Dissimilar catalytic behavior of molecular or colloidal palladium systems with a new NHC ligand†

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In this work, we describe the synthesis of a new N-heterocyclic carbene (NHC) ligand, derived from a hybrid pyrazole-imidazolium scaffold, namely 1-{2-(3,5-dimethylpyrazol-1-yl)ethyl}-3-[(5)-(1-phenylethyl)-3H-imidazol-2-ylidene (L). This ligand has been used as a stabilizer for the organometallic synthesis of palladium(0) nanoparticles (Pd NPs). L presents a better stabilizing effect than its pre-carbenic HLCI counterpart, allowing the formation of isolated Pd NPs while HLCI yields aggregated ones. Additionally, molecular Pd(ii) coordination compounds of L and HLCI were synthesized and characterized to better understand the coordination modes of these ligands. Both molecular and colloidal Pd systems have been further tested in catalytic C–C coupling processes. Three different types of reactions have been observed depending on the catalytic system: (i) the Suzuki–Miyaura reaction takes place with Pd molecular complexes; (ii) a secondary reaction, the dehalogenation of the substrate, is always detected and (iii) the C–C homocoupling between two molecules of bromoarenes is observed with colloidal catalysts.

Introduction

During the last few years, the use of N-heterocyclic carbenes (NHCs) as primary ligands has emerged in catalysis and beyond. Amongst other catalytic processes, organometallic compounds containing these ligands have been applied in the cross-coupling reactions of un-activated substrates.1 This can be explained not only by their remarkably strong σ-binding and steric tunability,2 but also by their ability to stabilize highly unusual and hitherto elusive reactive species such as metal nanoparticles (MNPs) thanks to their stability under oxidative conditions once coordinated.3 Thus, NHCs have become ligands of paramount importance in nanochemistry given their advantageous behavior for the stabilization and functionalization of MNPs.4 Although different families of NHCs have been largely explored in various important organic transformations when combined with metal pre-catalysts, imidazolium salts are the most frequently employed as the core structures for NHCs given their straightforward syntheses and feasible tuning properties.5

Different methodologies can be followed to obtain and stabilize NPs in different media while controlling their size, shape and composition, which, in turn, can tune their unique properties.6 The use of coordinating ligands is of particular interest to prepare MNPs because it gives the possibility of modulating their surface properties as known for the synthesis of molecular complexes.7 As a consequence, ligand-stabilized MNPs became very attractive for applications.8 MNPs are able to catalyze not only reactions that can also be catalyzed by molecular complexes (i.e. C–C coupling or hydrogenation of olefins) but also reactions that cannot be catalyzed by molecular complexes (i.e. hydrogenation of arenes).

Furthermore, palladium is the most versatile transition metal in chemical catalytic reactions since many of these processes cannot be catalyzed by other transition metals.9 Thus, Pd(0) NPs have shown large catalytic efficiency in C–C coupling...
Reactions specially when non-aggregated homogeneous NPs of 1–4 nm size are used as catalysts.\textsuperscript{19} The Suzuki–Miyaura reaction is one of the most important cross-coupling processes from an industrial point of view.\textsuperscript{11} It allows to easily obtain biaryl products, important intermediates in the organic syntheses of various target products ranging from performance materials to pharmaceuticals.\textsuperscript{12} Although noble metal complexes are usually employed as catalysts for this reaction, MNPs merit study since playing with stabilizing ligands may tune their catalytic performance.\textsuperscript{13}

Our research group has focused on discerning the catalytic behavior of colloidal and molecular palladium systems in C–C coupling reactions. For example, we have recently studied Pd molecular/colloidal systems containing new hybrid pyrazole derived ligands with alkylether, alkylthioether or alkylamino moieties leading to different catalytic outputs depending on the system.\textsuperscript{14} Here we present improved Pd systems based on a new NHC–pyrazole hybrid ligand. Interestingly, as it will be described hereafter, different behaviors were observed in C–C coupling catalysis that illustrates the possibility of optimizing the catalytic system according to the final aim.

Results and discussion

Synthesis of the ligand (L)

For the synthesis of 1-[2-(3,5-dimethylpyrazol-1-yl)ethyl]-3-((S)-1-phenylethyl)-3H-imidazol-1-ium chloride (HLCl), 1-(2-chloroethyl)-3,5-dimethyl-1H-pyrazole and 1-(S)-(phenylethyl)imidazol-2-ylidine (L) was achieved by reacting HLCl with NaH and a catalytic amount of BuOK in anhydrous dichloromethane (Scheme 1). Both L and HLCl have been fully characterized by NMR and IR spectroscopies as well as by ESI-MS (Fig. S1–S6 in the ESI\textsuperscript{†}).

