CHEMISTRY
A EUROPEAN JOURNAL

FULL PAPER

DOI: 10.1002/chem.201103719

# PEPPSI-Type Palladium Complexes Containing Basic 1,2,3-Triazolylidene Ligands and Their Role in Suzuki–Miyaura Catalysis

**Daniel Canseco-Gonzalez,[a] Andrzej Gniewek,[b] Michal Szulmanowicz,[b] Helge Müller-Bunz,[a] Anna M. Trzeciak,*[b] and Martin Albrecht*[a]**

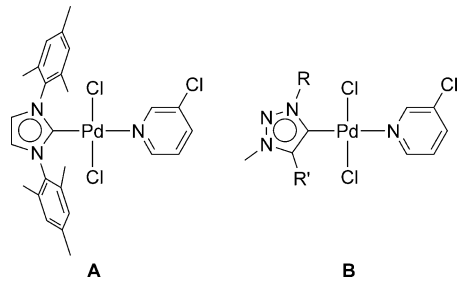
**Abstract:** A series of PEPPSI-type palladium(II) complexes was synthesized that contain 3-chloropyridine as an easily removable ligand and a triazolylidene as a strongly donating mesoionic spectator ligand. Catalytic tests in Suzuki–Miyaura cross-coupling reactions revealed the activity of these complexes towards aryl bromides and aryl chlorides at moderate temperatures (50 °C). However, the impact of steric shielding was the inverse of that observed with related normal N-heterocyclic carbenes (imidazol-2-ylidenes) and sterically congested mesityl substituents induced lower activity than small alkyl groups. Mechanistic investigations, including mercury poisoning experiments, TEM analyses, and ESI mass spectrometry, provide evidence for ligand dissociation and the formation of nanoparticles as a catalyst resting state. These heterogeneous particles provide a reservoir for soluble palladium atoms or clusters as operationally homogeneous catalysts for the arylation of aryl halides. Clearly, the substitution of a normal N-heterocyclic carbene for a more basic triazolylidene ligand in the precatalyst has a profound impact on the mode of action of the catalytic system.

**Keywords:** cross-coupling · heterogeneous catalysis · homogeneous catalysis · mesoionic carbene · palladium

## Introduction

Palladium complexes have found widespread academic and industrial application as catalyst precursors for carbon–carbon cross-coupling and for C–N and C–O bond-forming reactions.[1] Typically, a C–X bond (X = halide or pseudohalide) is required in the carbon precursor, although substantial progress has also recently been made in the direct functionalization of C–H bonds.[2] Cross-coupling of cheap and readily available chlorocarbons (X = Cl) generally involves oxidative addition of the C–Cl bond to a low-valent and coordinatively unsaturated palladium species as the rate-limiting step.[3] Appropriate balancing of the stability of the critical palladium(0) species is thus an essential aspect in designing better catalysts. This stability should be high enough to prevent decomposition, yet sufficiently low to favor oxidative C–Cl addition. Following these generic guidelines, ligands with enhanced basicity and increased steric demand have been developed over the last few years that have indeed boosted the catalytic activity of the palladium center, including P(*o*-tol)$_3$ (tol = tolyl),[4] P(*t*Bu)$_3$,[5] PCy$_2$-(biaryl) (Cy = cyclohexyl,[6] and 1,3-dimesitylimidazol-2-ylidene (IMes).[7] In particular, the combination of IMes, as a strongly electron-donating and bulky N-heterocyclic carbene (NHC), and 3-chloropyridine, as an easily removable ligand, with $PdCl_2$ gave a highly active catalyst precursor for cross-coupling reactions (**A**, Figure 1).[8] Because of the beneficial role of the pyridine ligand, the term PEPPSI (pyridineenhanced precatalyst preparation, stabilization, and initiation) was coined.

Recent work has shown that the electron-donor properties of N-heterocyclic carbene ligands[9] substantially increase when the heteroatoms of the ring are positioned at remote positions.[10] For example, mesoionic[11] 1,2,3-triazol-5-ylidenes (**B**, Figure 1) bear only one nitrogen adjacent to




A B

Figure 1. PEPPSI-type IMes palladium(II) complex **A** and its triazolylidene congener **B** (PEPPSI = pyridine-enhanced precatalyst preparation, stabilization, and initiation).

[a] D. Canseco-Gonzalez, Dr. H. Müller-Bunz, Prof. Dr. M. Albrecht
School of Chemistry and Chemical Biology
University College Dublin
Belfield, Dublin 4 (Ireland)
Fax: (+353) 1716-2501
E-mail: martin.albrecht@ucd.ie

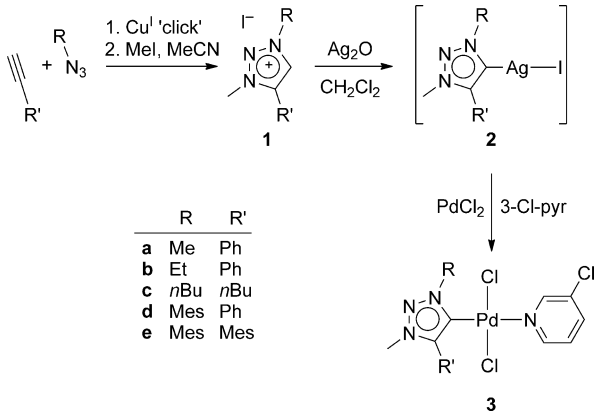
[b] Dr. A. Gniewek, M. Szulmanowicz, Prof. Dr. A. M. Trzeciak
Faculty of Chemistry, University of Wroclaw
14 F. Joliot-Curie St., 50-383 Wroclaw (Poland)
E-mail: anna.trzeciak@chem.uni.wroc.pl

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201103719.

the carbene bonding site and are more basic than classical imidazol-2-ylidene NHCs.[12] This type of triazolylidene[13] has recently been applied in the development of a variety of catalytic systems.[14] The triazolium ligand precursor is readily available through versatile copper-catalyzed [2+3] cycloaddition (click chemistry)[15] and subsequent N-alkylation. This synthetic flexibility paired with the stronger electron-donor properties suggests that these ligands will facilitate C–Cl oxidative addition in cross-coupling chemistry. Based on these considerations, we became interested in synthesizing a set of PEPPSI-type palladium complexes **B** with different triazolylidene ligands, as well as in evaluating their catalytic activity. Remarkably, the modification of the heterocyclic carbene ligand has a profound impact on the working mode of the catalyst, which may be rationalized by a decreased Pd–$C_{carbene}$ bond stability in the triazolylidene system.[16]

## Results and Discussion

**Synthesis of the complexes**: The triazolium salts **1a–e** were conveniently accessible through conventional and versatile Cu-catalyzed click cycloaddition of the appropriate azide and alkyne, followed by chemoselective methylation of the N3 position by using MeI (Scheme 1).[17] Metalation of the




Scheme 1. Synthesis of complexes **3**.

triazolium salts with $Ag_2O$ and subsequent transpalladation in 3-chloropyridine as the solvent afforded the PEPPSI-type palladium complexes **3a–e** as air- and moisture-stable solids. Yields of the pure materials ranged between only 20 and 60%, partially because of the formation of an insoluble pale-yellow side product, and partially because product fractions were washed away during purification. The complexes are highly soluble in chlorinated solvents, and also dissolve substantially in $Et_2O$ and similar low-polarity solvents that are typically used for precipitation of organometallic compounds.

Successful palladation was indicated spectroscopically by the absence of the low-field triazolium proton resonance in the $^1$H NMR spectrum, and by the presence of stoichiometric quantities of the diagnostic set of four resonances due to the 3-chloropyridine ligand. In addition, the resonance of the N3-bound $CH_3$ group is shifted upfield by 0.3–0.4 ppm, and the α-protons of the N1-bound alkyl group become more shielded (complexes **3a–c**). In contrast, the $^{13}$C NMR resonances are barely affected by the palladation reaction. The chemical shift of the C5 nucleus moves by between 0.2 and 8 ppm upon changing its substituent from hydrogen (in **1**) to palladium (in **3**), and the C4 frequency did not vary by more than 1 ppm. The absolute chemical shift of the C5 nucleus does not correlate with the electronic impact of the *ortho* substituents at N1 and C4,[18] suggesting that the resonance frequency is governed by a combination of steric and electronic factors.

