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PAPER

An *N*-heterocyclic carbene ligand based on a β-cyclodextrin–imidazolium salt: synthesis, characterization of organometallic complexes and Suzuki coupling†‡

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A new ligand based on permethylated β-cyclodextrin bearing a methylimidazole group was synthesized. In the presence of this N-heterocyclic carbene ligand, silver or palladium complexes were generated. Interestingly, palladium species based on this ligand are more active than palladium species based on TPP or IMes,Cl for a Suzuki cross-coupling reaction.

The first isolation of stable carbene by Bertrand *et al.*[1] followed by the discovery of *N*-heterocyclic carbene (NHC) by Arduengo *et al.* inspired the development of organometallic and coordination chemistry of NHC ligands.[2] NHCs have emerged as stronger binding and less oxidizable alternative ligands to classical phosphanes.[3] The shape of NHCs significantly differs from that of their phosphane counterparts. In the case of transition-metal phosphane complexes, the phosphane substituents point away from the metal center, forming a cone. In transition-metal NHC complexes, the substituents bound to the carbene nitrogen atom point toward the metal center and thereby surround the metal. NHC ligands possessing bulky groups are therefore particularly interesting. Indeed, successful transformations often require low coordinated organometallic complexes and the sterically demanding NHC ligands favour the formation of such complexes.[4]

In this context, the association of an NHC ligand with a cyclodextrin (CD) moiety is promising, as it would bring together steric crowding around the metal, water-solubility and a spatially close recognition site.[5] Although synthesis of imidazolium CDs has been thoroughly reported in the literature, they have never been used to generate an NHC and used in an organometallic catalytic process. In fact, these compounds were prepared to be used as chiral selectors[6] or linkers for a CD dimer.[7]

We report herein, the first synthesis of an NHC-appended CD, the study of the solubility, aggregation and recognition properties of its imidazolium precursor as well as its coordination and catalytic behaviors.

PM-β-CD-MIM,Cl (**1**) was synthesized in two steps from mono(6-*O*-tosyl)-β-CD (β-CD-OTs), which is easily prepared by the tosylation of β-CD on a large scale.[8] β-CD-OTs was permethylated in the presence of methyl iodide and NaH to give permethylated β-CD-OTs (PM-β-CD-OTs; yield: 50%).[9] PM-β-CD-OTs and 1-methylimidazole (MIM) reacted in DMF to give PM-β-CD-MIM,OTs. Attempts to precipitate this product were unsuccessful, so a dialysis technique was used to separate PM-β-CD-MIM,OTs from DMF and unreacted MIM. To finish, PM-β-CD-MIM,OTs was converted to its chloride salt (**1**) by being passed through an anion-exchange resin. The compound **1** was obtained as a pale yellow solid (yield: 48%) and fully characterized by mass (MALDI-TOF) and NMR spectroscopies (see ESI‡) (Scheme 1).

First of all, solubility tests have shown that **1** is highly soluble in organic solvents such as chloroform (>50 mM at 20 °C), methanol (>100 mM at 20 °C), dichloromethane (>20 mM at 20 °C), dioxane (>100 mM at 20 °C), THF (>20 mM at 20 °C) or DMF (>100 mM at 20 °C) and in water (>40 mM at 20 °C). The compound **1** was firstly characterized by NMR spectroscopy. NMR spectra recorded in $CDCl_3$ show that the chemical shifts of the three protons of the imidazolium ring (H-2, H-4 and H-5) depend on the concentration of **1** (Fig. 1). These concentration-dependent shifts were already observed in the literature and were attributed to π–π stacking interactions between the imidazolium rings.[10] Moreover, ^{1}H NMR spectra recorded in D_2O displayed that deuterium exchange of the proton H-2 of the imidazolium ring was observed as illustrated by the disappearance of the signal for this proton (Fig. 2).[11] This disappearance was also confirmed

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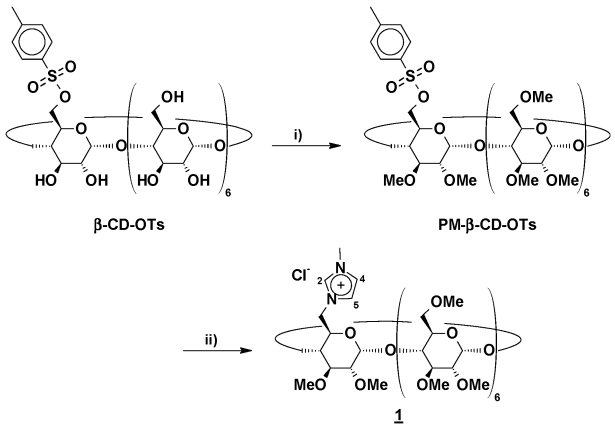


Scheme 1 Synthetic pathway of the cyclodextrin-based imidazolium **1**. Reagents and conditions: (i) CH_3I, NaH, anhyd. DMF, 6 h at 0 °C then 12 h at RT, 50%; (ii) (a) 1-methylimidazole, anhyd. DMF, 72 h at 80 °C; (b) dialysis; (c) ion exchange, 96%.