Synthesis of Pd(0) nanoparticles (Pd NPs)

Ligand L has been used to prepare Pd NPs according to the organometallic approach under mild reaction conditions.\textsuperscript{15} The syntheses have been carried out by reacting [Pd\textsubscript{2}(dba)\textsubscript{3}] (dba = dibenzylideneacetone) and L ([L]/[Pd] molar ratios varying from 0.1 to 1.0) in anhydrous dichloromethane for 18 h in a Fisher-Porter reactor, under 3 bar of dihydrogen at room temperature. Finally, Pd NPs were precipitated and washed with cold pentane and dried under reduced pressure.

TEM (transmission electron microscopy) and SEM (scanning electron microscopy) analyses (after deposition/drying of a drop of crude colloidal solutions onto a holey carbon-covered copper grid) were performed with all the obtained samples. The results showed that the Pd NPs are aggregated into superstructures when a L/Pd ratio of 0.1 is used (HR-TEM images are shown in Fig. 1a and SEM-FEG images are shown in ESI, Fig. S7a\textsuperscript{†}). The single NPs are spherical and have a mean size of 3.6(0.9) nm but the superstructures do not have a preferential shape and their size varies from 50 to 250 nm. For L/Pd ratios of 0.3, 0.5 and 1.0, only isolated NPs were observed (Fig. 1b–d). In all these cases, NPs are spherical and present similar mean sizes in the range of 2.1–2.4 nm. These similar sizes indicate that a minimum L/Pd molar ratio of 0.3 is needed to have stable isolated NPs, but the addition of a higher ligand/metal ratio does not have a significant effect on the size of the NPs.

For comparative purposes, the stabilization of the NPs has also been attempted with the protonated ligand HLCl (see HR-TEM images in Fig. 2 and SEM-FEG images in ESI, Fig. S7b–d\textsuperscript{†}). In this case, a molar ratio of 0.1 failed to afford stable NPs. For molar ratios of 0.3 and 0.5 Pd NPs appeared organized into superstructures, and for the molar ratio of 1.0, a mixture of isolated and aggregated NPs was observed. The mean sizes of these NPs are 3.0(0.7), 3.2(0.9) and 2.1(0.9) nm for HLCl/Pd molar ratios of 0.3, 0.5 and 1.0, respectively.

Thus, with HLCl a higher ratio of ligand is needed to successfully stabilize the NPs. From these results and given the main difference of the two ligands (L is a carbene while HLCl is not deprotonated), we believe that the stabilization of the Pd NPs takes place by the coordination of L through the carbene (M–C) and pyrazolic (M–N) groups to the surface of the Pd NPs whereas HLCl would only coordinate through the pyrazolic group (Scheme 1).
The presence of the ligands \( L \) or \( HLCl \) in \( N1 \) or \( N2 \) (those prepared with \( L \) and \( HLCl \), respectively, in a ligand/Pd molar ratio equal to 0.5) has been demonstrated by IR spectroscopy (Fig. S8† and the Experimental section), and ICP-OES and elemental analyses. The Pd/ligand ratios found are Pd\(_{561}L_{37}\) and Pd\(_{1415}HLCl_{93}\) for \( N1 \) and \( N2 \), respectively.

Wide-angle X-ray scattering (WAXS) measurements have been performed on nanoparticles \( N1 \) and \( N2 \). The two radial distribution functions (RDFs) (Fig. 3a) are very similar and in good agreement with the fcc structure of bulk Pd. However, significant distances can be observed of at least up to 4 nm, thus being in disagreement with the sizes obtained from HR-TEM (2.1(0.9) and 3.2(0.9) for \( N1 \) and \( N2 \), respectively). Indeed, when compared with the RDF computed (Fig. 3b) from a spherical model 2.0 nm in diameter, the agreement does not go beyond 1.5 nm. A much better result can be obtained with a dual size model, including a small amount (10%) of much bigger spherical particles (5 nm in diameter). Actually, this dual size model is likely itself oversimplified and different combinations including a large majority of 2 nm particles and a minority of bigger ones should probably lead to the same level of agreement. This result, however, is not in contradiction with the TEM results taking into account not only the mean sizes but also the relatively large tail on the bigger size side.

**Synthesis and characterization of Pd(II) molecular complexes (C1–C2)**

Pd(II) molecular complexes of \( L \) and \( HLCl \) have been synthesized in order to better understand the coordination properties of these ligands (Scheme 1).

