarylation reaction (right cycle),²³ including the proposed formation of product (**b**) (left cycle).

Synthesis of the ligand precursors

3,3'-Methylene-di-(4,5-dichloroimidazole) (1a).¹¹ In a round-bottomed flask were added 4,5-dichloroimidazole (4.01 g, 29.3 mmol), anhydrous K₂CO₃ (4.08 g, 29.5 mmol) and CH₃CN (100 ml) under an inert atmosphere. The mixture was stirred for 5 minutes, then dibromomethane (2.51 g, 1.02 ml, 14.4 mmol) was added and the resulting suspension was heated at reflux for 24 h. The mixture was then filtered and the solid was washed with 3 × 3 ml CH₃CN. The combined organic phases were evaporated to dryness yielding a bordeaux coloured powder. Finally, the product was washed with 3 × 10 ml cold EtOH, which yielded 2.75 g (9.63 mmol) crystalline, colourless powder, 67% yield. The spectroscopic characterization data exactly matched those previously published.¹¹

1,1'-Dimethyl-3,3'-methylene-di-(4,5-dichloroimidazolium)-bis(tetrafluoroborate) (2a). In a pressure tube were added **1a** (1.19 g, 4.14 mmol), trimethyloxonium tetrafluoroborate (1.32 g, 8.89 mmol) and CH₃CN (5 ml) under an inert atmosphere. The mixture was stirred for 5 minutes and then it was heated at 85 °C for 24 h. The mixture was cooled down to room temperature and the volatiles were removed under reduced pressure yielding a brown powder. The product was purified by fractional recrystallization from CH₃CN/Et₂O, which resulted in the isolation of 1.02 g (2.07 mmol) colourless crystalline solid, 46% yield. Anal. Calc. for C₉H₁₀B₂Cl₄F₈N₄: C, 22.08; H, 2.06; N, 11.44%. Found C, 21.83; H, 1.94; N, 11.24%. ¹H NMR (DMSO-d₆): δ = 9.76 (s, 2H, NCHN), 6.94 (s, 2H, CH₂), 3.94 (s, 6H, CH₃). ¹³C NMR (DMSO-d₆): δ = 138.5 (NCHN), 120.4 (C_{4/5}), 119.0 (C_{4/5}), 55.8 (CH₂), 35.5 (CH₃). ¹⁹F NMR (DMSO-d₆): δ = -148.96, -149.01.

3,3'-Propylene-di-(4,5-dichloroimidazole) (1b).¹¹ In a round-bottomed flask were added 4,5-dichloroimidazole (2.01 g, 14.7 mmol), anhydrous K₂CO₃ (2.02 g, 14.6 mmol) and CH₃CN (50 ml) under an inert atmosphere. The mixture was well stirred for 5 minutes, then 1,3-dibromopropane (1.47 g, 0.70 ml, 7.33 mmol) was added and the resulting suspension was heated at reflux for 24 h. The mixture was filtered and the solid was washed with 3 × 3 ml CH₃CN. The combined organic phases were evaporated to dryness yielding 1.98 g (6.31 mmol) yellow powder which was further employed without additional purification, 88% yield. The spectroscopic characterization data exactly matched those previously published.¹¹

1,1'-Dimethyl-3,3'-propylene-di-(4,5-dichloroimidazolium)-bis(tetrafluoroborate) (2b). In a pressure tube were added **1b** (0.50 g, 1.6 mmol), trimethyloxonium tetrafluoroborate (0.47 g, 3.2 mmol) and CH₃CN (5 ml). The mixture was well stirred for 5 minutes and then it was heated at 90 °C for 24 h. The mixture was cooled down to room temperature, 100 ml Et₂O were added and the solution was stored in the fridge overnight; after filtering and drying, colourless crystals were obtained. The product was purified by fractional recrystallization from CH₃CN/Et₂O, yielding 0.32 g (0.61 mmol) colourless crystalline solid, 38% yield. The spectroscopic characterization data matched those previously published for

the compound with iodide as counteranion.¹¹ Anal. Calc. for C₁₁H₁₄B₂Cl₄F₈N₄: C, 25.52; H, 2.73; N, 10.82%. Found C, 25.15; H, 2.41; N, 10.66%. ¹H NMR (DMSO-d₆): δ = 9.44 (s, 2H, NCHN), 4.37 (t, 4H, NCH₂), 3.86 (s, 6H, CH₃), 2.42–2.29 (m, 2H, CH₂). ¹³C NMR (DMSO-d₆): δ = 136.5 (NCHN), 119.4 (C_{4/5}), 118.1 (C_{4/5}), 44.8 (NCH₂), 35.9 (CH₃), 27.2 (CH₂). ¹⁹F NMR (DMSO-d₆): δ = -148.95, -149.00.