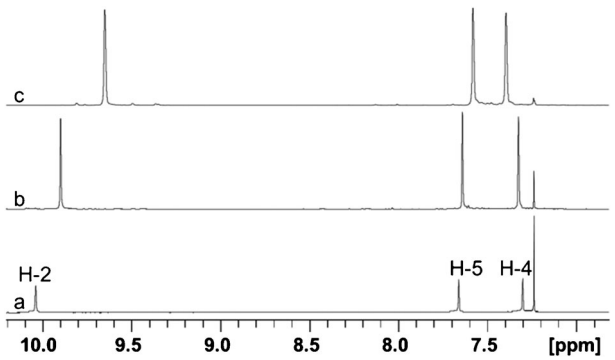


Fig. 1 Partial ^{1}H NMR spectra (20 °C, 700.13 MHz, $CDCl_3$) of **1** recorded at (a) 1.5 mM; (b) 8.0 mM; (c) 40 mM.

by the modification of the H-4 and H-5 NMR signals. Initially, the H-4 and H-5 protons appeared in the form of a pseudo-singlet due to a ^3J coupling between H-4 and H-5 protons and a ^4J coupling between H-2 and H-4 (or H-5) protons (Fig. 2a). Indeed, after complete deuteriation of the acidic site of the imidazolium cycle, the H-4 and H-5 imidazolium protons appeared in the form of a doublet due to a ^3J coupling between H-4 and H-5 protons (Fig. 2c). In this case, a value of 1.77 Hz was determinated for the $^3J_{H\text{-}4/H\text{-}5}$ constant coupling. In order to determine the rate constant for the hydrogen–deuterium exchange reaction, ^{1}H NMR spectra were also recorded at repeated time intervals (see ESI‡). The $k_{H/D}$ rate constant was found to be equal to 4.53×10^{-3} min^{-1} by considering a first order kinetic ($t_{1/2}$ = 2 h 30 min).

The surface active behavior of **1** was investigated by measuring the evolution of the surface tension (γ) *versus* the concentration of **1** in water (Fig. 3). Surprisingly, the curve exhibited two inflection points at 0.02 and 0.37 mM and a plateau was observed at 1.5 mM. The inflection points are characteristic of aggregation phenomena and the plateau corresponds to the formation of micelles in water. In order to have a better insight into the mechanism of aggregates formation, off-resonance ROESY experiments were performed.[12] No dipolar contact was observed between the protons of the imidazolium ring and the internal protons of

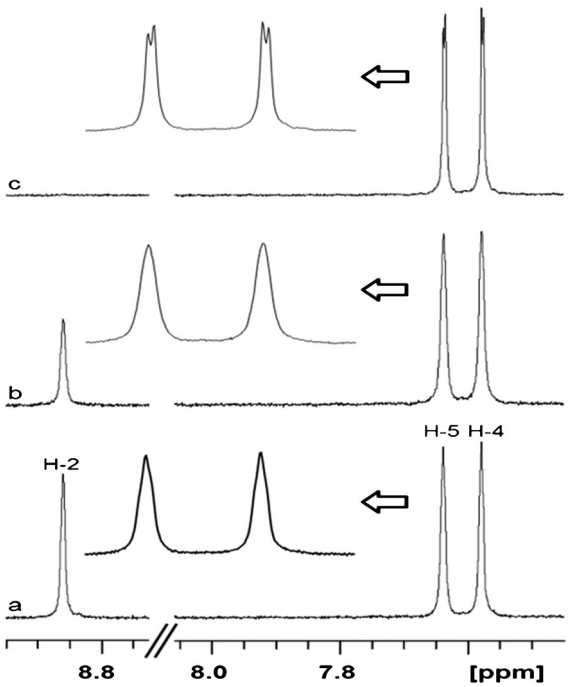


Fig. 2 Partial ^{1}H NMR spectra (20 °C, 700.13 MHz, 2.0 mM, D_2O) of **1** recorded initially (a), after 2 h 30 min (b) and after 22 h (c).