The silver carbene transmetallation reaction is a general procedure for the preparation of palladium–carbene complexes\(^{16}\) and was considered to obtain the Pd complex with \( L \). The silver complex of \( L \) (CAg) was prepared by reacting silver dioxide and \( HLCl \) in anhydrous dichloromethane. The \(^1H\) NMR spectrum of this complex shows that the pre-carbene proton of the imidazolium salt is no longer present, thus confirming the deprotonation of the imidazolium group and formation of the Ag–NHC bond (Fig. 4 and Fig. S9†). Also, the formation of CAg has been confirmed by ESI-MS and IR spectroscopy (Fig. S10 and S11† respectively). The next step consisted of the reaction of CAg with [PdCl\(_2\)(cod)] in anhydrous...
dichloromethane (Scheme 1) to obtain the carbenic Pd complex [PdCl$_2$L] (C1). The absence of the pre-carbene proton in the $^1$H-NMR spectrum of C1 confirms the formation of the Pd–NHC bond (Fig. 4 and Fig. S12†). The formation of the complex has been attested by HR-ESI-MS and IR spectroscopy (Fig. S13 and S14,† respectively). Moreover, the NMR data also evidence the chelation of the ligand to the metallic centre through the NHC and pyrazolic groups. The rigidity imposed by this coordination mode causes the two protons of each CH$_2$ in the N–CH$_2$CH$_2$–N moiety (H$_8$ and H$_9$) to become diastereotopic, resulting in four visible signals assigned to a single hydrogen atom each (see high-resolution NMR spectra of C1 including $^1$H and $^{13}$C NMR spectroscopy chemical shift assignments in Fig. S12a and b†). It is also noticeable that some proton signals split, which is a single quote labeled in Fig. S12a.† This splitting is due to conformational exchange between a major and a minor component with a ratio of approximately 70/30, as deduced from signal integration.

In order to study further this chemical exchange process, a 2D ROESY (Rotating Frame Overhauser Effect Spectroscopy) spectrum was recorded.17 Briefly explained, in this NMR experiment ROE and occasionally chemical exchange cross peaks are observed.18 The former are indicative of through space distance proximity, and the latter are detected when protons experience distinct chemical environments, which is commonly the case when a conformational equilibrium is present. The distinction of the above mentioned different cross peaks families is possible from the opposite signal phase in the ROESY spectrum. Fig. 5 and S12d† show the 2D ROESY spectrum of C1, where chemical exchange cross peaks are detected in the negative phase (blue color), while ROE cross peaks are positive phased (red color). Thus, protons H$_8$ and H$_9$ in the ethyl chain undergo a pronounced chemical environment exchange, with cross peaks situated notably separated from the spectrum diagonal. This conformational exchange

Fig. 3 WAXS measurements on Pd nanoparticles for N1 and N2 and comparison with Pd fcc in reciprocal space (a) and real space (b).

Fig. 4 $^1$H-NMR of HLCl, L and CAg registered at 360 MHz (CDCl$_3$, 298 K) and C1 registered at 600 MHz (CDCl$_3$, 298 K).

Fig. 5 2D ROESY spectrum of C1 registered at 600 MHz (CDCl$_3$, 298 K). Arrows pointing negative cross peaks (blue color) indicate chemical exchange between H$_8$ and H$_9$ protons.
might be explained on the basis of a slow conformational equilibrium of the new seven-membered ring formed. Other protons (H₄, H₆, H₇, H₁₃, H₁₄ and H₁₆) also exhibit chemical exchange cross peaks, which are closer to the spectrum diagonal, indicating that chemical exchange is taking place between less differentiated chemical environments. This latter effect could be explained as a side-effect from the mentioned seven ring conformational exchange. On the other side, neither benzyl ring protons H₁₈–H₂₂ nor H₁₅ show any chemical exchange cross peaks, suggesting that these protons are situated far enough from the conformational exchange described.

On the other hand, the direct reaction of HLCl with PdCl₂ in acetonitrile yielded the complex [PdCl₃(HL)] (C₂, Scheme 1), which has been characterized by NMR and IR spectroscopies and ESI-MS (Fig. S15–S17†), thus confirming its stoichiometry. Interestingly, the existence of the protonated ligand HL⁺ is confirmed by the singlet ¹H NMR spectroscopy resonance appearing at 9.03 ppm for the H₁₁ pre-carbene proton (Fig. S15†).

Crystal and molecular structure of trichloro[(S)-3-(2-(3,5-dimethyl-1H-pyrazol-1-yl)(ethyl)-1(1-phenylethyl)-1H-imidazol-3-ium-κ¹N]palladium(u) (C₂)

Single crystals of C₂ suitable for X-ray diffraction analysis were obtained by slow evaporation of a concentrated acetonitrile solution of the complex at RT. The structure of C₂ consists of monomeric [PdCl₃(HL)] units (Fig. 6a), linked by van der Waals forces (Fig. 6b). The palladium center is coordinated by three terminal chloride ligands and one pyrazolic nitrogen from a 1-[2-(3,5-dimethylpyrazol-1-yl)ethyl]-3-(1-phenylethyl)-3H-imidazol-1-ium cation in a slightly distorted square-planar geometry. Crystallographic data are listed in Table S1† and the data on selected bond lengths and angles are gathered in Table S2.† The positive charge generated by the imidazolium cation is canceled by the negative charge provided by the third chloride ion coordinated to Pd(u), thus forming a zwitterionic structure.