Complexes **3b**, **3c**, and **3d** were analyzed by single-crystal X-ray diffraction (Figure 2). In all three complexes, the ligands around the square-planar palladium center adopt the expected *trans* arrangement. The Pd–$C_{trz}$ (trz = triazolylidene) bond length in all complexes is 1.96(1) Å, which is in line with those of related triazolylidene–palladium complexes (Table 1).[14e,f,19] The Pd–$N_{pyr}$ (pyr = pyridine) bond

Table 1. Selected bond lengths [Å] and angles [°] in complexes **3b**, **3c**, and **3d**.

| | **3b** | **3c** | **3d** | |
|---|---|---|---|---|
| | | | molecule 1 | molecule 2[a] |
| Pd–C(1) | 1.9601(16) | 1.9650(13) | 1.957(3) | 1.967(3) |
| Pd–N(4) | 2.1105(13) | 2.1192(11) | 2.129(3) | 2.126(3) |
| Pd–Cl(1) | 2.3028(4) | 2.3103(3) | 2.3115(8) | 2.2961(9) |
| Pd–Cl(2) | 2.3051(4) | 2.3054(3) | 2.3046(9) | 2.2969(9) |
| C(1)-Pd-N(4) | 178.87(6) | 177.70(4) | 175.81(11) | 178.71(12) |
| C(1)-Pd-Cl(1) | 88.63(5) | 89.27(4) | 88.18(10) | 89.63(9) |
| N(4)-Pd-Cl(1) | 90.45(4) | 91.83(3) | 92.12(8) | 89.76(9) |
| C(1)-Pd-Cl(2) | 88.68(5) | 88.67(4) | 88.76(10) | 90.23(9) |
| N(4)-Pd-Cl(2) | 92.25(4) | 90.36(3) | 90.75(8) | 90.48(9) |
| C(4)-Pd-Cl(2) | 88.68(5) | 88.67(4) | 88.76(10) | 90.23(9) |
| Cl(1)-Pd-Cl(2) | 176.732(16) | 175.849(12) | 176.04(3) | 174.89(4) |

[a] Second independent molecule in the unit cell, atom labeling adapted.

length is weakly affected by the substitution pattern on the triazolylidene ligand and increases slightly in the series **3b** < **3c** < **3d**. The effect is very small and may indicate enhanced steric congestion in this series. The most pronounced distinction between the three complexes pertains to the different twist angle of the heterocycles out of the palladium coordination plane. The dihedral angle of the two heterocycles is nearly identical in **3b** and **3c**, 30.6(2)° and 27.57(16)°, respectively, and yet it is significantly larger in **3d**, 68.2(3)°. This almost perpendicular arrangement is probably a direct consequence of the shielding properties of the *ortho*-methyl groups of the mesityl substituent in **3d**. This shielding factor may also explain the fact that the torsion angle of the pyridine ligand out of the metal plane is smallest for **3d** (29.3(3)°), and increases for **3c** (36.54(11)°) and **3b** (45.55(13)°). In all three complexes, the dihedral angle between the palladium square plane and the triazolylidene

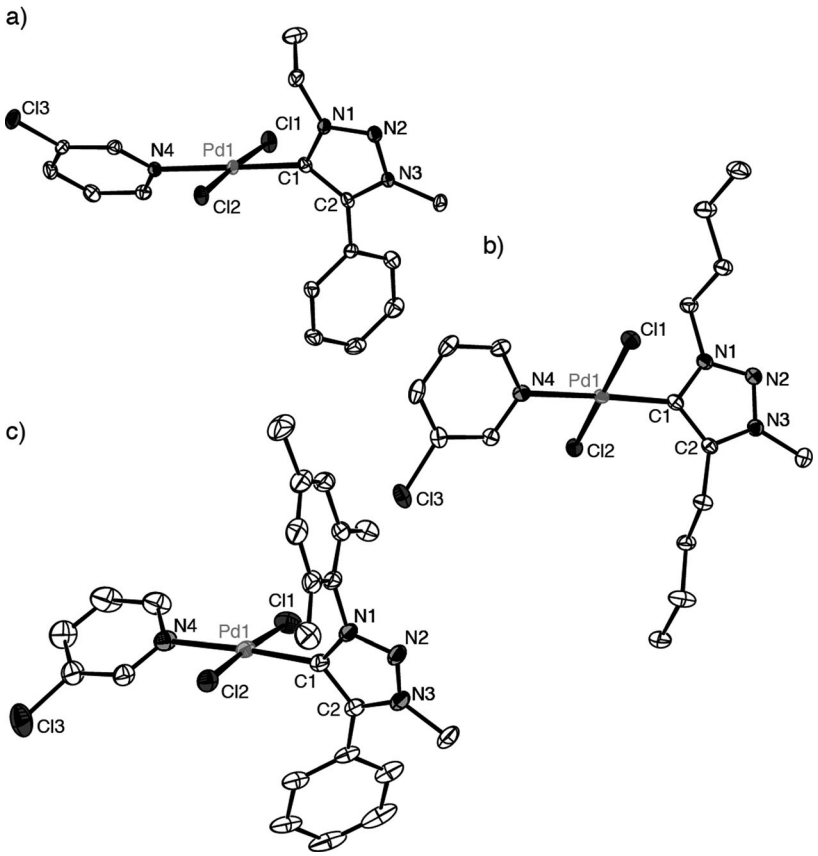
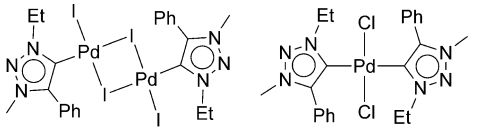



Figure 2. ORTEP diagrams of complex a) **3b**, b) **3c**, and c) one of the two crystallographically independent molecules of complex **3d** (50% probability level; co-crystallized solvent molecules and hydrogen atoms omitted for clarity).

ligand is significantly larger (68–79°) than the 29–46° between the palladium coordination plane and the pyridine heterocycle.

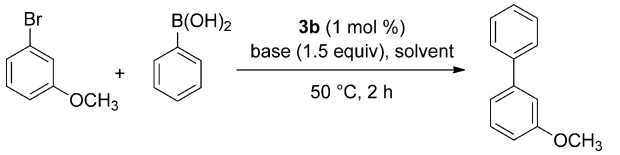
**Catalytic application**: The PEPPSI-type complexes were tested as catalyst precursors in Suzuki–Miyaura cross-coupling reactions by using *meta*-bromoanisole and phenylboronic acid as model substrates. A first set of experiments was aimed at identifying the most suitable reaction conditions to achieve this coupling at mild reaction temperatures (50 °C). The activity of complex **3b** was evaluated by determining the conversion after 2 h. Initial variations included the solvent (dimethylacetamide (DMA), dioxane, and *i*PrOH) and the base ($K_2CO_3$, NaOAc, *t*BuOK, and $Bu_4NF$; Table 2). These experiments indicated that the best performance occurred with $Bu_4NF$ in *i*PrOH, and further catalytic evaluations were thus carried out by using this combination. The reaction is sensitive to thermal variations. At 50 °C, the catalytic solution remained transparent over extended periods of time. When heated to 80 °C, however, the catalytic reaction mixture became cloudy within the first 10 min, and a black precipitate gradually started to appear. In contrast, reducing the temperature to 30 °C preserved the transparent appearance, yet significantly compromised the conversion (33% after 2 h, 58% after 4 h).