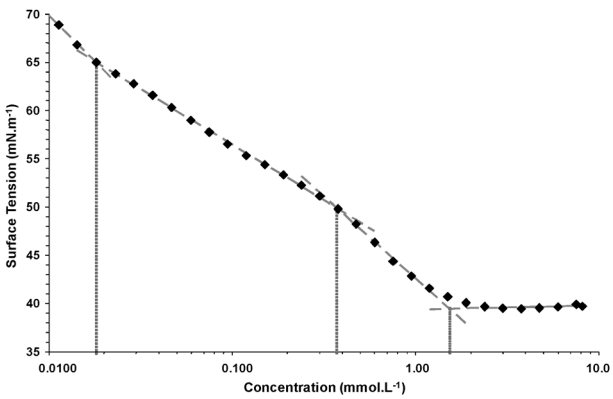


Fig. 3 Surface tension curves of an aqueous solution of **1** at 25 °C.

the CD moiety (see ESI‡). These data clearly indicated that the imidazolium ring is not included into the CD cavity. So, the formation of aggregates are probably due to π–π stacking interactions between imidazolium rings.[13] As no self-inclusion phenomenon was evidenced, the cavity should be able to accommodate a guest. 1-Adamantol was selected to check the inclusion properties because of its high affinity for the β-CD cavity.[14] An off-resonance ROESY experiment performed on a mixture **1**/1-adamantol displayed dipolar contacts between 1-adamantol and CD cavity protons proving that **1** is able to include a guest (Fig. 4). Assuming a 1 : 1 stoichiometry, the value of the association constant between 1-adamantol and **1** was determined by UV-vis spectroscopy and was found to be equal to 5940 M^{-1} (see ESI‡).

The coordination properties of the NHC complexes using **1** as a precursor were also studied. The silver complex (**2**) was prepared in degassed CH_2Cl_2 by mixing **1** (2 eq.) with Ag_2O

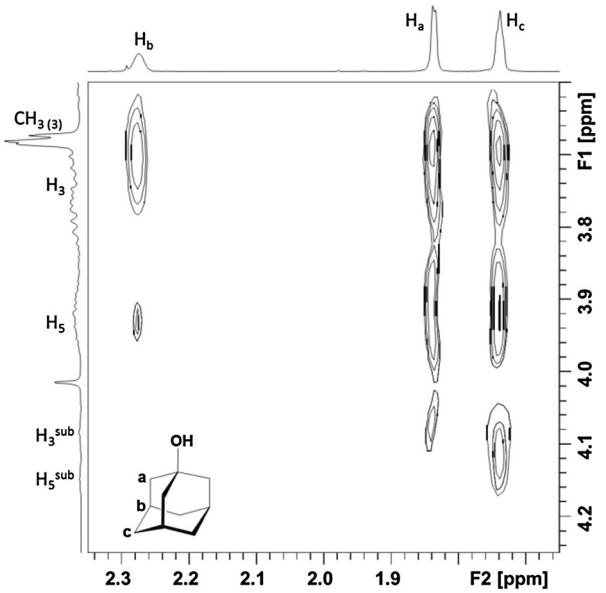
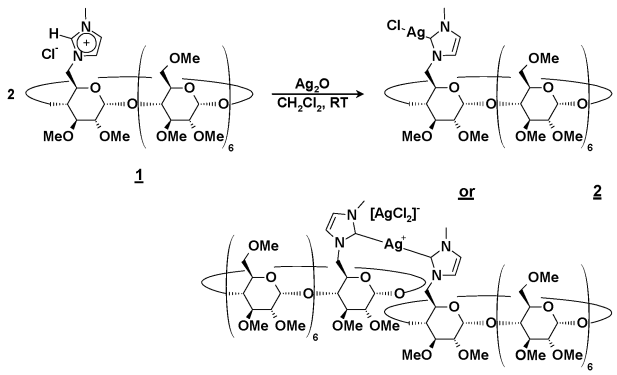


Fig. 4 Partial contour plot of an off-resonance ROESY experiment (15 °C, 599.94 MHz, D_2O, effective angle: 54.7°, mixing time: 300 ms) recorded on a mixture of **1** (0.75 mM) and 1-adamantol (2.25 mM). Horizontal part: 1-adamantol region; vertical part: cyclodextrine region of the spectra.



Scheme 2 Proposed structures for **2**.

(Scheme 2). **2** was sufficiently stable to be characterized by ^1H and ^{13}C NMR spectroscopy. The ^1H and $^{13}C\{^1H\}$ JMOD NMR data reflect significant changes between the imidazolium salts and the carbene complex (Fig. 5 and 6). Indeed, the ^1H NMR spectrum showed the disappearance of the H-2 proton resonance at 10.0 ppm together with a shielding of the aromatic protons (Fig. 5). The formation of the silver(I) carbene complex was confirmed in the $^{13}C\{^1H\}$ JMOD NMR spectra by the disappearance of the C-2 resonance at 139.5 ppm for **1** and the appearance of the C-2 resonance at 171.4 ppm for **2** (Fig. 6). This value is similar to the chemical shifts seen in other silver imidazolylidene complexes.[15] However, no coupling was observed between C-2 and the silver atom. The lack of coupling may be due to reversible coordination of the carbene to the silver center in solution.[16] By analogy with the characterized structures of silver complexes described in the literature, complex **2** can be assigned to a mono or a bis-(imidazol-2-ylidene)silver structure. Unfortunately, attempts to obtain the exact structure were unsuccessful. Indeed, the