3,3'-o-Phenylenedimethylene-di-(4,5-dichloroimidazole) (1c). In a round-bottomed flask were added 4,5-dichloroimidazole (4.00 g, 29.2 mmol), anhydrous K₂CO₃ (4.81 g, 34.8 mmol) and CH₃CN (100 ml) under an inert atmosphere. The mixture was well stirred for 5 minutes, then α,α'-dibromo-o-xylene (3.78 g, 14.3 mmol) was added and the resulting suspension was heated at reflux for 24 h. The mixture was filtered and the solid was washed with 3 × 3 ml CH₃CN. The combined organic phases were evaporated to dryness. The solid residue was washed with 3 × 10 ml cold EtOH, which yielded 3.49 g (9.28 mmol) pure product as an ivory coloured solid, 67% yield. Anal. Calc. for C₁₄H₁₀Cl₄N₄: C, 44.71; H, 2.68; N, 14.90%. Found C, 44.39; H, 2.48; N, 14.83%. ¹H NMR (DMSO-d₆): δ = 7.97 (s, 2H, NCHN), 7.39 (dd, 2H, ArH), 6.83 (dd, 2H, ArH), 5.47 (s, 4H, CH₂). ¹³C NMR (DMSO-d₆): δ = 136.6 (NCHN), 133.0 (ArC_{ipso}), 128.5 (ArC), 126.8 (ArC), 124.8 (C_{4/5}), 112.7 (C_{4/5}), 46.1 (CH₂).

1,1'-Dimethyl-3,3'-o-phenylenedimethylene-di-(4,5-dichloroimidazolium)bis(tetrafluoroborate) (2c). In a pressure tube were added **1c** (1.15 g, 3.06 mmol), trimethyloxonium tetrafluoroborate (0.91 g, 6.1 mmol) and CH₃CN (5 ml) under an inert atmosphere. The mixture was well stirred for 5 minutes, and then it was heated at 85 °C for 24 h. The mixture was cooled down to room temperature and the volatiles were removed under reduced pressure, yielding a beige powder. The product was purified by fractional recrystallization from CH₃CN/Et₂O, yielding 0.56 g (0.96 mmol) compound as a colourless solid, 31% yield. Anal. Calc. for C₁₆H₁₆B₂Cl₄F₈N₄: C, 33.15; H, 2.78; N, 9.66%. Found C, 33.01; H, 2.48; N, 9.74%. ¹H NMR (DMSO-d₆): δ = 9.31 (s, 2H, NCHN), 7.53 (dd, 2H, ArH), 7.26 (dd, 2H, ArH), 5.67 (s, 4H, CH₂), 3.89 (s, 6H, CH₃). ¹³C NMR (DMSO-d₆): δ = 136.8 (NCHN), 130.6 (ArC_{ipso}), 129.7 (ArC), 128.5 (ArC), 120.2 (C_{4/5}), 118.5 (C_{4/5}), 48.4 (CH₂), 35.2 (CH₃). ¹⁹F NMR (DMSO-d₆): δ = -148.91, -148.97.

3,3'-Methylene-di-(4,5-dicyanoimidazole) (1d). In a round-bottomed flask were added 4,5-dicyanoimidazole (3.00 g, 25.4 mmol), anhydrous K₂CO₃ (3.95 g, 28.6 mmol) and CH₃CN (100 ml) under an inert atmosphere. The mixture was well stirred for 5 minutes, then diiodomethane (3.00 g, 0.93 ml, 11.2 mmol) was added and the resulting suspension was heated at reflux for 24 h. The mixture was filtered and the solid was washed with 3 × 3 ml CH₃CN. The combined organic phases were evaporated to dryness yielding a brown/yellow powder. The product was re-crystallized from CH₃CN/Et₂O: a yellow solid was obtained, which proved to be still impure. The product was then further purified by column chromatography on silica gel (DCM/CH₃CN 4:1) which finally allowed to isolate 0.12 g (0.48 mmol) product as an ivory coloured solid, 4% yield. ¹H NMR (DMSO-d₆): δ = 8.61 (s, 2H, NCHN), 6.77

(s, 2H, CH₂). ¹³C NMR (DMSO-d₆): δ = 143.9 (NCHN), 122.5 (C_{4/5}), 112.7 (CN), 112.0 (CN), 107.9 (C_{4/5}), 55.8 (CH₂).