The role of the pyridine ligand as an activator was investigated by comparing the activity of **3b** to related complexes **4** and **5**. Complex **4** is a dimeric version of **3b** that may split into two coordinatively unsaturated [Pd(trz)$X_2$] fragments akin to the intermediate expected upon pyridine dissociation from complex **3b**. Under the optimized reaction conditions, complex **4** exhibits a lower catalytic activity and reaches only 60% conversion.[17] Complex **5**, comprising two triazolylidene ligands, gave an appreciable 75% conversion, only marginally lower than the conversions achieved with complex **3b**.[20] The high activity of complex **5** is in agreement with earlier studies on an analogous complex derived from **1e**[14b] and may be related to that observed for a mixed C2-/C4-bound bis(imidazolylidene) system,[21] in which the C4-bound imidazolylidene is supposed to be less strongly bound to the palladium




**4** **5**

Table 2. Conversion [%] of 3-bromoanisole in the Suzuki–Miyaura cross-coupling catalyzed by **3b**.[a]




| | Base | | | |
|---|---|---|---|---|
| Solvent | $K_2CO_3$ | NaOAc | *t*BuOK | $Bu_4NF$ |
| DMA | 30 | 9 | 4 | 3 |
| dioxane | 8 | 2 | 2 | 4 |
| *i*PrOH | 64 | 10 | 14 | 80 |

[a] General reaction conditions: bromoanisole (1.0 mmol), $PhB(OH)_2$ (1.2 mmol), base (1.5 mmol), and complex **3b** (5 mmol, 0.5 mol%) in the appropriate solvent (3.0 mL) at 50 °C for 2 h.

center than the C2-bound analogue.[22] In complex **5**, one triazolylidene ligand may thus mimic the activating role of 3-chloropyridine in **3b**, thus also generating a [Pd(trz)$X_2$] species.

Variation of the substituents at the triazolylidene ligand revealed a moderate dependence on steric factors (Figure 3). The smallest substituents (**3a** and **3b**) induced

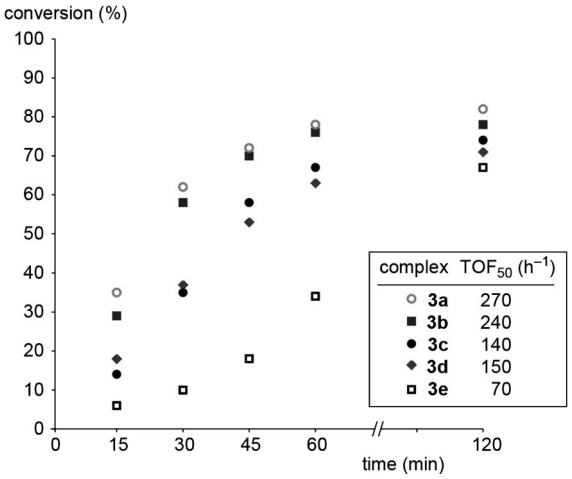



Figure 3. Time–conversion profile for the coupling of bromoanisole (1.0 mmol) and phenylboronic acid (1.2 mmol) catalyzed by complex **3** (0.5 mol%) with $Bu_4NF$ (1.5 mmol) in *i*PrOH (3 mL) at 50°C. The inset shows approximate turnover frequencies at 50% conversion ($TOF_{50}$).

the highest activity, whereas the di(mesityl)-substituted triazolylidene palladium complex **3e** displayed comparably slow conversion. For example, 35% conversion was reached with complex **3a** after 15 min, whereas 60 min were required with **3e** to accomplish the same conversion. The low performance of **3e** is remarkable when considering the excellent catalytic activity of its imidazol-2-ylidene analogue (compare with **A**, Figure 1).[8,23] Complexes **3c** and **3d**, comprised of moderately demanding triazolylidene substituents, display activities that are between those of **3a** and **3e**. These results suggest that the bulkiness around the palladium center matters, either for catalyst activation, or for substrate conversion.

The most active complexes **3a** and **3b** were subsequently tested for the conversion of more demanding aryl chlorides. With *para*-chlorobenzaldehyde as the substrate, the activity of **3a**, containing a small Me substituent at the triazolylidene ligand, was distinctly higher than that of **3b**. At 50°C and a 2 mol% loading of palladium complex (vs. aryl chloride), **3a** gave appreciable catalytic activity with a turnover frequency at 50% conversion ($TOF_{50}$) of 53 $h^{-1}$. In contrast, complex **3b**, comprising an ethyl *ortho* substituent at the triazolylidene, was markedly less active ($TOF_{50} = 17\ h^{-1}$). With both complexes, conversion ceased at about 60%, which suggests a limited lifetime of the catalytically active species. No improvement in conversion was achieved when increasing the loading of the catalyst precursor from 2 to 5 mol%.

**Mechanistic insights**: Aryl chloride conversion under relatively mild conditions, as applied herein, typically suggests homogeneous catalysis.[24] However, the delicate impact of temperature, as well as the trend observed in the steric demand of the triazolylidene ligand, which is inverse to the trend observed for normal NHC–palladium complexes,[8] suggest a catalytic mechanism that differs from classical PEPPSI-type systems. To further elucidate the mode of action, a set of analyses was performed, including microscopy, mass spectrometry, and mercury-poisoning experiments.[25]

In a representative experiment by using complex **3b** under the standard conditions (bromoanisole as the substrate, see Figure 3), a large excess of elemental mercury (about 7 g, 35 mmol, ca. 7000 mol equiv vs. palladium) was added after 5 min (14% conversion). This addition efficiently stalled the catalytic activity, and the same 14% conversion was determined after 120 min. In contrast, a parallel mercury-free reaction reached 80% over the same period. The outcome was qualitatively identical when the substrate was replaced with chlorobenzaldehyde. In this case, addition of mercury after 5 min (4% conversion) inhibited further catalytic coupling and no biaryl product was formed during the subsequent 120 min (compare with the 47% yield in a parallel unpoisoned reaction run over the same time span). These results indicate that the catalytic working mode is not fundamentally different when changing the substrate from an aryl bromide to an aryl chloride. Moreover, the well-known capability of mercury to poison heterogeneous, but not homogeneous catalysts[26] is in apparent contradiction with the assumption that palladium-catalyzed cross-coupling of aryl chlorides under mild conditions requires molecular palladium.[1,24]

Analysis of catalytic reaction mixtures by transmission electron microscopy (TEM) revealed further details. A micrograph of a sample taken from the cross-coupling of bromoanisole by using **3b** after 35 min (Figure 4a) is represen-

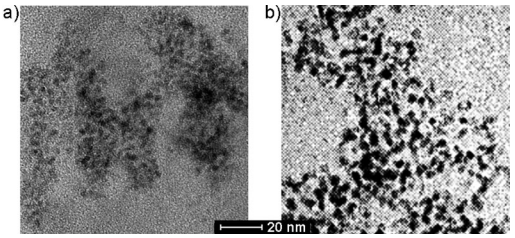



Figure 4. TEM micrographs of post-reaction mixtures after the Suzuki–Miyaura reaction with a) **3b** and bromoanisole and b) **3a** and chlorobenzaldehyde.

tative of all of the complexes (**3a–e**) and indicates the formation of palladium nanoparticles with an average size of 2–3 nm. Slightly larger particles were formed in the conversion of chlorobenzaldehyde (3–5 nm when using **3a**, Figure 4b). Nanoparticle formation was also observed when either of the two coupling partners was omitted. In the absence of phenylboronic acid, the particles were consistently larger (4–8 nm). In addition, some redispersion was noted

by the presence of larger crystallites, suggesting Ostwald ripening under these conditions. In the absence of the aryl halide, the particle size does not differ significantly from that of the original catalytic mixture, which suggests that the phenylboronic acid may play a role in stabilizing the nanoparticles and in controlling their size. The observed Ostwald ripening may provide an explanation for the catalytic activity of the system because the particle size redistribution requires partial dissolution of particles, thus generating a dissolved palladium(0) species[27] that either undergoes oxidative addition with an aryl halide and thus enters the catalytic cycle, or aggregates with a nanoparticle to contribute to the Ostwald ripening process.[28]

Electron-spray ionization mass spectrometry (ESI-MS) measurements were performed to validate the mechanistic hypothesis. In agreement with the TEM data and with the formation of colloidal palladium(0), ESI-MS spectra of the catalytic reaction mixture did not show any signals in the low-molecular range that would indicate the presence of defined molecular species. Irrespective of the sampling time (after 10, 20, and 35 min), only signals in the *m*/*z* 900–1600 range were detected. The spectra were almost identical for all complexes (**3a**–**e**) and do not indicate a correlation to the observed catalytic conversions. For example, when using complex **3b**, signals at *m*/*z* 1020, 1443, 1490, and 1534 were measured. Their isotopic distribution pattern indicates the presence of up to four palladium atoms per species. Moreover, the *m*/*z* 1443 and 1490 signals were observed when using different triazolylidene palladium complexes as catalyst precursors, suggesting that these species do not contain a triazolylidene ligand.