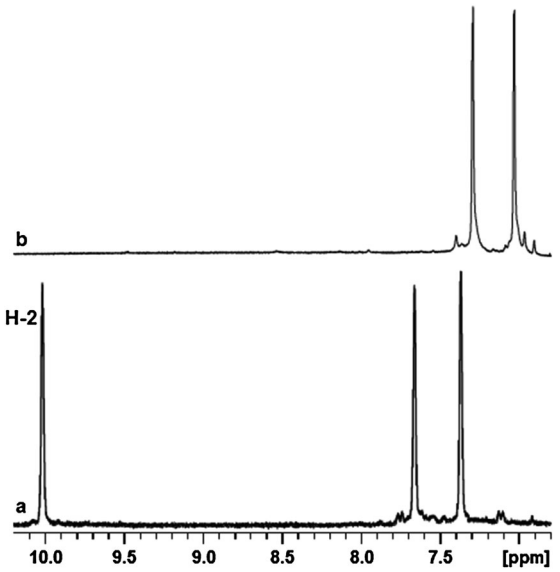


Fig. 5 Partial ^1H NMR spectra (20 °C, 300.13 MHz, 30 mM, CD_2Cl_2) of (a) **1** and (b) **2**.

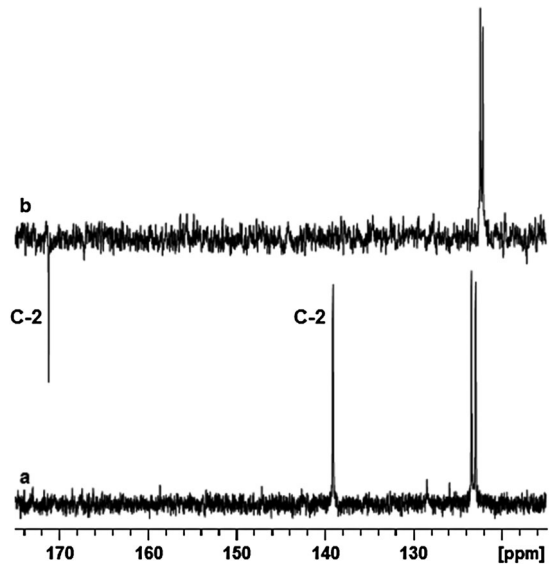


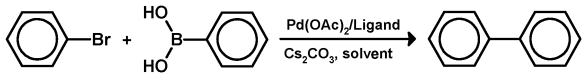
Fig. 6 Partial $^{13}C\{^1H\}$ JMOD NMR spectra (20 °C, 300.13 MHz, 30 mM, CD_2Cl_2) of (a) **1** and (b) **2**.

electrospray mass spectrum of **2** only showed the signal of **1** probably due to the poor stability of the complex under the ESI‡ conditions. Moreover, no X-ray structure was obtained because of difficulties to obtain the crystallisation of **2**.

Finally, catalytic behaviour of the system was probed. The palladium catalyzed Suzuki coupling reaction of phenyl bromide with phenylboronic acid was chosen as model reaction to evaluate the capacity of **1** to stabilize active catalytic species.[17]

All reactions were carried out with $Pd(OAc)_2$ as a palladium source and Cs_2CO_3 as a base. No catalytic activity was observed without the ligand in a control experiment (Table 1, entry 1). For the following experiments, the catalyst was formed *in situ* from **1** (or other ligand) and $Pd(OAc)_2$ in the presence of Cs_2CO_3. A first set of reactions was performed in 1,4-dioxane (entries 1–7), THF being a less suitable solvent

Table 1 Suzuki cross-coupling of phenylbromide and phenylboronic acid to yield biphenyl[a]



Entry	Solvent	Ligand	L/Pd	Yield[b] (%)
1	Dioxane	(–)	(–)	0
2	Dioxane	**1**	1	52
3[c]	Dioxane	**1**	1	60
4	Dioxane	**1**	2	39
5[c]	Dioxane	**1**	2	99
6[d]	Dioxane	TPP	5	17
7	Dioxane	IMes,Cl	2	25
8	THF	**1**	2	22
9	Water	**1**	2	1
10	Dioxane/water[e]	**1**	2	15
11	Toluene/water[f]	**1**	2	5
12	Dioxane	β-CD-MIM,Cl	2	2

[a] Experimental conditions: $Pd(OAc)_2$ (2.22×10^{-2} mmol), solvent (5 mL), bromobenzene (3.34 mmol), phenylboronic acid (4.01 mmol), Cs_2CO_3 (6.68 mmol), *T*: 50 °C; time: 6 hours. [b] Yield calculated from bromobenzene. [c] Time: 16 hours. [d] For a ratio Pd/TPP inferior to 5, the catalytic system was unstable (presence of black palladium precipitate). [e] *v*(dioxane)/*v*(water) = 75/25. [f] *v*(toluene)/*v*(water) = 50/50.