3,3'-Propylene-di-(4,5-dicyanoimidazole) (1e). In a round bottomed flask were added 4,5-dicyanoimidazole (2.54 g, 21.5 mmol), anhydrous K₂CO₃ (3.17 g, 22.9 mmol) and CH₃CN (50 ml) under an inert atmosphere. The mixture was well stirred for 5 minutes, then 1,3-dibromopropane (2.31 g, 1.16 ml, 11.4 mmol) was added and the resulting suspension was heated at reflux for 24 h. The mixture was filtered and the solid was washed with 3 × 3 ml CH₃CN. The combined organic phases were evaporated to dryness yielding an orange powder. The raw product was recrystallized from CH₃CN/Et₂O, which yielded 2.10 g (7.60 mmol) product as an ivory coloured solid, yield 66%. ¹H NMR (DMSO-d₆): δ = 8.38 (s, 2H, NCHN), 4.30 (m, 4H, NCH₂), 2.48–2.33 (m, 2H, CH₂). ¹³C NMR (DMSO-d₆): δ = 143.3 (NCHN), 121.3 (C_{4/5}), 112.4 (CN), 112.3 (CN), 108.5 (C_{4/5}), 44.4 (NCH₂), 29.2 (CH₂).

1,1'-Dimethyl-3,3'-propylene-di-(4,5-dicyanoimidazolium)bis-(tetrafluoroborate) (2e). In a pressure tube were added **1e** (2.03 g, 7.35 mmol), trimethyloxonium tetrafluoroborate (2.46 g, 16.6 mmol) and CH₃CN (7 ml) under an inert atmosphere. The mixture was well stirred for 5 minutes, and then it was heated at 100 °C for 24 h. The mixture was cooled down to room temperature and the volatiles were removed under reduced pressure, yielding a brown oil. The product was washed with acetone, yielding 1.30 g (2.71 mmol) compound as an ivory coloured solid, yield 37%. Anal. Calc. for C₁₅H₁₄B₂F₈N₈: C, 37.54; H, 2.94; N, 23.35%. Found C, 37.36; H, 2.75; N, 23.54%. ¹H NMR (DMSO-d₆): δ = 9.78 (s, 2H, NCHN), 4.58 (t, 4H, NCH₂), 4.11 (s, 6H, CH₃), 2.58–2.46 (m, 2H, CH₂). ¹³C NMR (DMSO-d₆): δ = 142.5 (NCHN), 116.1 (CN), 114.8 (CN), 106.0 (C_{4/5}), 47.2 (NCH₂), 37.2 (CH₃), 27.7 (CH₂). ¹⁹F NMR (DMSO-d₆): δ = −148.94, −149.00.

3,3'-o-Phenylenedimethylene-di-(4,5-dicyanoimidazole) (1f). In a round bottomed flask were added 4,5-dicyanoimidazole (3.00 g, 25.4 mmol), anhydrous K₂CO₃ (3.36 g, 24.3 mmol) and CH₃CN (120 ml) under an inert atmosphere. The mixture was well stirred for 5 minutes, then α,α'-dichloro-o-xylene (2.14 g, 12.2 mmol) was added and the resulting suspension was heated at reflux for 24 h. The mixture was filtered and the solid was washed with 3 × 3 ml cold, dry EtOH. The combined organic phases were evaporated to dryness yielding an orange powder. The raw product was recrystallized from CH₃CN/Et₂O, which provided 3.54 g (10.5 mmol) compound as an ivory coloured solid, yield 87%. Anal. Calc. for C₁₈H₁₀N₈: C, 63.90; H, 2.98; N, 33.12%. Found C, 64.09; H, 3.00; N, 32.90%. ¹H NMR (DMSO-d₆): δ = 8.43 (s, 2H, NCHN), 7.53 (dd, 2H, ArH), 7.22 (dd, 2H, ArH), 5.72 (s, 4H, CH₂). ¹³C NMR (DMSO-d₆): δ = 143.7 (NCHN), 132.2 (ArC_{ipso}), 129.6 (ArC), 129.0 (ArC), 122.2 (C_{4/5}), 112.3 (CN), 112.2 (CN), 108.3 (C_{4/5}), 47.9 (CH₂).