In contrast, ESI-MS measurements on solutions, in *i*PrOH, containing only the complex and neither cross-coupling substrates nor $Bu_4NF$, revealed signals for various low-molecular weight species resulting from loss of chloride, and from triazolylidene ligand transfer. For example, a solution of **3b** gave signals at *m*/*z* 479.1, attributed to $[Pd(trz)(py\text{-}Cl)Cl]^+$ and at *m*/*z* 517.1, assigned to $[Pd(trz)_2Cl]^+$. The latter species again underlines the activating role of the chloropyridine ligand. Transfer of the triazolylidene ligand may be a consequence of the sample ionization in the mass spectrometer, since no indications of ligand transfer were obtained from NMR measurements in solution. Similar effects have been observed previously with imidazolylidene–palladium complexes.[29] Warming of a solution of **3b** in *i*PrOH to 50 °C, that is, to the catalytic reaction temperature, resulted in substantially more signals in the ESI-MS spectra, including dimeric species, such as $[Pd_2(trz)_3Cl_3]^+$ (*m*/*z* 880.1) and $[Pd_2(trz)_3(py\text{-}Cl)_2Cl_3+3H]^{4+}$ (*m*/*z* 1109.2). The increased number of species and the presence of dimetallic systems that were not detected when keeping the solution at room temperature suggest that the complexes are thermally unstable. Indeed, $^1H$ NMR spectrum monitoring of the stability of **3b** in $[D_8]$-*i*PrOD at 50 °C by using hexamethylbenzene as the internal standard revealed a drop in the concentration of **3b** to 57(±1)% after 2 h. In addition, a yellow precipitate was formed, but no palladium black. No further decrease in concentration was observed upon prolonged heating.

The interplay between NHC metal complexes and nanoparticles has received considerable attention recently. Potentially in relation to our observations, the degradation of NHC ruthenium complexes into nanoparticles in the presence of N-heterocyclic carbenes has been reported.[30] Moreover, it was shown that solid metals can be used as a precursor to generate a variety of molecular carbene–metal complexes.[31] Whilst imidazolium and ammonium salts effectively stabilize palladium nanoparticles and prevent their aggregation,[32] ammonium salts have also been shown to facilitate the formation of soluble palladium species from palladium(0) nanoparticles in the presence of aryl halides.[33] Taking these precedents into account, it seems plausible that colloidal palladium is the resting state of the catalyst derived from complex **3**,[34] although the catalytically active species results from dissociation of a palladium cluster or of single palladium atoms, either as a solvated palladium(0) species, or as triazolylidene adducts.

Heterogenization of the molecular precatalyst to palladium nanoparticles and subsequent dissolution of palladium atoms from these nanoparticles constitutes a model that accounts for all of the observations detailed above. Such a model has been suggested, although only rarely underpinned with experimental evidence.[35] The dissociated "naked" or triazolylidene-bound palladium atoms are expected to be sufficiently activated to oxidatively add both aryl bromides and aryl chlorides under mild conditions.[36] Elemental mercury poisons the reaction by preventing dissociation of a palladium atom from the colloidal reservoir and thus shuts down the activation step from the catalyst resting state. In addition, *i*PrOH may be the solvent of choice because of its potentially reducing character,[37] thus providing smooth access to low-valent palladium. Formation of colloidal palladium may further explain the delicate role of the temperature, since elevated temperatures accelerate colloid formation and eventually lead to aggregation of the colloids into large particles that cannot easily expel a palladium atom. In contrast, too low a temperature appears to compromise the decomposition of the precursor complex **3**, leading to low activity. Likewise, the substituents on the triazolylidene system may fulfill a role that is different from the steric protection of the metal center, as in PEPPSI-type imidazol-2-ylidene palladium catalysts **A**.[8] In the catalytic system described herein, a low steric impact of the carbene ligand facilitates palladium dissociation, and little steric congestion also provides triazolium salts that may assist in stabilizing the palladium colloids. In addition to this effect on the catalytic reaction rate,[26e] this type of stabilization is supposed to be essential to keep the nanoparticles small and to enhance the propensity for a palladium atom to dissociate from the particle and hence enter the catalytic cycle.

## Conclusion

We have developed a straightforward synthetic methodology to obtain a series of C5-bound 1,2,3-triazolylidene palladium complexes containing a 3-chloropyridine ligand as an easily cleavable ligand. The activity of these complexes in Suzuki–Miyaura cross-coupling can be tailored by varying the substituents on the triazolylidene ring. Steric effects govern the catalytic activity and less bulky substituents induce better catalytic activity than bulkier IMes-type analogues comprising two mesityl groups in the *ortho* positions, which is in contrast to the trends observed with the imidazol-2-ylidene congeners. Mechanistic work has demonstrated that this opposite trend originates from a fundamentally different mode of action of the triazolylidene complexes. In contrast to the homogeneous catalysis observed with the original PEPPSI system, all experimental evidence indicates that the triazolylidene complexes undergo a heterogenization process that generates palladium nanoparticles as the resting state of the catalyst. Leaching of palladium atoms from these nanoparticles provides a molecular, catalytically active species that is able to convert aryl chlorides under relatively mild conditions. This type of mechanism may be relevant for a range of catalyst precursors, and care should be taken when using aryl chloride conversion as a probe because spectator ligands may not be preserved, but may instead be involved in a heterogenization–homogenization pathway, and could also assist in reconstituting a dissolved active species from a colloidal reservoir. Moreover, this work highlights substantial differences between abnormal triazolylidenes and classical NHCs, such as imidazol-2-ylidenes, in metal bonding.

## Experimental Section

**General**: 1-Methyl-4-phenyl-1,2,3-triazole, 1-mesityl-4-phenyl-1,2,3-triazole, the triazolium salt **1c**, and the silver carbenes **2b** and **2e** have been described previously.[12,14b,38] All other reagents are commercially available and were used as received. Microwave reactions were carried out by using a Biotage Initiator 2.5, operating at 100 W irradiation power. Unless otherwise specified, NMR spectra were recorded at 25 °C on Varian Innova spectrometers operating at 300, 400, or 500 MHz ($^1$H NMR) and 75, 100, or 125 MHz ($^{13}$C{1H} NMR). Chemical shifts ($\delta$ in ppm and coupling constants $J$ in Hz) were referenced to residual solvent resonances. Assignments are based on homo- and heteronuclear shift correlation spectroscopy. Elemental analyses were performed by the Microanalytical Laboratory at University College Dublin, Ireland, by using an Exeter Analytical CE-440 Elemental Analyzer.