(entries 4 *vs.* 8). Although the kinetics of the reaction is faster during the first 6 hours using one equivalent of **1**, two equivalents lead to a better stabilization of the catalytic species (compare entries 2 and 4) and allow a total conversion after 16 hours (compare entries 3 and 5).[18]

Two comparison experiments were conducted in the presence of the classical ligand triphenylphosphane (TPP) and the typical NHC ligand 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (IMes,Cl). Interestingly, the catalytic activity observed in the presence of **1** is 1.5 and 2-fold higher than in the presence of IMes,Cl and TPP, respectively (compare entry 4 with entries 6 and 7). As **1** is water-soluble, the catalytic activity of Pd–NHC complexes derived from **1** was also evaluated in water. Indeed, only few hydrophilic metal–NHC complexes have been used during organometallic catalytic processes.[19] In pure water, the catalytic activity dramatically decreased (entry 9). The same tendency was also observed in a mixture of dioxane/water or toluene/water (entries 10 and 11). From these results, it appears that the catalytic system is unstable in water. An experiment performed in dioxane by replacing **1** by its hydroxylated equivalent (β-CD-MIM,Cl; the hydroxyl groups of CD are not methylated) confirmed that the presence of labile protons has a disastrous influence on the catalytic activity (entry 12).

As a summary, we have prepared a new CD-appended imidazolium salt ligand (**1**), which is soluble in water and in organic solvents and displays aggregation properties depending on concentration. Its cavity is however available for inclusion of a hydrophobic guest. Silver complexes could also be generated with **1**. Furthermore, a Suzuki cross-coupling reaction was performed using **1** generating catalytic active species with a palladium precursor. It is important to underline that palladium species based on **1** are more active than those based on the classical ligand such as TPP or IMes,Cl. Unfortunately, the catalytic experiments performed in water failed probably due to the unstability of this carbene in the presence of labile protons. Work is currently in progress to synthesize isolable NHC appended to CDs for organometallic catalysis.

Experimental

Synthesis of 6^A-deoxy-6^A-(3-*N*-methylimidazolium)-$2^A,2^B,2^C,2^D,2^E,2^F,2^G,3^A,3^B,3^C,3^D,3^E,3^F,3^G,6^B,6^C,6^D,6^E,6^F,6^G$-eicosa-*O*-methyl-β-cyclodextrin chloride salt 1

N-Methylimidazole (2.63 g *i.e.* 2.55 mL, 32 mmol) was added under an inert atmosphere to a stirred solution of dried PM-β-CD-OTs (5.0 g, 3.2 mmol) in dry DMF (10 mL). The reaction mixture was stirred for 72 h at 80 °C under nitrogen. After evaporation of most of the solvent under reduced pressure, the residual syrup was then purified by dialysis (MWCO 1000 Da, Spectra/Por® 7 dialysis membrane, Spectrum Laboratories) against 5 L deionized water while stirring at 20 °C. The water was changed after 2 h followed by an additional 2 h of dialysis. The last step was repeated all five times to give after evaporation under reduced pressure the tosylate salt of **1** as a yellow powder. Finally, this powder was dissolved in deionised water and replacement of tosylate by chloride was performed by using an Amberlite® IRA-900 Cl resin. The solution was filtered and the corresponding filtrate was collected and the solvent was removed by evaporation under reduced pressure to give the desired product, chloride salt **1** as a yellow amorphous solid (4.45 g, 96%).

