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Palladium complexes of amido-functionalized N-heterocyclic carbenes as effective precatalysts for the Suzuki–Miyaura C–C cross-coupling reactions of aryl bromides and iodides

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ABSTRACT

A series of air-stable, robust and highly active palladium based precatalysts of amido-functionalized N-heterocyclic carbenes for the Suzuki–Miyaura C–C cross-coupling reaction has been designed. In particular, the [1-R-3-{*N*-(benzylacetamido)imidazol-2-ylidene]$_2$PdCl$_2$ [R = *i*-Pr (**1c**) and CH$_2$Ph (**2c**)] complexes efficiently carried out the Suzuki–Miyaura coupling of the aryl bromide and iodide substrates with phenyl boronic acid in good to excellent yields in air at 90 °C in 12 h. Quite interestingly, of these palladium precatalysts, the *i*-propyl derivative (**1c**) exhibited superior activity as compared to the benzyl derivative (**2c**). The density functional theory (DFT) studies carried out on the **1c** and **2c** complexes revealed the strong σ-donating nature of the NHC ligand as reflected in their high *d*/*b* ratio [*i.e.* forward σ-donation (*d*) to backward π-donation (*b*)] of these complexes and, thus, point towards greater stability of the Pd–NHC interaction in these complexes.

1. Introduction

As a convenient approach to accessing the "biaryl frameworks", so ubiquitous in many important bioactive molecules as well as in value-added chemical feedstock, the Suzuki–Miyaura C–C cross-coupling reaction, today, has emerged as a major work horse in synthetic organic chemistry [1–7]. In particular, the famed reaction involves highly efficient C–C cross-coupling of aryl halide with aryl boronic acid in a catalytic fashion aided by palladium in presence of a base. The extreme popularity of the Suzuki–Miyaura reaction stems form its regio- and stereoselectivity, functional group tolerance, ready availability of the boron based starting materials, its non-toxic nature and its air and moisture stability. Thus, because of its utility as an important synthetic methodology, a significant amount of research focus had been devoted to designing improved catalysts for the Suzuki–Miyaura cross-coupling reaction. In this regard it is noteworthy that though numerous catalysts of phosphine based systems [8,9] have been reported for the coupling reaction, the use of N-heterocyclic carbenes based ones is a relatively new affair [10,11]. The N-heterocyclic carbene based precatalysts posses distinct advantages that arise from the tight binding of the NHC ligand to the metal, leading to a greater stability of the complex under the catalysis conditions, and which in turn helps suppress the leaching of the catalysts [12–14]. The tight binding of the NHC ligand to the metal is reflected in the high NHC–metal bond dissociation energy *eg.* 74.8 kcal/mol in *trans*-[1-benzyl-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene]$_2$PdBr$_2$, [15] 75.1 kcal/mol in *cis*-[1-benzyl-3-(*N*-*t*-butylacetamido)imidazol-2-ylidene]$_2$PdCl$_2$ [15] and 81.9 kcal/mol in *trans*-[1-(benzyl)-3-(*N*-*t*-butylacetamido)imidazol-2-ylidene]Pd(pyridine)Cl$_2$ [16] etc. The additional advantages of the N-heterocyclic carbenes arise from their easy tunability and from their behavior as good "spectator" ligands, which while influencing the catalysis, do not get consumed or chemically react in the process.

In continuing with our efforts on designing new precatalysts for a host of C–C bond forming reactions namely, the Hiyama [17], Sonogashira [15,17,18], Suzuki–Miyaura [16,19] and the base-free Michael reactions [20,21], we were in look out for new N-heterocyclic carbene based scaffolds for stabilizing palladium precatalysts for the coupling reactions. More specifically, with regard to the Suzuki–Miyaura coupling, we demonstrated the use of the *trans*-(NHC)$_2$PdX$_2$ (X = halide) and the famed PEPPSI [22–27] themed (NHC)PdX$_2$(pyridine) type complexes, of which the former ones showed ultra high activity [16,19]. Thus, the present efforts are directed along the line of developing new *trans*-(NHC)$_2$PdX$_2$ (X = halide) type complexes for application in the Suzuki–Miyaura cross-coupling reaction. In this connection, we additionally emphasized on employing well-defined N-heterocyclic carbene based precatalysts for the said study as opposed to performing it

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under the more common "Ligand Assisted Catalysis" (LAC) conditions is because the use of well-characterized catalysts display shorter reaction times and also significantly reduces the unwanted side reactions.