**General procedure for the synthesis of the triazolium iodides 1**: MeI was added to a solution of triazole in MeCN and the mixture was stirred under microwave irradiation at 90 °C for 5 h. All volatiles were then removed in vacuo. The residue was washed several times with copious amounts of $Et_2O$ and dried in vacuo to afford the crude triazolium salt **1**. Microanalytically pure samples were obtained by recrystallization from hot acetone. Analytical data for the new triazolium salts are compiled in the Supporting Information.

**General procedure for the synthesis of the carbene–silver complexes 2**: $Ag_2O$ (0.5 equiv) was added to a solution of the triazolium salt **1** (1.0 equiv) in $CH_2Cl_2$. The mixture was stirred in the absence of light at room temperature for 2 h and then filtered through Celite. The solvent was removed in vacuo at room temperature and the residue was washed with pentane (3×25 mL) and dried in vacuo. Analytical data for the new triazolium salts are compiled in the Supporting Information.

**General procedure for the synthesis of the carbene–palladium complexes 3**: The carbene–silver complex **2** and $PdCl_2$ were suspended in 3-chloropyridine (7 mL) and stirred at 100 °C for 16 h. The reaction mixture was cooled to RT, diluted with $CH_2Cl_2$ (7 mL) and passed through a short column of $SiO_2$ covered with a pad of Celite. After product elution with $CH_2Cl_2$ was complete (TLC), all volatiles were evaporated under reduced pressure. The product was precipitated from pentane, collected by filtration, and dried in vacuo. The residue was dissolved in a minimum amount of $CH_2Cl_2$ and poured into $Et_2O$ (50 mL). The precipitate was removed by filtration and the filtrate was evaporated to dryness, affording pure complex **3**.

**Complex 3a**: The reaction of **2a** (500 mg, 0.61 mmol) and $PdCl_2$ (217 mg, 1.23 mmol) according to the general procedure afforded **3a** as a yellow solid (200 mg, 35 %). $^1$H NMR ($CDCl_3$ 500 MHz): $\delta$ = 9.00 (d, $^4J_{HH}$ = 2.3 Hz, 1H; $H_{Py}$), 8.89 (dd, $^3J_{HH}$ = 5.5, $^4J_{HH}$ = 1.2 Hz, 1H; $H_{Py}$), 7.93 (dd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.4 Hz, 2H; $H_{Ar}$), 7.72 (ddd, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 2.3, 1.2 Hz, 1H; $H_{Py}$), 7.56 (m, 3H; $H_{Ar}$), 7.28 (ddd, $^3J_{HH}$ = 8.2, 5.5, $^5J_{HH}$ = 0.4 Hz, 1H; $H_{Py}$), 4.59 (s, 3H; $NCH_3$), 3.98 ppm (s, 3H; $NCH_3$); $^{13}$C{$^1$H} NMR ($CDCl_3$, 125 MHz): $\delta$ = 150.6 ($C_{Py}$), 149.5 ($C_{Py}$), 144.2 ($C_{trz}$Ph), 139.0 ($C_{Py}$), 138.0 ($C_{trz}$Pd), 132.7 ($C_{Py}$), 131.3 (*m*-$C_{Ar}$), 130.9 (*p*-$C_{Ar}$), 129.8 (*o*-$C_{Ar}$), 128.3 (*i*-$C_{Ar}$), 126.6 ($C_{Py}$), 41.8 ($NCH_3$), 37.5 ppm ($NCH_3$); elemental analysis calcd for $C_{15}H_{17}Cl_3N_4Pd$ (466.10): C 38.65, H 3.68, N 12.02; found: C 38.16, H 3.49, N 11.64.

**Complex 3b**: The reaction of **2b** (500 mg, 0.59 mmol) and $PdCl_2$ (217 mg, 1.23 mmol) according to the general procedure afforded **3b** as a yellow solid (226 mg, 40 %). $^1$H NMR ($CDCl_3$ 500 MHz): $\delta$ = 9.00 (d, $^4J_{HH}$ = 2.2 Hz, 1H; $H_{Py}$), 8.89 (dd, $^3J_{HH}$ = 5.5, $^4J_{HH}$ = 1.2 Hz, 1H; $H_{Py}$), 7.93 (dd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.4 Hz, 2H; $H_{Ar}$), 7.72 (ddd, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 2.2, 1.2 Hz, 1H; $H_{Py}$), 7.56 (m, 3H; $H_{Ar}$), 7.28 (ddd, $^3J_{HH}$ = 8.2, 5.5, $^5J_{HH}$ = 0.4 Hz, 1H; $H_{Py}$), 5.03 (q, $^3J_{HH}$ = 7.3 Hz, 2H; $NCH_2Me$), 3.99 (s, 3H; $NCH_3$), 1.86 ppm (t, $^3J_{HH}$ = 7.3 Hz, 3H; $NCH_2CH_3$); $^{13}$C{$^1$H} NMR ($CDCl_3$, 125 MHz): $\delta$ = 150.5 ($C_{Py}$), 149.5 ($C_{Py}$), 143.8 ($C_{trz}$Ph), 138.0 ($C_{Py}$), 136.6 ($C_{trz}$Pd), 133.0 ($C_{Py}$), 131.3 (*m*-$C_{Ar}$), 130.9 (*p*-$C_{Ar}$), 129.1 (*o*-$C_{Ar}$), 126.7 (*i*-$C_{Ar}$), 124.7 ($C_{Py}$), 50.6 ($NCH_2Me$), 37.6 ($NCH_3$), 15.4 ppm ($NCH_2CH_3$); elemental analysis calcd for $C_{16}H_{19}Cl_3N_4Pd$ (480.13): C 40.03, H 3.99, N 11.67, found: C 40.25, H 3.91, N 11.54.

**Complex 3c**: The reaction of **2c** (670 mg, 0.78 mmol) and $PdCl_2$ (276 mg, 1.56 mmol) according to the general procedure afforded **3c** as a yellow powder (400 mg, 53 %). $^1$H NMR ($CDCl_3$ 500 MHz): $\delta$ = 9.10 (d, $^4J_{HH}$ = 2.0 Hz, 1H; $H_{Py}$), 8.98 (dd, $^3J_{HH}$ = 5.4, $^4J_{HH}$ = 1.2 Hz, 1H; $H_{Py}$), 7.75 (ddd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 2.0, 1.2 Hz, 1H; $H_{Py}$), 7.31 (ddd, $^3J_{HH}$ = 8.1, 5.4, $^5J_{HH}$ = 0.4 Hz, 1H; $H_{Py}$), 4.82 (m, 2H; $NCH_2$), 3.95 (s, 3H; $NCH_3$), 3.04 (t, $^3J_{HH}$ = 7.8 Hz, 2H; $C_{trz}CH_2$), 2.27 (quint, $^3J_{HH}$ = 7.5 Hz, 2H; $NCH_2CH_2$), 2.00 (quint, $^3J_{HH}$ = 7.8 Hz, 2H; $C_{trz}CH_2CH_2$), 1.50 (m, 4H; $NCH_2CH_2CH_2$, $C_{trz}CH_2CH_2CH_2$), 1.03, 1.02 ppm (2×t, $^3J_{HH}$ = 7.3 Hz, 3H; $NCH_2CH_2CH_2CH_3$, $C_{trz}CH_2CH_2CH_2CH_3$); $^{13}$C{$^1$H} NMR ($CDCl_3$, 125 MHz): $\delta$ = 150.6 ($C_{Py}$), 149.5 ($C_{Py}$), 144.2 ($C_{trz}$Bu), 138.0, 134.9, 132.8 (3×$C_{Py}$), 129.2 ($C_{trz}$Pd), 54.6 ($NCH_2$), 36.3 ($NCH_3$), 32.0 ($NCH_2CH_2$), 31.4 ($C_{trz}CH_2$), 25.0 ($C_{trz}CH_2CH_2$), 22.8, 20.1 ($C_{trz}CH_2CH_2CH_2$, $NCH_2CH_2CH_2$), 14.0, 13.8 ppm ($C_{trz}CH_2CH_2CH_2CH_3$, $NCH_2CH_2CH_2CH_3$); elemental analysis calcd for $C_{16}H_{25}Cl_3N_4Pd$ (480.13): C 39.53, H 5.18, N 11.52; found: C 39.46, H 5.09, N 11.36.