1,1'-Dimethyl-3,3'-o-phenylenedimethylene-di-(4,5-dicyanoimidazolium)bis(tetrafluoroborate) (2f). In a pressure tube were added **1f** (2.00 g, 5.93 mmol), trimethyloxonium tetrafluoroborate (1.80 g, 12.2 mmol) and CH₃CN (7 ml) under an inert atmosphere. The mixture was well stirred for 5 minutes, and then it was heated at 90 °C for 24 h. The mixture was

cooled down to room temperature and the volatiles were removed under reduced pressure, yielding an ivory coloured powder. The raw product was purified by fractional re-crystallization CH₃CN/Et₂O, yielding 1.28 g (2.37 mmol) pure product as a colourless solid, yield 41%. Anal. Calc. for C₂₀H₁₆B₂F₈N₈: C, 44.32; H, 2.98; N, 20.67%. Found C, 44.09; H, 2.76; N, 20.80%. ¹H NMR (DMSO-d₆): δ = 9.65 (s, 2H, NCHN), 7.68 (dd, 2H, ArH), 7.44 (dd, 2H, ArH), 5.91 (s, 4H, CH₂), 4.12 (s, 6H, CH₃). ¹³C NMR (DMSO-d₆): δ = 142.6 (NCHN), 130.7 (ArC_{ipso}), 130.3 (ArC), 130.2 (ArC), 117.1 (CN), 114.3 (CN), 106.0 (C_{4/5}), 105.9 (C_{4/5}), 50.5 (CH₂), 37.2 (CH₃). ¹⁹F NMR (DMSO-d₆): δ = −148.97, −149.03.

Synthesis of the palladium complexes

1,1'-Dimethyl-3,3'-methylene-di-(4,5-dichloro-imidazol-2-ylidene)palladium(II)dibromide (3a). In a Schlenk tube were added **2a** (0.51 g, 1.0 mmol), anhydrous potassium bromide (0.28 g, 2.3 mmol), palladium(II) acetate (0.21 g, 0.93 mmol) and dry DMSO (5 ml). The mixture was well stirred at 40 °C for 24 hours, and then the solution was heated at 60 °C for 2 h, at 80 °C for 2 h and at 110 °C for 2 h. The mixture was cooled down to room temperature and the DMSO was removed under reduced pressure. The obtained yellow solid was washed with 2 × 10 ml CH₃OH, 2 × 10 ml CH₃CN and 3 × 10 ml Et₂O, yielding after drying a yellow powder. The product was further purified by fractional recrystallization from CH₃CN/Et₂O, yielding 0.40 g (0.69 mmol) product as a light yellow solid, yield 75%. Anal. Calc. for C₉H₈Br₂Cl₄N₄Pd: C, 18.63; H, 1.39; N, 9.66%. Found C, 18.77; H, 1.33; N, 9.77%. ¹H NMR (DMSO-d₆): δ = 6.39 (d, 1H, CH₂), 6.04 (d, 1H, CH₂), 3.88 (s, 6H, CH₃). ¹³C NMR (DMSO-d₆): δ = 161.6 (NCN), 117.2 (C_{4/5}), 116.5 (C_{4/5}), 58.9 (CH₂), 37.6 (CH₃). IR (neat, cm^{−1}): ν = 2250, 1591, 1509, 1447, 1395, 1366, 1299, 1149, 1131, 1088, 1018, 1007, 865, 718, 671, 652.