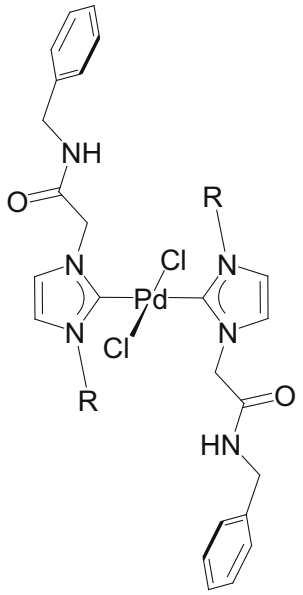
Here in this contribution, we report a series of robust and highly efficient palladium complexes of amido-functionalized N-heterocyclic carbenes namely, [1-R-3-{*N*-(benzylacetamido)imidazol-2-ylidene]$_2$PdCl$_2$ [R = *i*-Pr (**1c**) and CH$_2$Ph (**2c**)], for the Suzuki–Miyaura cross-coupling reactions of aryl bromides and iodides with phenyl boronic acid in air (Fig. 1).

2. Results and discussion

Two new amido-functionalized N-heterocyclic carbene ligands were designed with the intent of stabilizing palladium complexes for use as precatalysts for the Suzuki–Miyaura cross-coupling reaction. In this regard the following new N-heterocyclic carbene precursors, 1-R-3-*N*-(benzylacetamido)imidazolium chloride salts [R = *i*-Pr (**1a**) and CH$_2$Ph (**2a**)], were synthesized by the direct reaction of the *N*-benzyl-2-chloro-acetamide with the respective 1-R-imidazole (R = *i*-Pr and CH$_2$Ph) in 81–84% yield (Scheme 1). The appearance of the downfield shifted peaks at *ca.* 9.97–10.05 ppm in the ^{1}H NMR and at *ca.* 132.6–135.5 ppm in ^{13}C{^{1}H} NMR, that are characteristics of the NCHN resonances, indicated the clean formation of the imidazolium chloride salts **1a** and **2a**.

The palladium complexes [1-R-3-{*N*-(benzylacetamido)imidazol-2-ylidene]$_2$PdCl$_2$ [R = *i*-Pr (**1c**) and CH$_2$Ph (**2c**)] were obtained by following the transmetallion route form the silver complexes {[1-R-3-{*N*-(benzylacetamido)imidazol-2-ylidene]$_2$Ag}$^+$Cl$^-$ [R = *i*-Pr (**1b**) and CH$_2$Ph (**2b**)] by treatment with (COD)PdCl$_2$ (COD = *cis*,-*cis*-1,5-cyclooctadiene) in 52–64% yield. The silver complexes **1b** and **2b** were in turn synthesized from the respective imidazolium chloride salt **1a** and **2a** by the reaction with Ag$_2$O in 61–67% yield. Of interest, are the diagnostic M–C$_{carbene}$ resonances that appeared downfield shifted [M = Ag, 179.8 ppm (**1b**) and 182.2 ppm (**2b**); M = Pd, 169.2 ppm and 169.3 ppm (**1c**) and 159.0 ppm and 156.8 ppm (**2c**)] in the ^{13}C{^{1}H} NMR spectrum.

Quite expectedly, the molecular structure of the **1c** and **2c** complexes revealed monomeric square-planar geometry at the metal consistent with a d^8 palladium(II) metal center (Figs. 2 and 3 and Supplementary material Table S1). The Pd–C$_{carbene}$ bond distances [2.029 (3) Å (**1c**) and 2.032 (6) Å (**2c**)] are comparable to the sum of the individual covalent radii of Pd and C (2.055 Å) [28] and also to other related structurally characterized (NHC)$_2$PdCl$_2$ type examples namely, *trans*-[1-benzyl-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene]$_2$PdBr$_2$ [2.018(9) Å] [15], *cis*-[1-benzyl-3-(*N*-*t*-butylacetamido)imidazol-2-ylidene]$_2$PdCl$_2$ [1.998(2) Å] [15], and *trans*-[1-benzyl-3-*t*-butylimidazol-2-ylidene]$_2$PdCl$_2$ [2.044(4) Å] [29]. The Pd–Cl distances in **1c** and **2c** are 2.3167(8) Å and 2.309(2) Å, respectively. The other notable aspects of the **1c** and **2c** structures are the *trans* disposition of the of the N1 and N3 substituents of the imidazole rings, that make a coplanar arrangement to each other.