There are three complexes reported in the literature with a PdCl₃N core (terminal chloride ligands and pyrazolic nitrogen).¹⁹–²¹ The Pd–N and Pd–Cl bond lengths here observed are comparable to the values found in the literature, and the N–Pd–Cl and Cl–Pd–Cl bond angles slightly deviate from the square planar angles (Table S2†).

In compound C₂, chlorine atoms (Cl₂ and Cl₃, Fig. 6b) form three different hydrogen bonds: C₃–H₃A⋯Cl₂ (2.707 Å, 146.11°) and C₁₅–H₁₅⋯Cl₃ (2.935 Å, 154.30°) interacting with hydrogens from the ethylene group of an adjacent C₂ unit, and C₁₁–H₁₁⋯Cl₂ (2.840 Å, 138.45°) interacting with a hydrogen atom from the imidazole aromatic ring of another adjacent C₂ complex. These interactions are responsible for the expansion in the crystallographic a direction.

Catalytic experiments with Pd molecular or colloidal systems

C₁ and C₂ Pd complexes (with L and HLCl ligands, respectively) as well as N₁ and N₂ Pd nanoparticles have been evaluated as catalysts for the Suzuki–Miyaura reaction (Scheme 2, Table 1).²²,²³

4-Halogenotoluene derivatives (4-chlorotoluene, 4-bromotoluene or 4-iodotoluene) and an excess of phenylboronic acid were chosen as substrates in order to easily distinguish between cross-coupling and homocoupling products. Under the catalytic reaction conditions applied (Scheme 2),¹⁴ two different by-products can be formed besides the expected cross-coupled product [4-methylbiphenyl; BT] as follows: (i) toluene (PhMe) arising from the dehalogenation of the substrates and (ii) 4,4′-dimethylbiphenyl (TT), resulting from the 4-bromotoluene homocoupling. Once optimized, 4-halogenotoluene (substrate/Pd = 2500), phenylboronic acid (PhB(OH)₂/Pd = 3125 or 0), and ⁴BuOK (base/Pd = 5000) were employed in a DMF/water mixture (4/1) as the solvent. As a general trend,
higher conversions were obtained with 4-iodotoluene compared to 4-bromotoluene in both molecular and colloidal systems (Table 1), as expected from the respective C(Ph)–X bond energies (X = Br, 84 kcal mol−1; X = I, 67 kcal mol−1).24

Unfortunately, 4-chlorotoluene could not be activated probably due to the higher C(Ph)–Cl bond energy value (97.1 kcal mol−1)24 and the Suzuki–Miyaura coupling reaction was unsuccessful.

Interestingly, in the presence of the molecular catalysts C1 and C2, toluene was the only side product observed in a significant amount using both 4-bromotoluene and 4-iodotoluene as substrates (Table 1, entries 1–4). The homocoupling reaction does not take place, as otherwise predictable according to the literature on Pd molecular complexes.14 Also, 4-bromotoluene yields BT as the major product, while the amount of the dehalogenation product (toluene) significantly increases when 4-iodotoluene is used.

Recently, V. P. Ananikov et al. have demonstrated the formation of Pd NPs when molecular Pd complexes with NHC ligands are used in the Mizoroki–Heck reaction.25 In our case, even if it is not a definite proof, TEM control analyses of the solutions after catalysis with C1 or C2 did not show the presence of Pd nanoparticles. In any case, Hg poisoning tests carried out using these systems (vide infra) confirm the molecular nature of the real catalyst when C1 or C2 is used.

When 4-iodotoluene was used as a substrate with nanocatalysts N1 and N2, complete conversions were achieved in 6 h in both cases. In the case of N1, the formation of the cross-coupling product (4-methylbiphenyl; BT) was mainly observed together with a small amount of toluene (Table 1, entry 5). The formation of toluene increases to 53% in the case of N2 (Table 1, entry 6). In contrast, N1 and N2 behave similarly against 4-bromotoluene, with the formation of 4,4′-dimethylbiphenyl (TT), arising from the homocoupling reaction, together with toluene and small amounts of BT (Table 1, entries 9 and 10). Furthermore, for the two halogenotoluene substrates, both conversion and chemoselectivities are higher for the Pd NP/L system (N1) than that for the Pd NP/HCl system (N2). These differences can be explained by the binding of the carbene group at the Pd NP surface in the case of N1 compared to N2. Indeed, the different coordination modes (by C and N in N1 and only by N in N2) may tune both electronic and steric properties at the surface and consequently the catalytic behavior of N1.