1,1'-Dimethyl-3,3'-propylene-di-(4,5-dichloro-imidazol-2-ylidene)palladium(II)dibromide (3b). In a Schlenk tube were added **2b** (0.20 g, 0.39 mmol), anhydrous potassium bromide (93 mg, 0.78 mmol), palladium(II) acetate (87 mg, 0.39 mmol) and dry DMSO (3 ml). The mixture was well stirred at 40 °C for 24 hours, and then the solution was stirred at 60 °C for 2 h, at 80 °C for 2 h and at 110 °C for 2 h. The mixture was cooled down to room temperature and the DMSO was removed under reduced pressure. The obtained ivory solid was washed with 2 × 10 ml CH₃OH, 2 × 10 ml CH₃CN and 3 × 10 ml Et₂O, yielding after drying an ivory powder. The product was further purified by fractional recrystallization from CH₃CN/Et₂O, yielding 85 mg (0.14 mmol) complex as a colourless solid, yield 36%. Anal. Calc. for C₁₁H₁₂Br₂Cl₄N₄Pd: C, 21.72; H, 1.99; N, 9.21%. Found C, 21.65; H, 1.67; N, 9.14%. ¹H NMR (DMSO-d₆): δ = 4.95 (m, 2H, NCH₂), 4.49 (m, 2H, NCH₂), 3.93 (s, 6H, CH₃), 2.41 (m, 1H, CH₂), 1.76 (m, 1H, CH₂). ¹³C NMR (DMSO-d₆): δ = 162.2 (NCN), 117.0 (C_{4/5}), 116.4 (C_{4/5}), 50.1 (NCH₂), 36.8 (CH₃), 28.5 (CH₂). IR (neat, cm^{−1}): ν = 2935, 1589, 1509, 1472, 1453, 1406, 1390, 1355, 1340, 1144, 1088, 972, 891, 690, 676, 645.

1,1'-Dimethyl-3,3'-*o*-phenylenedimethylene-di-(4,5-dichloroimidazol-2-ylidene)palladium(II) dibromide (3c). In a Schlenk tube were added **2c** (0.30 g, 0.52 mmol), anhydrous potassium bromide (0.15 g, 1.3 mmol), palladium(II) acetate (0.11 g, 0.47 mmol) and dry DMSO (3 ml). The mixture was well stirred at 40 °C for 24 hours, and then the solution was stirred at 60 °C for 2 h, at 80 °C for 2 h and at 110 °C for 2 h. The mixture was cooled down to room temperature and the DMSO was removed under reduced pressure. The obtained yellow solid was washed with 2 × 10 ml CH₃OH, 2 × 10 ml CH₃CN and 3 × 10 ml Et₂O, yielding after drying a colourless crystals. The product was further purified by fractional recrystallization from CH₃CN/Et₂O, followed by an additional washing with 3 ml water at 120 °C (pressure tube). 118 mg (0.18 mmol) of the product were obtained as a colourless solid yield 37%. Anal. Calc. for C₁₆H₁₄Br₂Cl₄N₄Pd·0.9H₂O·0.08 C₂H₆OS: C, 28.41; H, 2.36; N, 8.04; S, 0.37%. Found C, 28.09; H, 2.03; N, 7.71; S, 0.46%. ¹H NMR (DMSO-d₆): δ = 8.19–7.87 (m, 2H, ArH), 7.63–7.47 (m, 2H, ArH), 6.65 (d, 2H, CH₂), 5.42 (d, 2H, CH₂), 3.98 (s, 6H, CH₃). ¹³C NMR (DMSO-d₆): δ = 134.6 (ArC_{ipso}), 134.2 (ArC), 129.6 (ArC), 118.4 (C_{4/5}), 116.2 (C_{4/5}), 51.6 (CH₂), 37.4 (CH₃). IR (neat, cm⁻¹): ν = 3431, 2951, 1632, 1591, 1450, 1435, 1387, 1322, 1295, 1218, 1196, 1096, 1071, 895, 846, 791, 745, 707, 679, 653.