$[\alpha]_D^{20} = +267.5°$ (*c* 2.0, H_2O); ^{1}H NMR (700.13 MHz, $CDCl_3$, 293.0 K): δ = 9.85 (ps, 1H, N–CH═N), 7.64 (ps, 1H, CH_2–N–CH═CH), 7.32 (ps, 1H, CH_3–N–CH═CH), 5.15 (d, 1H, $^3J_{H_1-H_2}$ = 3.3 Hz, H_{1sub}), 5.13 (d, 1H, $^3J_{H_1-H_2}$ = 3.6 Hz, H_1), 5.10 (d, 1H, $^3J_{H_1-H_2}$ = 3.4 Hz, H_1), 5.08 (d, 1H, $^3J_{H_1-H_2}$ = 3.4 Hz, H_1), 5.05 (d, 1H, $^3J_{H_1-H_2}$ = 3.3 Hz, H_1), 5.05 (vt, 2H, $^3J_{H_1-H_2}$ = 4.5 Hz, H_1), 4.79 (dd, 1H, $^3J_{H_5-H_{6'}}$ = 2.8 Hz, $^2J_{H_6-H_{6'}}$ = 14.7 Hz, $H_{6'sub}$), 4.57 (dd, 1H, $^3J_{H_5-H_6}$ = 2.7 Hz, $^2J_{H_6-H_{6'}}$ = 14.7 Hz, $H_{6'sub}$), 4.16 (s, 3H, N–CH_3), 4.12 (m, 1H, H_{5sub}), 3.98–3.22 (m, 91H, H_{3sub}, H_3, H_4, H_5, H_6, $H_{6'}$, Me_2, Me_3, Me_6), 3.21–3.12 (m, 6H, H_2), 3.00 (dd, 1H, $^3J_{H_1-H_2}$ = 3.3 Hz, $^3J_{H_2-H_3}$ = 10.3 Hz, H_{2sub}), 2.98 (t, 1H, $^3J_{H_3-H_4} \approx {}^3J_{H_4-H_5}$ = 9.5 Hz, H_{4sub}); ^{13}C NMR (176.06 MHz, $CDCl_3$, 293.0 K): 139.51 (1 × N–CH═N), 123.83 (1 × CH_2–N–CH═CH), 122.66 (1 × CH_3–N–CH═CH), 100.42, 100.22, 99.30, 99.19, 99.12 (6 × C_1), 98.02 (1 × C_{1sub}), 82.48, 82.34, 82.25, 82.09, 81.85, 81.78, 81.73, 81.45, 81.42, 81.28, 81.08, 80.84, 80.78, 80.58, 80.04, 79.87 (7 × C_2, 7 × C_3, 7 × C_4), 72.75, 71.99, 71.53, 71.42, 71.39, 71.35, 71.18, 71.15, 71.03 (6 × C_5, 6 × C_6), 68.77 (1 × C_{5sub}), 61.92, 61.72, 61.65, 61.59, 61.54, 61.32 (6 × Me_6), 60.11, 59.42, 59.24, 59.12, 59.06, 58.80, 58.59, 58.54, 58.47 (7 × Me_2, 7 × Me_3), 49.92 (1 × C_{6sub}), 37.21 (1 × N–CH_3); MALDI-TOF-MS: *m*/*z* = 1479.576 (calcd. 1479.733 for $[C_{66}H_{115}O_{34}N_2Cl–Cl]^+$); UV-vis (water, 293.15 K); λ_{max} = 211 nm, log ε = 3.71.

Synthesis of silver(I)–carbene complex 2

The silver(I)–carbene complex **2** was synthesised from **1** *via* a procedure adapted from the literature.[20] Briefly, Ag_2O (6 mg, 0.025 mmol) was added to a degassed solution of **1** (76 mg, 0.05 mmol) in anhydrous dichloromethane (1 mL). The reaction mixture was stirred at room temperature in the dark,

by recovering the Schlenk flask with aluminium foil, until discoloration of the dark solution. After this stirring period, the mixture was filtered through Celite® to give a pale yellow filtrate. The solvent was removed under reduced pressure and the resulting solid was dried under reduced pressure to afford a pale yellow material (97% yield).

^{1}H NMR (300.13 MHz, CD_2Cl_2, 295.1 K): δ = 7.30 (d, 1H, $^3J_{H-H}$ = 1.6 Hz, CH_2–N–CH=CH), 7.03 (d, 1H, $^3J_{H-H}$ = 1.6 Hz, CH_3–N–CH=CH), 5.14–5.08 (m, 4H, H_1), 5.07 (d, 1H, $^3J_{H1-H2}$ = 3.5 Hz, H_1), 5.03 (d, 1H, $^3J_{H1-H2}$ = 3.3 Hz, H_1), 5.00 (d, 1H, $^3J_{H_1-H_2}$ = 3.5 Hz, H_1), 4.81 (dd, 1H, $^3J_{H_5-H_{6'}}$ = 1.5 Hz, $^2J_{H_6-H_{6'}}$ = 13.9 Hz, $H_{6'\,sub}$), 4.43 (dd, 1H, $^3J_{H_5-H_6}$ = 1.9 Hz, $^2J_{H_6-H_{6'}}$ = 13.9 Hz, $H_{6'sub}$), 4.06–2.96 (m, 103H, N–CH_3, H_2, H_3, H_4, H_5, H_6, $H_{6'}$, Me_2, Me_3, Me_6); ^{13}C NMR (75.49 MHz, CD_2Cl_2, 295.1 K): 171.38 (1 × N–C(Ag)=N), 122.59 (1 × CH_2–N–CH=CH), 122.31 (1 × CH_3–N–CH=CH), 99.76, 99.73, 99.45, 99.08, 98.98, 98.94, 98.45 (7 × C_1), 84.21, 82.77, 82.72, 82.67, 82.61, 82.51, 82.47, 82.40, 82.36, 82.21, 82.08, 80.83, 80.62, 80.47, 80.36, 80.33, 79.73 (7 × C_2, 7 × C_3, 7 × C_4), 73.12, 72.32, 72.13, 71.90, 71.81, 71.70, 71.63, 71.61, 71.39, 71.25, 71.00 (7 × C_5, 6 × C_6), 62.03, 61.80, 61.70, 61.65, 61.52, 61.41 (6 × Me_6), 59.65, 59.54, 59.50, 59.44, 59.33, 59.19, 59.18, 58.98, 58.90, 58.80, 58.59, 58.44 (7 × Me_2, 7 × Me_3), 53.8 (1 × C_{6sub}, resonance overlapped by solvent signals), 39.24 (1 × N–CH_3).