**Complex 3d**: The reaction of complex **2d** (975 mg, 0.95 mmol) and $PdCl_2$ (338 mg, 1.90 mmol) according to the general procedure afforded **3d** as a light yellow powder (184 mg, 18 %). $^1$H NMR ($CDCl_3$ 500 MHz): $\delta$ = 8.80 (d, $^4J_{HH}$ = 2.2 Hz, 1H; $H_{Py}$), 8.68 (dd, $^3J_{HH}$ = 5.5, 1.1 Hz, 1H; $H_{Py}$), 8.11 (d, $^3J_{HH}$ = 7.0 Hz, 2H; $H_{Ar}$), 7.59 (m, 3H; $H_{Ar}$), 7.56 (m, 1H; $H_{Py}$), 7.11 (m, 1H; $H_{Py}$), 7.06 (m, 2H; $H_{Mes}$), 4.13 (s, 3H; $NCH_3$), 2.39 (s, 3H; $ArCH_3$), 2.30 ppm (s, 6H; $ArCH_3$); $^{13}$C{$^1$H} NMR ($CDCl_3$, 125 MHz): $\delta$ = 150.6 ($C_{Py}$), 149.6 ($C_{Py}$), 144.3 ($C_{trz}$Mes), 140.6 ($C_{Ar}$), 140.4 ($C_{Ar}$), 137.7 ($C_{Py}$), 136.1 ($C_{Py}$), 135.3 ($C_{Ar}$), 132.3 ($C_{trz}$Pd), 130.8 ($C_{Ar}$), 130.4 ($C_{Ar}$), 129.5 ($C_{Ar}$), 129.1 ($C_{Ar}$), 127.1 ($C_{Py}$), 124.6 ($C_{Ar}$), 37.9 ($NCH_3$), 21.5 ($ArCH_3$), 19.0 ppm ($ArCH_3$); elemental analysis calcd for $C_{23}H_{23}Cl_3N_4Pd{\cdot}H_2O$ (568.23): C 47.12, H 4.30, N 9.56, found: C 46.96, H 4.21, N 9.10.

**Complex 3e**: The reaction of complex **2e** (200 mg, 0.18 mmol) and $PdCl_2$ (64 mg, 0.36 mmol) according to the general procedure afforded **3e** as a yellow powder (125 mg, 57%). $^1$H NMR ($CDCl_3$ 500 MHz): $\delta = 8.75$ (d, $^4J_{HH} = 2.2$ Hz, 1H; $H_{Py}$), 8.65 (dd, $^3J_{HH} = 5.5$, $^4J_{HH} = 1.1$ Hz, 1H; $H_{Py}$), 7.56 (ddd, $^3J_{HH} = 8.1$, $^4J_{HH} = 2.2$, 1.1 Hz, 1H; $H_{Py}$), 7.08 (m, 1H; $H_{Py}$), 7.07 (s, 2H; $H_{Mes}$), 7.05 (s, 2H; $H_{Mes}$), 3.82 (s, 3H; $NCH_3$), 2.39, 2.38 (2×s, 3H; $ArCH_3$), 2.32 ppm (s, 12H; $ArCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): $\delta = 150.7$ ($C_{Py}$), 149.8 ($C_{Py}$), 143.6 ($C_{trz}$Mes), 140.8 ($C_{Ar}$), 140.6 ($C_{Ar}$), 140.5 ($C_{Ar}$), 139.5 ($C_{Ar}$), 137.5 ($C_{Py}$), 136.1 ($C_{Py}$), 135.6 ($C_{Ar}$), 132.1 ($C_{trz}$Pd), 129.5 ($C_{Ar}$), 129.1 ($C_{Ar}$), 124.4 ($C_{Py}$), 122.9 ($C_{Ar}$), 36.6 ($NCH_3$), 21.6 ($ArCH_3$), 21.5 ($ArCH_3$), 21.2 ($ArCH_3$), 19.0 ppm ($ArCH_3$); elemental analysis calcd for $C_{26}H_{29}Cl_3N_4Pd{\cdot}H_2O$ (610.30): C 49.70, H 4.97, N 8.92, found: C 50.12, H 4.61, N 8.85.

**General procedures for Suzuki–Miyaura Cross-Coupling**: Phenylboronic acid (147 mg, 1.2 mmol), base (1.5 mmol), 3-bromoanisole (127 μL, 1.0 mmol), and 2-propanol (3.0 mL) were added to a Schlenk tube containing complex **3** (0.5 mol% or 1.0 mol%) and a magnetic stirring bar. The Schlenk tube was placed in a preheated (50°C) oil bath and stirred for the time indicated. The mixture was quenched with water, extracted with $CH_2Cl_2$, dried over $MgSO_4$, and filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was analyzed by $^1$H NMR spectroscopy. Chemical shifts of the starting materials and products were compared with data reported previously.[39]

**ESI-MS analyses**: Complex **3** (1 mg) was dissolved in *i*PrOH (3 mL) at 50°C and phenylboronic acid (7 mg), $Bu_4NF$ (50 μL), and 3-bromoanisole (7 mg) were added. MS spectra were recorded after 5, 20, and 35 min for samples (10 μL) diluted with *i*PrOH (1.5 mL) on an Apex-Qe Ultra 7T instrument (Bruker Daltonics, Germany) equipped with an ESI source. The potential between the spray needle and the orifice was set to 4.5 kV, the source accumulation time was 0.5 s and the ion accumulation time was 0.5 s.

**Transmission electron microscopy**: Complex **3** (1 mg), phenylboronic acid (7 mg) and 3-bromoanisole (7 mg) were placed in a test tube and subsequently *i*PrOH (3 mL) and $Bu_4NF$ (50 μL) were added. The tube was sealed with a plastic stopper and heated at 50°C for 35 min with magnetic stirring. A droplet of the reaction mixture was placed on a carbon-coated microscope grid and dried for 40 min. TEM measurements were carried out by using a FEI Tecnai $G^2$ 20 X-TWIN electron microscope (TEM) operating at 200 kV.

**Crystallographic details**: Crystal data for complexes **3b**, **3c**, and **3d** were collected by using an Agilent Technologies SuperNova A diffractometer fitted with an Atlas detector that uses monochromated $Mo_{K\alpha}$ radiation (0.71073 Å). A complete dataset was collected, assuming that the Friedel pairs are not equivalent. An analytical numeric absorption correction was performed.[40] The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares fitting on $F^2$ for all data using SHELXL-97.[41] Hydrogen atoms were added at calculated positions and refined by using a riding model. Anisotropic thermal displacement parameters were used for all nonhydrogen atoms. Further crystallographic details are compiled in the Supporting Information (Tables S1–S3). CCDC-855567 (**3d**), CCDC-855568 (**3b**), and CCDC-855569 (**3c**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## Acknowledgements

We thank Dr. Ewa Mieczyńska and Mr. Marek Jon (Faculty of Chemistry, University of Wrocław) for experimental assistance. Financial support from Science Foundation Ireland, the European Research Council (ERC Starting Grant), the Polish Ministry of Science and Higher Education (N164/COST/2008), and COST D40 is gratefully acknowledged.