1,1'-Dimethyl-3,3'-propylene-di-(4,5-dicyanoimidazol-2-ylidene)palladium(II)dibromide (3e). In a Schlenk tube were added **2e** (0.65 g, 1.35 mmol), anhydrous potassium bromide (0.40 g, 3.4 mmol), palladium(II) acetate (0.30 g, 1.35 mmol) and dry DMSO (5 ml). The mixture was well stirred at 40 °C for 24 hours, and then the solution was stirred at 60 °C for 2 h, at 80 °C for 2 h and at 110 °C for 2 h. The mixture was cooled down to room temperature and the DMSO was removed under reduced pressure. The obtained yellow solid was washed with 2 × 10 ml CH₃OH, 2 × 10 ml CH₃CN, 3 × 10 ml Et₂O, and 2 × 25 ml water at 95 °C, yielding after drying 0.61 g (1.1 mmol) of product as a colourless solid, yield 79%. Anal. Calc. for C₁₅H₁₂Br₂N₈Pd·0.2H₂O·0.02 C₂H₆OS: C, 31.38; H, 2.19; N, 19.46%; S, 0.11%. Found C, 31.16; H, 1.79; N, 19.04; S, 0.28%. ¹H NMR (DMSO-d₆): δ = 5.11 (dd, 2H, NCH₂), 4.57 (dd, 2H, NCH₂), 4.13 (s, 6H, CH₃), 2.28 (m, 2H, CH₂). ¹³C NMR (DMSO-d₆): δ = 170.9 (NCN), 116.2 (CN), 115.5 (CN), 107.4 (C_{4/5}), 107.1 (C_{4/5}), 52.3 (CH₂), 38.4 (CH₃), 28.0 (CH₂). IR (neat, cm⁻¹): ν = 2955, 2246, 1601, 1473, 1458, 1411, 1374, 1358, 1284, 1209, 1168, 1100, 975, 904, 810, 698, 677.

1,1'-Dimethyl-3,3'-*o*-phenylenedimethylene-di-(4,5-dicyanoimidazol-2-ylidene)palladium(II)dibromide (3f). In a Schlenk tube were added **2f** (0.50 g, 0.92 mmol), anhydrous potassium bromide (0.27 g, 2.3 mmol), palladium(II) acetate (0.21 g, 0.92 mmol) and dry DMSO (5 ml). The mixture was well stirred at 40 °C for 24 hours, and then the solution was heated at 60 °C for 2 h, at 80 °C for 2 h and at 110 °C for 2 h. The mixture was cooled down to room temperature and the DMSO was removed under reduced pressure. The obtained yellow solid was washed with 2 × 10 ml CH₃OH, 2 × 10 ml CH₃CN and 3 × 10 ml Et₂O, yielding after drying a white powder. The

product was further purified by fractional recrystallization from CH₃CN/Et₂O, followed by an additional washing with 3 ml water at 120 °C (pressure tube). 0.42 g (0.67 mmol) complex were obtained as a colourless crystalline solid, yield 72%. Anal. Calc. for C₂₀H₁₄Br₂N₈Pd·0.39 H₂O: C, 37.56; H, 2.33; N, 17.52%. Found C, 37.92; H, 1.92; N, 17.11%. ¹H NMR (DMSO-d₆): δ = 7.95 (dd, 2H, ArH), 7.63 (dd, 2H, ArH), 6.81 (d, 2H, CH₂), 5.71 (d, 2H, CH₂), 4.17 (s, 6H, CH₃). ¹³C NMR (DMSO-d₆): δ = 172.1 (NCN), 134.3 (ArC_{ipso}), 133.6 (ArC), 130.3 (ArC), 118.1 (CN), 114.1 (CN), 107.9 (C_{4/5}), 106.9 (C_{4/5}), 52.8 (CH₂), 38.8 (CH₃). IR (neat, cm⁻¹): ν = 2240, 1452, 1405, 1334, 1249, 1180, 1089, 1038, 885, 802, 751, 747, 744, 734, 691, 671, 630.

Catalytic tests in the hydroarylation reaction

General procedure: in a Schlenk tube were placed pentamethylbenzene (13.20 mmol), the Pd complex (0.013 mmol) and AgTFA (0.026 mmol). The flask was evacuated and filled with argon, after which trifluoroacetic acid (13.20 mmol) and 1,2-dichloroethane (the quantity necessary to reach a total volume of 6.3 mL) were added. Finally, the alkyne (13.20 mmol) was introduced and the flask was placed in a water bath thermostated at 25 °C and vigorously stirred. Aliquots of the reaction mixture (around 0.2 ml) were periodically withdrawn from the reactor and analyzed by ¹H NMR. Yields were determined by comparison of the integrals of prominent peaks of reagents and products.

Acknowledgements

P.P. thanks the European Commission for a scholarship within the framework of the ERASMUS program.

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