General procedure for the Suzuki–Miyaura cross-coupling reaction

The first step was the preparation of the catalytic solutions under nitrogen using standard Schlenk techniques. In a typical experiment, $Pd(OAc)_2$ (2.22×10^{-2} mmol), **1** (4.44×10^{-2} mmol) and caesium carbonate (6.68 mmol) were dissolved in 10 mL of deoxygenated 1,4-dioxane and stirred for about one hour at 1250 rpm. Then, after this incubation step, the catalytic solution was added to degassed bromobenzene (3.34 mmol) and phenylboronic acid (4.01 mmol). The glass reactor was then heated at 50 °C, stirred with a magnetic stirrer at 1250 rpm. For kinetic measurements the time corresponding to the desired temperature was considered as the beginning of the reaction. The reaction medium was sampled during the reaction by GC analyses.

Acknowledgements

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Notes and references

1 A. Igau, H. Grutzmacher, A. Baceiredo and G. Bertrand, *J. Am. Chem. Soc.*, 1988, **110**, 6463.
2 A. J. Arduengo, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361.
3 S. Leuthäusser, D. Schwarz and H. Plenio, *Chem.–Eur. J.*, 2007, **13**, 7195; A. Azua, S. Sanz and E. Peris, *Organometallics*, 2010, **29**, 3661.
4 S. Würtz and F. Glorius, *Acc. Chem. Res.*, 2008, **41**, 1523.
5 For cyclodextrin-phosphane used during organometallic catalytic processes, see: M. T. Reetz and S. R. Waldvogel, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 865; M. T. Reetz, *Catal. Today*, 1998, **42**, 399; M. T. Reetz, *J. Heterocycl. Chem.*, 1998, **35**, 1065–1073; M. T. Reetz and C. Frömbgen, *Synthesis*, 1999, 1555; D. Armspach and D. Matt, *Chem. Commun.*, 1999, 1073; Y. T. Wong, C. Yang, K. C. Ying and G. Jia, *Organometallics*, 2002, **21**, 1782; E. Engeldinger, D. Armspach, D. Matt and P. G. Jones, *Chem.–Eur. J.*, 2003, **9**, 3091–3105; L. Poorters, D. Armspach, D. Matt and L. Toupet, *Dalton Trans.*, 2007, 3195; C. Machut-Binkowski, F. X. Legrand, N. Azaroual, S. Tilloy and E. Monflier, *Chem.–Eur. J.*, 2010, **16**, 10195; S. Guieu, E. Zaborova, Y. Blériot, G. Poli, A. Jutand, D. Madec, G. Prestat and M. Sollogoub, *Angew. Chem., Int. Ed.*, 2010, **49**, 2314; R. Gramage-Doria, D. Armspach, D. Matt and L. Toupet, *Angew. Chem., Int. Ed.*, 2011, **50**, 1554; F. X. Legrand, N. Six, C. Slomianny, H. Bricout, S. Tilloy and E. Monflier, *Adv. Synth. Catal.*, 2011, DOI: 10.1002/adsc.201000917.
6 For examples, see: G. Galaverna, R. Corradini, A. Dossena, R. Marchelli and G. Vecchio, *Electrophoresis*, 1997, **18**, 905; T. T. Ong, T. Weihua, W. Muderawan, S. C. Ng and H. Sze On Chan, *Electrophoresis*, 2005, **26**, 3839; K. Huang, X. Zhang and D. W. Armstrong, *J. Chromatogr., A*, 2010, **1217**, 5261.
7 R. Breslow and S. Halfon, *Proc. Natl. Acad. Sci. U. S. A.*, 1992, **89**, 6916; R. Breslow, S. Halfon and B. Zhang, *Tetrahedron*, 1995, **51**, 377.
8 R. C. Petter, J. S. Salek, C. T. Sikorski, G. Kumaravel and F. T. Lin, *J. Am. Chem. Soc.*, 1990, **112**, 3860.