[1] a) *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed. (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**; b) *Modern Arylation Methods* (Ed.: L. Ackermann), Wiley-VCH, Weinheim, **2009**; c) *Palladacycles: Synthesis, Characterization and Applications* (Eds.: J. Dupont, M. Pfeffer), Wiley-VCH, Weinheim, **2010**; d) A. Suzuki, *Angew. Chem.* **2011**, *123*, 6854–6869; *Angew. Chem. Int. Ed.* **2011**, *50*, 6722–6737; e) E. Negishi, *Angew. Chem.* **2011**, *123*, 6870–6897; *Angew. Chem. Int. Ed.* **2011**, *50*, 6738–6764; f) I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009–3066; g) J. F. Hartwig, *Nature* **2008**, *455*, 314–319; h) J.-P. Corbet, G. Mignani, *Chem. Rev.* **2006**, *106*, 2651–2710; i) J. Magano, J. R. Dunetz, *Chem. Rev.* **2011**, *111*, 2177–2250.

[2] For examples, see: a) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174–238; b) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147–1169; c) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem.* **2009**, *121*, 5196–5217; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094–5115.

[3] a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483; b) M. Portnoy, D. Milstein, *Organometallics* **1993**, *12*, 1665–1673.

[4] M. Beller, H. Fischer, W. A. Herrmann, K. Öfele, C. Brossmer, *Angew. Chem.* **1995**, *107*, 1992–1993; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1848–1849.

[5] A. F. Littke, G. C. Fu, *Angew. Chem.* **1998**, *110*, 3586–3587; *Angew. Chem. Int. Ed.* **1998**, *37*, 3387–3388.

[6] D. W. Old, J. P. Wolfe, S. L. Buchwald, *J. Am. Chem. Soc.* **1998**, *120*, 9722–9723.

[7] C. Zhang, J. Huang, M. L. Trudell, S. P. Nolan, *J. Org. Chem.* **1999**, *64*, 3804–3805.

[8] a) M. G. Organ, S. Avola, I. Dubovyk, N. Hadei, E. A. B. Kantchev, C. J. O'Brien, C. Valente, *Chem. Eur. J.* **2006**, *12*, 4749–4755; b) C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson, M. G. Organ, *Chem. Eur. J.* **2006**, *12*, 4743–4748; c) E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem.* **2007**, *119*, 2824–2870; *Angew. Chem. Int. Ed.* **2007**, *46*, 2768–2813; for a related concept, see: d) O. Navarro, N. Marion, J. Mei, S. P. Nolan, *Chem. Eur. J.* **2006**, *12*, 5142–5148; e) M.-T. Chen, D. A. Vicic, M. L. Turner, O. Navarro, *Organometallics* **2011**, *30*, 5052–5056.

[9] a) *N-Heterocyclic Carbenes in Synthesis* (Ed.: S. P. Nolan), Wiley-VCH, Weinheim, **2006**; b) *Catalysis by Complexes, Vol. 32, Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis* (Ed.: C. S. J. Cazin), Springer, Berlin, **2010**; c) *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools* (Ed.: S. Diez-Gonzalez), RSC, Cambridge, **2010**; d) D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91; e) W. A. Herrmann, C. Köcher, *Angew. Chem.* **2002**, *114*, 1342–1363; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309; f) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; g) special issue: A. J. Arduengo, G. Bertrand, *Chem. Rev.* **2009**, *109*, 3209–3210.

[10] a) P. L. Arnold, J. Pearson, *Coord. Chem. Rev.* **2007**, *251*, 596–609; b) M. Albrecht, *Chem. Commun.* **2008**, 3601–3610; c) O. Schuster, L. Yang, M. Albrecht, H. G. Raubenheimer, *Chem. Rev.* **2009**, *109*, 3445–3478; d) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem.* **2010**, *122*, 8992–9032; *Angew. Chem. Int. Ed.* **2010**, *49*, 8810–8849; e) D. G. Gusev, *Organometallics* **2009**, *28*, 6458–6461; f) Y. Han, H. V. Huynh, *Dalton Trans.* **2011**, *40*, 2141–2147; g) M. Iglesias, M. Albrecht, *Dalton Trans.* **2010**, *39*, 5213–5215.

[11] a) A. Lawson, C. E. Searle, *J. Chem. Soc.* **1957**, 1556–1561; b) A. D. McNaught, A. Wilkinson in *IUPAC Compendium of Chemical Terminology (the "Gold Book")* 2nd ed., Blackwell Scientific Publications, Oxford, **1997**.

[12] P. Mathew, A. Neels, M. Albrecht, *J. Am. Chem. Soc.* **2008**, *130*, 13534–13535.

[13] G. Guisado-Barrios, J. Bouffard, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2010**, *122*, 4869–4872; *Angew. Chem. Int. Ed.* **2010**, *49*, 4759–4762.

[14] a) R. Lalrempuia, N. D. McDaniel, H. Müller-Bunz, S. Bernhard, M. Albrecht, *Angew. Chem.* **2010**, *122*, 9959–9962; *Angew. Chem. Int. Ed.* **2010**, *49*, 9765–9768; b) T. Nakamura, K. Ogata, S. Fukuzawa, *Chem. Lett.* **2010**, *39*, 920–922; c) K. J. Kilpin, U. S. D. Paul, A.-L.

Lee, J. D. Crowley, *Chem. Commun.* **2011**, *47*, 328–330; d) T. Nakamura, T. Terashima, K. Ogata, S. Fukuzawa, *Org. Lett.* **2011**, *13*, 620–623; e) A. Poulain, D. Canseco-Gonzalez, R. Hynes-Roche, H. Müller-Bunz, O. Schuster, H. Stoeckli-Evans, A. Neels, M. Albrecht, *Organometallics* **2011**, *30*, 1021–1029; f) A. Prades, E. Peris, M. Albrecht, *Organometallics* **2011**, *30*, 1162–1167; g) R. Saravanakumar, V. Ramkumar, S. Sankararaman, *Organometallics* **2011**, *30*, 1689–1694; h) J. Bouffard, B. K. Keitz, R. Tonner, G. Guisado-Barrios, G. Frenking, R. H. Grubbs, G. Bertrand, *Organometallics* **2011**, *30*, 2617–2627; i) L. Bernet, R. Lalrempuia, W. Ghattas, H. Mueller-Bunz, L. Vigara, A. Llobet, M. Albrecht, *Chem. Commun.* **2011**, *47*, 8058–8060; j) J. D. Crowley, A.-L. Lee, K. J. Kilpin, *Aust. J. Chem.* **2011**, *64*, 1118–1132.

[15] a) R. Huisgen, *Angew. Chem.* **1963**, *75*, 604–637; *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 565–598; b) H. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem.* **2001**, *113*, 2056–2075; *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021; c) M. Meldal, C. W. Tornoe, *Chem. Rev.* **2008**, *108*, 2952–3015; d) special issue: M. G. Finn, V. V. Fokin, *Chem. Soc. Rev.* **2010**, *39*, 1231–1232.

[16] Similar observations have recently been reported in ruthenium-catalyzed olefin metathesis: B. K. Keitz, J. Bouffard, G. Bertrand, R. H. Grubbs, *J. Am. Chem. Soc.* **2011**, *133*, 8498–8501.

[17] See the Supporting Information for details.

[18] The pertinent $^{13}$C NMR chemical shifts for C–Pd are 138.0 (**3a**), 136.6 (**3b**), 129.2 (**3c**), 132.3 (**3d**), and 132.1 ppm (**3e**).

[19] A. Poulain, M. Iglesias, M. Albrecht, *Curr. Org. Chem.* **2011**, *15*, 3325–3336.

[20] Similar to **3b**, complexes **4** and **5** exhibit poor catalytic performance when DMA or dioxane were used as the solvent. See the Supporting Information for a time–conversion profile of **4** and **5**.

[21] H. Lebel, M. K. Janes, A. B. Charette, S. P. Nolan, *J. Am. Chem. Soc.* **2004**, *126*, 5046–5047.

[22] a) D. Bacciu, K. J. Cavell, I. A. Fallis, L.-I. Ooi, *Angew. Chem.* **2005**, *117*, 5416–5418; *Angew. Chem. Int. Ed.* **2005**, *44*, 5282–5284; b) M. Heckenroth, A. Neels, M. G. Garnier, P. Aebi, A. W. Ehlers, M. Albrecht, *Chem. Eur. J.* **2009**, *15*, 9375–9386.