In order to determine the influence of phenylboronic acid in C–C coupling reactions catalyzed by the colloidal systems, catalytic experiments were also carried out in the absence of the boron reagent. Besides that BT was not detected, it is remarkable that full conversion to the dehalogenated product (PhMe) is observed in the case of the reaction carried out with 4-iodotoluene catalyzed by N1 (Table 1, entry 7). However, when 4-bromotoluene was employed a significant increase in the yield of the TT homocoupling product is observed for both nanocatalysts (from 34% to 60%; Table 1, entries 9 and 11, respectively, for N1, and from 13% to 26% for N2, entries 10 and 12). When performed with the molecular complexes, the same reaction of 4-halotoluene in the absence of phenylboronic acid reagent did not yield homocoupling products at all.

A recurrent discussion with Pd NPs as catalysts for C–C coupling reactions is whether the real catalysts are the NPs or molecular Pd species leached from them.10 There are several publications that support either a surface-based26 or atom-leaching mechanism.27 In this context, three different tests have been carried out to assess the nature of the active species during the catalytic process. First of all, in the mercury poisoning test,28 100 equivalents of Hg were added to the catalytic mixtures after 10 min of reaction. For molecular systems (C1 and C2) the conversions were not affected, while for the colloidal systems (N1 and N2) the catalytic reactions ceased completely. These data suggest that C1 and C2 act as real molecular catalysts when starting with them, whereas Pd NPs are the active species when N1 and N2 are introduced into the catalysis. This is in accordance with the different results observed in catalysis depending on the molecular or colloidal

Table 1  Suzuki–Miyaura reactions with palladium catalysts

<table>
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<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>X</th>
<th>[PhB(OH)2][Pd]</th>
<th>Conv. (%)</th>
<th>BT (%)</th>
<th>TT (%)</th>
<th>PhMe (%)</th>
<th>Yield BT (%)</th>
<th>Yield TT (%)</th>
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<td>1</td>
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<td>I</td>
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<td>59</td>
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a Reaction conditions: 1 × 10−3 mmol of Pd, 2.5 mmol of 4-halogenotoluene, 5.0 mmol BuOK and 0.5 mmol naphthalene as an internal standard in 8.0 mL of DMF and 2.0 mL of H2O. Temperature, 100 °C. b Conversion after 6 h reaction. c Chemoselectivity in 4-methylbiphenyl (BT), 4,4′-dimethylbiphenyl (TT) and toluene (PhMe), respectively.
nature of the introduced catalysts. However, the mercury poisoning test is not definitive, since the amalgam of Hg and Pd from the NPs could prevent potential Pd molecular species from leaching. For this reason, additional experiments have been performed with systems from entries 9 and 10 in Table 1 (Suzuki–Miyaura reaction conditions, p-bromotoluene as the haloderivative and N1 or N2 as the catalyst, respectively). First of all, TEM grids were prepared after the catalytic experiments, observing the existence of Pd NPs (Fig. S18). The mean size of these NPs (2.7(0.7) and 3.3(0.6) nm for N1 and N2 after catalysis, respectively) is similar to those found for the same NPs prior to the catalytic tests (2.1(0.9) and 3.2(0.9) nm for N1 or N2, respectively). Even if no restructuring of the NPs seems to have taken place (which could indicate a leaching/deposition mechanism through the Ostwald ripening process), it is important to note that for N2 the NPs appear isolated after catalysis, in contrast with the aggregation observed prior to catalysis.

Secondly, ICP-MS analyses of the solutions after catalysis for entries 9 and 10 in Table 1 were carried out in order to know the amount of Pd leached from the NPs to the solution. The concentrations of Pd in these solutions are 0.17 and 1.8 ppm for N1 or N2, respectively, meaning that 0.7% and 15% of Pd have leached to the solution for N1 or N2, respectively. The differences on the percentage of leached Pd can be explained by the different coordinative properties of the ligands on each system. For N1, the carbene and pyrazolyl groups from L can coordinate to the surface of the NPs, and better stabilize them from Pd leaching than in N2, where only the pyrazolyl group from HLCI can coordinate to the surface of the NPs.

Moreover, the leached molecular Pd species can be responsible for the small amount of C–C heterocoupling reaction observed in entries 9 and 10 of Table 1 (5% and 7%, respectively).

All in all, these experiments indicate that C1 and C2 act as molecular catalysts in Suzuki–Miyaura C–C heterocoupling and N1 and N2 are the real active species for the C–C homocoupling reaction.

**Experimental section**

**General procedure and reagents**

All manipulations were carried out under an argon atmosphere using standard Schlenk tubes or Fisher-Porter reactors and vacuum line techniques, or in a glove-box. [Pd2(dba)3] was purchased from Strem Chemicals, and [PdCl2(CH2CN)2]10 and [PdCl2(cod)]11 (cod = 1,5-cyclooctadiene) were prepared as described in the literature. Solvents were purchased from SDS and dried using a purification machine (M Braun MB SPS-800) or distilled prior to use: tetrahydrofuran and diethyl ether over sodium/benzophenone, and pentane, n-hexane, acetonitrile and dichloromethane over calcium hydride.