9 J. A. Faiz, N. Spencer and Z. Pikramenou, *Org. Biomol. Chem.*, 2005, **3**, 4239.
10 L. Leclercq and A. R. Schmitzer, *J. Phys. Chem. A*, 2008, **112**, 4996.
11 T. L. Amyes, S. T. Diver, J. P. Richard, F. M. Rivas and K. Toth, *J. Am. Chem. Soc.*, 2004, **126**, 4366; T. Fahlbusch, M. Frank, J. Schatz and D. T. Schühle, *J. Org. Chem.*, 2006, **71**, 1688.
12 H. Desvaux, P. Berthault, N. Birlirakis and M. Goldman, *J. Magn. Reson., Ser. A*, 1994, **108**, 219; H. Desvaux, P. Berthault, N. Birlirakis, M. Goldman and M. Piotto, *J. Magn. Reson., Ser. A*, 1995, **113**, 47; H. Desvaux and P. Berthault, *J. Chim. Phys. Phys.-Chim. Biol.*, 1996, **93**, 403; H. Desvaux and P. Berthault, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1999, **35**, 295.
13 L. Leclercq and A. R. Schmitzer, *J. Phys. Chem. B*, 2008, **112**, 11064.
14 M. V. Rekharsky and Y. Inoue, *Chem. Rev.*, 1998, **98**, 1875.
15 A. J. Arduengo, III, H. V. R. Dias, J. C. Calabrese and F. Davidson, *Organometallics*, 1993, **12**, 3405.
16 L. C. Moore, S. M. Cooks, M. S. Anderson, H. J. Schanz, S. T. Griffin, R. D. Rogers, M. C. Kirk and K. H. Shaughnessy, *Organometallics*, 2006, **25**, 5151.
17 For reviews, see: N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457; S. P. Stanforth, *Tetrahedron*, 1998, **54**, 263; A. Suzuki, *J. Organomet. Chem.*, 1999, **576**, 147.
18 Black palladium precipitate is observed after 6 hours of reaction with one equivalent of **1** explaining the decrease in catalytic activity.
19 For examples, see: W. A. Herrmann, M. Elison, J. Fischer and C. Kocher, *US Pat.* 5 663 451, 1997; I. Özdemir, B. Yigit, B. Cetinkaya, D. Ülkü, M. N. Tahir and C. Arici, *J. Organomet. Chem.*, 2001, **633**, 27; M. T. Zarka, M. Bortenschlager, K. Wurst, O. Nuyken and R. Weberskirch, *Organometallics*, 2004, **23**, 4817; D. Schönfelder, O. Nuyken and R. Weberskirch, *J. Organomet. Chem.*, 2005, **690**, 4648; D. Schönfelder, K. Fischer, M. Schmidt, O. Nuyken and R. Weberskirch, *Macromolecules*, 2005, **38**, 254; J. P. Gallivan, J. P. Jordan and R. H. Grubbs, *Tetrahedron Lett.*, 2005, **46**, 2577; S. H. Hong and R. H. Grubbs, *J. Am. Chem. Soc.*, 2006, **128**, 3508; J. W. Kim, J. H. Kim, D. H. Lee and Y. S. Lee, *Tetrahedron Lett.*, 2006, **47**, 4745; C. Fleckenstein, S. Roy, S. Leuthäußer and H. Plenio, *Chem. Commun.*, 2007, 2870; J. P. Jordan and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2007, **46**, 5152; F. Tewes, A. Schlecker, K. Harms and F. Glorius, *J. Organomet. Chem.*, 2007, **692**, 4593; H. Ohta, T. Fujihara and Y. Tsuji, *Dalton Trans.*, 2008, 379; M. Meise and R. Haag, *ChemSusChem*, 2008, **1**, 637; J. Mesnager, P. Lammel, E. Jeanneau and C. Pinel, *Appl. Catal., A*, 2009, **368**, 22; J. Mesnager, C. Quettier, A. Lambin, F. Rataboul, A. Perrard and C. Pinel, *Green Chem.*, 2010, **12**, 475; A. Almássy, C. E. Nagy, A. C. Bényei and F. Joó, *Organometallics*, 2010, **29**, 2484; S. Roy and H. Plenio, *Adv. Synth. Catal.*, 2010, **352**, 1014.
20 H. M. J. Wang and I. J. B. Lin, *Organometallics*, 1998, **17**, 972.