[23] J. Nasielski, N. Hadei, G. Achonduh, E. A. Kantchev, C. J. O'Brien, M. G. Organ, *Chem. Eur. J.* **2010**, *16*, 10844–10853.

[24] a) A. F. Littke, G. C. Fu, *Angew. Chem.* **2002**, *114*, 4350–4386; *Angew. Chem. Int. Ed.* **2002**, *41*, 4176–4211; b) R. B. Bedford, C. S. J. Cazin, D. Holder, *Coord. Chem. Rev.* **2004**, *248*, 2283–2321; nanoparticles have been reported to catalyze aryl chloride conversion: c) R. B. Bedford, M. E. Blake, C. P. Butts, D. Holder, *Chem. Commun.* **2003**, 466–467; d) N. E. Leadbeater, M. Marco, *Org. Lett.* **2002**, *4*, 2973–2976.

[25] I. Blaszczyk, A. Gniewek, A. M. Trzeciak, *J. Organomet. Chem.* **2011**, *696*, 3601–3607.

[26] a) D. R. Anton, R. H. Crabtree, *Organometallics* **1983**, *2*, 855–859; b) G. M. Whitesides, M. Hackett, R. L. Brainard, J. P. P. M. Lavalleye, A. F. Sowinski, A. N. Izumi, S. S. Moore, D. W. Brown, E. M. Staudt, *Organometallics* **1985**, *4*, 1819–1830; c) J. A. Widegren, R. G. Finke, *J. Mol. Catal. A: Chem.* **2003**, *198*, 317–341; d) R. H. Crabtree, *Chem. Rev.* **2012**, *112*, 1536–1554; mercury poisoning in palladium-catalyzed cross-coupling is not unambiguous, see: e) N. T. S. Phan, M. van der Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609–679.

[27] R. D. Glover, J. M. Miller, J. E. Hutchision, *ACS Nano* **2011**, *5*, 8950–8957.

[28] I. P. Beletskaya, A. N. Kashin, I. A. Khotina, A. R. Khokhlov, *Synlett* **2008**, 1547–1552.

[29] W. Zawartka, A. Gniewek, A. M. Trzeciak, J. J. Ziolkowski, J. Pernak, *J. Mol. Catal. A: Chem.* **2009**, *304*, 8–15.

[30] P. Lara, O. Rivada-Wheelaghan, S. Conejero, R. Poteau, K. Philippot, B. Chaudret, *Angew. Chem.* **2011**, *123*, 12286–12290; *Angew. Chem. Int. Ed.* **2011**, *50*, 12080–12084.

[31] B. Liu, Q. Xia, W. Chen, *Angew. Chem.* **2009**, *121*, 5621–5624; *Angew. Chem. Int. Ed.* **2009**, *48*, 5513–5516.

[32] C. C. Cassol, A. P. Umpierre, G. Machado, S. I. Wolke, J. Dupont, *J. Am. Chem. Soc.* **2005**, *127*, 3298–3299.

[33] A. Gniewek, A. M. Trzeciak, J. J. Ziolkowski, L. Kepinski, J. Wrzyszcz, W. Tylus, *J. Catal.* **2005**, *229*, 332–343.

[34] Heterogenization has been report to occur, although, generally, the catalytic activity has been attributed to the nanoparticles themselves and not to redissolved molecular palladium species. See: a) M. T. Reetz, J. G. de Vries, *Chem. Commun.* **2004**, 1559–1563; b) J. G. de Vries, *Dalton Trans.* **2006**, 421–429; c) D. Astruc, *Inorg. Chem.* **2007**, *46*, 1884–1894; d) Y. Tsuji, T. Fujihara, *Inorg. Chem.* **2007**, *46*, 1895–1902; e) A. Gniewek, J. J. Ziolkowski, A. M. Trzeciak, M. Zawadzki, H. Grabowska, J. Wrzyszcz, *J. Catal.* **2008**, *254*, 121–130; f) Y.-H. Chen, H.-H. Hung, M. H. Huang, *J. Am. Chem. Soc.* **2009**, *131*, 9114–9121; g) P. J. Ellis, I. J. S. Fairlamb, S. F. J. Hackett, K. Wilson, A. F. Lee, *Angew. Chem.* **2010**, *122*, 1864–1868; *Angew. Chem. Int. Ed.* **2010**, *49*, 1820–1824; h) A. N. Kashin, I. P. Beletskaya, *Russ. J. Org. Chem.* **2011**, *47*, 475–479; for critical reviews, see also: i) I. P. Beletskaya, A. V. Cheprakov, *J. Organomet. Chem.* **2004**, *689*, 4055–4082; j) L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133–173.

[35] Metal leaching from solid supports has been demonstrated for the Heck reaction at high temperatures: a) S. S. Pröckl, W. Kleist, M. A. Gruber, K. Köhler, *Angew. Chem.* **2004**, *116*, 1917–1918; *Angew. Chem. Int. Ed.* **2004**, *43*, 1881–1882; b) S. S. Pröckl, W. Kleist, K. Köhler, *Tetrahedron* **2005**, *61*, 9855–9859; c) J. M. Richardson, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 1207–1216; d) I. Pryjomska-Ray, A. Gniewek, A. M. Trzeciak, J. J. Ziolkowski, W. Tylus, *Top. Catal.* **2006**, *40*, 173–184; e) S. MacQuarrie, J. H. Horton, J. Barnes, K. McEleney, H.-P. Loock, C. M. Crudden, *Angew. Chem.* **2008**, *120*, 3324–3328; *Angew. Chem. Int. Ed.* **2008**, *47*, 3279–3282; f) P.-P. Fang, A. Jutand, Z.-Q. Tian, C. Amatore, *Angew. Chem. Int. Ed.* **2011**, *50*, 12184; for a relevant example in palladium-catalyzed addition reactions, see: g) V. P. Ananikov, N. V. Orlov, I. P. Beletskaya, V. N. Khrustalev, M. Y. Antipin, T. V. Timofeeva, *J. Am. Chem. Soc.* **2007**, *129*, 7252–7253; for an excellent review, see: h) V. P. Ananikov, I. P. Beletskaya, *Organometallics* **2012**, *31*, 1595–1604.

[36] a) M. Weck, C. W. Jones, *Inorg. Chem.* **2007**, *46*, 1865–1875; b) K. Köhler, W. Kleist, S. S. Pröckl, *Inorg. Chem.* **2007**, *46*, 1876–1883.

[37] a) G. Zassinovich, G. Mestroni, S. Gladiali, *Chem. Rev.* **1992**, *92*, 1051–1069; b) D. Klomp, U. Hanefeld, J. A. Peters, in *Handbook of Homogeneous Hydrogenation, Vol. 2* (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2007**, 585–630; c) S. Gladiali, E. Alberico, *Chem. Soc. Rev.* **2006**, *35*, 226–236; d) J. S. M. Samec, J.-E. Bäckvall, P. G. Andersson, P. Brandt, *Chem. Soc. Rev.* **2006**, *35*, 237–248.

[38] a) P. Appukkuttana, W. Dehaena, V. Fokin, M. Van der Eycken, *Org Lett.* **2004**, *6*, 4223–4225; b) K. Barral D. A. Moorhouse, J. E. Moses, *Org Lett.* **2007**, *9*, 1809–1811; c) D. Kumar, V. B. Reddy, *Synthesis* **2010**, 1687–1691.

[39] J. Jin, M. M. Cai, J. X. Li, *Synlett* **2009**, 2534–2538.

[40] *CrysalisPro, Version 1.171.34.36*, Oxford Diffraction Limited, **2010**.

[41] G. M. Sheldrick, *Acta Crystallogr. A* **2008**, *64*, 112–122.

Received: November 25, 2011
Revised: February 9, 2012
Published online: March 29, 2012