Elemental analyses (C, H, and N) were carried out by the Chemical Analyses Service of the Universitat Autònoma de Barcelona on a Eurovector 3011 instrument. The Pd weight percentages or concentrations were analyzed by the Chemical Analyses Service of the Universitat Autònoma de Barcelona using an inductively coupled plasma mass spectrometry (ICP-MS) Agilent 7500ce model system or an inductively coupled plasma optical emission spectrometry (ICP-OES) PerkinElmer Optima 4300DV model system. Infrared spectra were recorded on a PerkinElmer FT spectrophotometer, series 2000, as KBr pellets or polyethylene films in the range of 4000–150 cm⁻¹. 1H NMR, 13C {1H} NMR, HSQC, COSY, DOSY and NOESY spectra for all compounds but C1 were recorded on Bruker AVANCE 360 and 400 NMR spectrometers in CDCl3 solutions at room temperature. For C1, NMR spectroscopy experiments were performed on a Bruker Avance 600 spectrometer (Bruker Biospin, Rheinstetten, Germany) equipped with TXI HCN z-grad probes. The temperature for all measurements was set to 298 K. The NMR spectroscopy experiments performed for the structural characterization were the standard 1H, 13C, COSY, ROESY, multiplicity-edited HSQC and HMBC experiments (see the ESIF). All chemical shift values (δ) are given in ppm. Electrospray ionization mass spectra (ESI-MS) were obtained with an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics.

Specimens for TEM/HR-TEM and SEM-FEG analyses were prepared by slow evaporation of a drop of crude colloidal solution deposited under argon onto holey carbon-covered copper grids. TEM/HR-TEM analyses were performed at the Servei de Microscòpia de la UAB with a JEOL JEM 2010 electron microscope working at 200 kV with a resolution point of 2.5 Å. SEM-FEG analyses were performed at the Service Commun de Microscopie Electronique de l’Université Paul Sabatier in Toulouse with an MEB JSM6700F microscope. The size distributions were determined via manual analysis of enlarged micrographs by measuring ca. 200 particles on a given grid to obtain a statistical size distribution and a mean diameter.

Data collection for WAXS was performed at the CEMES-CNRS (Toulouse) on small amounts of powder. All samples were sealed in 1 mm diameter Lindemann glass capillaries. The measurements of the X-ray intensity scattered by the samples irradiated with graphite monochromatized MoKα (0.071069 nm) radiation were performed using a dedicated two-axis diffractometer. The measurement time was 15 h for each sample. Scattering data were corrected for polarization and absorption effects, then normalized to one Pd atom and Fourier transformed to obtain the RDFs. To make comparisons with the crystalline structure in real space, a model was generated from bulk Pd parameters. The classic Debye’s function was then used to compute the intensity values, subsequently Fourier transformed under the same conditions as the experimental ones.

**Synthesis and characterization of the ligands**

1-[2-(3,5-Dimethylpyrazol-1-yl)ethyl]-3-((S)-1-phenylethyl)-3H-imidazol-1-ium chloride (HLCI). A mixture of 1-(2-chloroethyl)-3,5-dimethyl-1H-pyrazole20 (0.942 g, 5.94 mmol) and 1-(S)-(phenylethyl)imidazole32 (1.023 g, 5.94 mmol) was heated and stirred at 120 °C for 64 hours. After cooling to room tempera-
ture, the product was dissolved in dichloromethane (5 mL) and precipitated with diethyl ether (50 mL). For complete precipitation, the system was stored overnight at −31 °C. The product was washed with diethyl ether (3 × 30 mL) and dried under vacuum. The product was obtained as a sticky orange solid. Yield: 1.79 g, 91%.

Anal. calec for C_{18}H_{24}N_{3}Cl: 1.5H_{2}O: C, 60.41; H, 7.32; N, 15.66. Found: C, 60.54; H, 7.27; N, 16.02. 1H-NMR: (CDCl_{3}, 360 MHz, 298 K) δ: 1.89 [s, 3H, H_{6} or H_{7}], 1.92 [br, 3H, H_{16}], 2.06 [s, 3H, H_{6} or H_{7}], 4.44 [br, 2H, H_{4}], 4.87 [br, 2H, H_{5}], 5.61 [s, 1H, H_{1}], 5.76 [q, 2H, J = 7.0 Hz, H_{3}], 7.00, 7.23 [2Br, 1H each one, H_{12}, H_{24}], 7.30 [br, 5H, H_{18}−H_{22}], 10.32 [s, 1H, H_{11}].