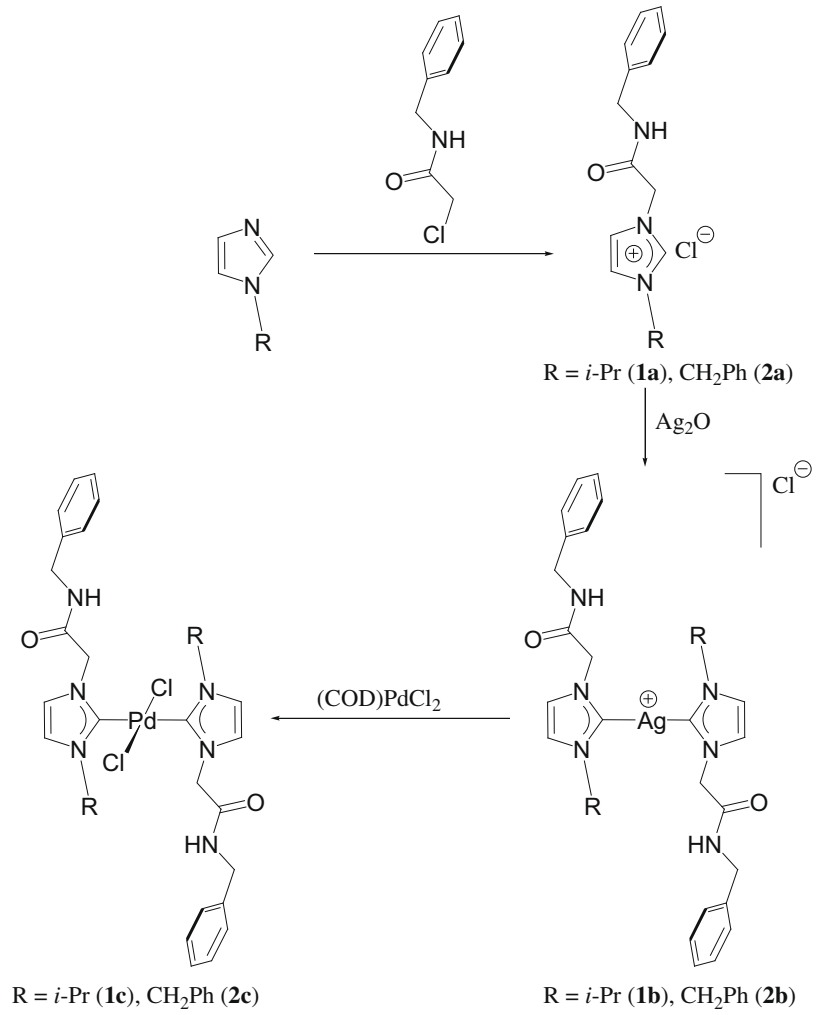
R = *i*-Pr (**1c**), CH$_2$Ph (**2c**)

Fig. 1. Palladium complexes of amido-functionalized N-heterocyclic carbenes.

Deeper understanding of the nature of the Pd–NHC interaction could be obtained by the density functional theory studies. Specifically, the respective geometry optimized structure of the palladium complexes, **1c** and **2c**, were obtained by computing at the B3LYP/SDD, 6-31G(d) level of theory using the atomic coordinates adopted from the X–ray analysis (Supplementary material Tables S2 and S3). Subsequent, single-point calculation was performed on the geometry optimized structure to obtain insight on the electronic properties of the complexes.

Quite interestingly, the NBO analysis indicated that the Pd–NHC bond is composed of an interaction of a C$_{carbene}$ sp^2 orbital with a *sd* orbital of the palladium center (Supplementary material Table S9). Indeed, a careful look at the electronic configuration of the palladium center in **1c** and **2c** relative to that in the PdCl$_2$ species as well as of the C$_{carbene}$ center in **1c** and **2c** relative to that in the free NHC ligand fragment reveal that electron donation occur from the free NHC ligand fragment on to the 5*s* orbital of the palladium center in **1c** and **2c** (Supplementary material Table S6). Corroborating the above mentioned observation, both the Mulliken and Natural Charge analysis showed that as a result of the σ-donation from the free NHC ligand fragment, the electron density at the palladium center increased from that in the PdCl$_2$ species to that in **1c** and **2c** (Supplementary material Tables S4 and S5). Also, attesting to the good σ-donating ability of the NHC ligand, the *d*/*b* ratio [1.96 (**1c**) and 2.98 (**2c**)], which is a measure of the relative extent of the NHC to metal σ-donation (*d*) and the metal to NHC π-back donation (*b*) and is computed using the Charge Decomposition Analysis (CDA) method, for the **1c** and **2c** complexes were found to be greater than unity (Supplementary material Table S8).