(DMSO, 360 MHz, 298 K) δ: 1.81 [d, 3H, J = 7.0 Hz, H_{6} and H_{7}], 1.99 [s, 3H, H_{6} and H_{7}], 4.42 [t, 2H, J = 5.0 Hz, H_{4}], 4.58 [t, 2H, J = 5.0 Hz, H_{5}], 5.73 [s, 1H, H_{1}], 5.85 [q, 1H, J = 7.0 Hz, H_{3}], 7.36 [br, 5H, H_{18}−H_{22}], 7.72, 7.92 [2Br, 1H each one, H_{12}, H_{13}], 9.39 [s, 1H, H_{11}]. 13C{1H}-NMR: (CDCl_{3}, 91 MHz, 298 K) δ: 10.7, 13.4 [C_{6}], 21.1 [C_{16}], 47.9 [C_{6}], 59.2 [C_{13}], 105.5 [C_{5}], 120.4, 123.0 [C_{13}, C_{14}], 126.8, 129.3, 137.8 [C_{17}−C_{22}], 136.6 [C_{19}], 140.5, 148.7 [C_{8}, C_{9}], 150.5 [C_{6}], 20.6 [C_{16}], 47.2 [C_{6}], 48.8 [C_{8}], 58.5 [C_{13}], 105.0 [C_{5}], 121.3, 123.2 [C_{13}, C_{14}], 126.5, 128.7, 129.0, [C_{17}−C_{22}], 136.0 [C_{19}], 139.4, 146.8 [C_{9}, C_{10}], IR (ATR) cm⁻¹: 3040, 2978 υ(C−H), 1552 (υ(C=–C)=, υ(C=−N)=)ar, 1455 (δ(C=C)=, δ(C=N)=)ar, 1160 (δ(C−H)=p), 703 δ (C−H)=oop. MS (ESI): m/z (%) 295.2 (100.0%) [C_{18}H_{23}N_{3}Cl = C].

1-[2-(3,5-Dimethylpyrazol-1-yl)ethyl]-3-(S)-phenylethyl)-3H-imidazol-2-ylidene (1). Under an argon atmosphere, sodium hydride (60% dispersion in mineral oil, 124.1 mg, 3.10 mmol) was added to anhydrous pentane twice (2 × 15 mL) and the residual solvent was evaporated under reduced pressure. Then, a catalytic amount of potassium tert-butoxide (95%, 10 mg, 0.08 mmol) and anhydrous dichloromethane (5 mL) was added. A solution of 1-[2-(3,5-dimethylpyrazol-1-yl)ethyl]-3-(S)-phenylethyl)-3H-imidazol-2-ylimidazolium iodide (HCl, 513.2 mg, 1.55 mmol) in anhydrous dichloromethane (20 mL) was added to the dispersion of NaH/KO'Bu. The resulting mixture was stirred overnight at room temperature. The reaction crude was then filtered through a small plug of Celite and the solvent was removed under reduced pressure. The product was obtained as a sticky dark orange solid. Yield: 333 mg, 73%.

1H-NMR: (CDCl_{3}, 400 MHz, 298 K) δ: 2.00 [d, 3H, J = 7.0 Hz, H_{16}], 2.16 [s, 3H, H_{6} or H_{7}], 4.55 [t, 2H, J = 5.0 Hz, H_{5}], 5.01 [t, 2H, J = 5.0 Hz, H_{4}], 5.65 [q, 1H, J = 7.0 Hz, H_{3}], 5.71 [s, 1H, H_{1}], 6.67, 7.90 [2d, 1H each one, J = 2.0 Hz, H_{12}, H_{24}], 7.31−7.42 [2m, 5H, H_{18}−H_{22}]. 13C{1H}-NMR: (CDCl_{3}, 100 MHz, 298 K) δ: 10.7, 13.5 [C_{6}], 21.2 [C_{16}], 48.0 [C_{6}], 49.2 [C_{8}], 60.2 [C_{13}], 105.6 [C_{5}], 120.4, 123.0 [C_{13}, C_{14}], 126.8, 129.5, 137.8 [C_{17}−C_{22}], 140.5, 148.8 [C_{9}, C_{10}], signal for [C_{11}] was not observed. IR (ATR) cm⁻¹: 3097, 2978 υ(C−H), 1555 (υ(C=–C)=, υ(C=−N)=)ar, 1452 (δ(C=C)=, δ(C=N)=)ar, 1180 (δ(C−H)=p), 694 δ (C−H)=oop. HRMS (ESI): m/z 399.0808 [C_{18}H_{26}N_{3}Cl_Pd = Cl−HCl].

**Synthesis and characterization of the Pd(n) or Ag(i) complexes**

**Chloro[S]-3-[2-(3,5-dimethyl-1H-pyrazol-1-yl)ethyl]-1-(1-phenylethyl)-1H-imidazol-2-ylidene]silver(i), (C_{Ag}).** A mixture of 1-[2-(3,5-dimethylpyrazol-1-yl)ethyl]-3-(S)-phenylethyl)-3H-imidazol-1-um chloride (HCl, 342 mg, 1.03 mmol) and silver(i) oxide (99%, 240 mg, 1.03 mmol) in anhydrous dichloromethane (25 mL) was stirred at room temperature for 24 hours in the dark. Then, the reaction crude was filtered through Celite. The filtrate solvent was removed under vacuum and the product was dried completely. The product was obtained as a sticky grey-brown solid. Yield: 361 mg, 80%.

**Dichloro[S]-3-[2-(3,5-dimethyl-1H-pyrazol-1-yl)ethyl]-1-(1-phenylethyl)-1H-imidazol-2-ylidene[κ’N]palladium(i), (C_{1}).** A mixture of C_{Ag} (242 mg, 0.55 mmol) and dichloro[15-cyclooctadiene]palladium(i) (158 mg, 0.55 mmol) in dichloromethane (30 mL) was kept under vigorous stirring for 24 hours at room temperature in the dark. The reaction crude was filtered through Celite. Then, the filtrate solvent was evaporated under vacuum and the resulting solid was washed with hexane (30 mL). The residue was purified by flash column chromatography (silica gel 60 Å) using ethyl acetate : diethyl ether 4:1 as the eluent and then by second column chromatography (silica gel 60 Å) using dichloromethane : hexane 9:1 as the eluent. The product was obtained as a pale yellow powder. Yield: 133 mg, 51%.

**Trichloro[S]-3-[2-(3,5-dimethyl-1H-pyrazol-1-yl)ethyl]-1-(1-phenylethyl)-1H-imidazol-3-um-κ’N]palladium(i), (C_{2}).** A mixture of 1-[2-(3,5-dimethylpyrazol-1-yl)ethyl]-3-(S)-phenylethyl)-3H-imidazol-1-um chloride (HCl, 205 mg, 0.62 mmol) and palladium(i) chloride (99.9%, 110 mg, 0.62 mmol) in acetonitrile (20 mL) was kept under vigorous stirring for 24 hours at room temperature. Then, the solution was filtered through Celite. The solvent volume was decreased to ca. 2 mL and diethyl ether (30 mL) was added to induce precipitation. The orange powder was filtered and washed with diethyl ether (3 × 30 mL), and dried under vacuum. The product was obtained as an
Crystallographic data for compound C2 were collected at low temperature (180 K) on a Bruker Kappa Apex II diffraclometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and equipped with an Oxford Cryosystems Cryostream Cooler device. Crystallographic data for C2 can be gathered in the ESI, Tables S1 and S2.

The structures have been solved by Direct Methods using SIR92,31 and refined by means of least-squares procedures on \( F^2 \) with the aid of the program SHELXL9734 included in the software package WinGX version 1.63.35 The atomic scattering factors were taken from International tables for X-ray crystallography.36,37 All hydrogen atoms were placed geometrically, and refined by using a riding model. All non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighing scheme was used, where weights are calculated from the following formula: \( w = 1/\left[\sigma^2(F_o^2) + (aF)^2 + bP\right] \) where \( P = (F_o^2 + 2F_c^2)/3 \).

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre, CCDC, with reference number 1432563 (C2).†

**Conclusions**

A new hybrid pyrazole-imidazol-2-ylidene ligand, 1-[2-(3,5-dimethylpyrazol-1-yl)ethyl]-3-((S)-1-phenylethyl)-3H-imidazol-2-ylidene (L), has been synthesized for the first time and proved to effectively stabilize small and isolated palladium(0) nanoparticles. A comparison with its counterpart HLCI as a stabilizer led to badly stabilized NPs which evidenced that the coordination of the yliden group is a key factor in the stabilization process of the colloidal system. The successful preparation and complete characterization of molecular Pd(II) coordination compounds with the same ligands confirmed a chelated coordination mode through the pyrazolic nitrogen.
and the ylide group for L but a terminal monodentate mode through pyrazolic nitrogen for HLCl. From our previous research with carbene or pyrazole-containing ligands as stabilizers, we can conclude that similar coordination modes of L and HLCl here take place for both the Pd NP particles and Pd complexes respectively. As a consequence, the coordination of L is stronger and leads to nanoparticles with well-controlled size.

All these systems have been tested in catalytic C–C coupling reactions. For colloidal systems (N1 and N2), we observed an improving effect, in terms of chemoselectivity and yield, of L containing NPs (N1) with respect to HLCl containing NPs (N2) as a result of the different coordination modes of the carbene group to the surface of the NPs. Interestingly, these systems are the only ones able to achieve the C–C homocoupling reaction between two molecules of bromoarenes or the complete dehalogenation reaction of iodoarenes. The Suzuki–Miyaura reaction is favored with the Pd molecular complexes.

Taking into account the advantages of the organometallic approach and the different attributes of these catalysts, we believe that these materials could find practical uses in C–C coupling reactions in the future.

Conflicts of interest
There are no conflicts to declare.

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Notes and references