A closer look at the Pd–NHC interaction could be obtained by constructing the molecular orbital (MO) correlation diagram from the individual fragment molecular orbitals (FMO) of the respective free NHC ligand fragment and the PdCl$_2$ species (Figs. 4 and 5 and Supplementary material Figs. S1 and S2). Quite interestingly, the molecular orbitals HOMO−39 (**1c**) and HOMO−45 (**2c**) represent the σ-orbital interaction between the palladium center and the free NHC ligand fragment. Specifically, the Pd–NHC σ-bonding orbital, HOMO−39 (25% NHC, 31% PdCl$_2$), in **1c** showed an interaction of the carbene lone pair (HOMO−1 of the free NHC fragments) with a metal based vacant LUMO (72% palladium with 28% *s* and 44% *d* character) of the PdCl$_2$ fragment (Fig. 4). In the **2c** complex, the Pd–NHC σ-bonding orbital, HOMO−45 (21% NHC, 29% PdCl$_2$) showed an interaction of the carbene lone pair (HOMO−1 of the free NHC fragments) with a metal based vacant LUMO (72% palladium with 28% *s* and 44% *d* character) of the PdCl$_2$ fragment (Fig. 5). It is worth noting that these low lying Pd–NHC σ-molecular orbitals signify stable interaction which are less vulnerable to the electrophilic or nucleophilic attacks. In this regard it is noteworthy that carbenes along with its metal complexes, as such, are highly reactive compounds that readily undergo reactions with electrophiles and nucleophiles.



Scheme 1.

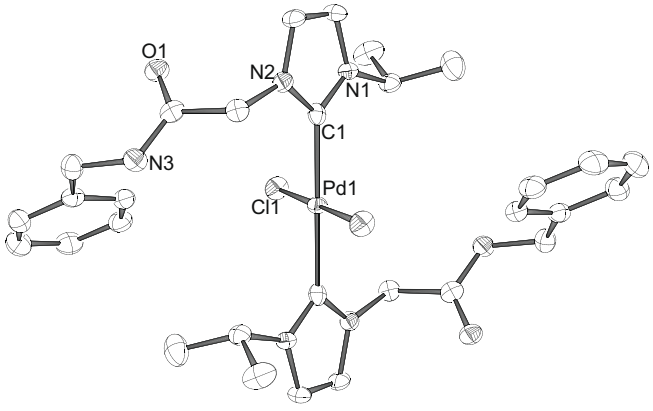


Fig. 2. ORTEP of **1c** with thermal ellipsoids drawn at 50% probability level. Selected bond length (Å) and bond angles (°): Pd1–C1 2.029(3), Pd1–Cl1 2.3161(8), C1–Pd1–C1 180.000(1), C1–Pd1–Cl1 90.41(8), C1–Pd1–Cl1_3 89.59(8), Cl1–Pd–Cl1 180.000(1), N1–C1–N2 104.4(2).

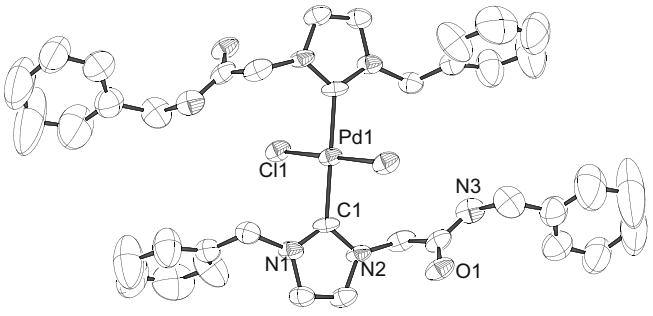


Fig. 3. ORTEP of **2c** with thermal ellipsoids drawn at 50% probability level. Selected bond length (Å) and bond angles (°): Pd1–C1 2.032(6), Pd1–Cl1 2.309(2), C1–Pd1–C1 180.00(14), C1–Pd1–Cl1 90.6(2), C1–Pd1–Cl1_3 89.4(2), Cl1–Pd–Cl1 180.0, N1–C1–N2 105.7(5).

Lastly, the strength of the Pd–NHC interaction could be gauged by estimating the Pd–$C_{carbene}$ bond dissociation energy (D_e) at B3LYP/SDD, 6-31G(d) level of theory and that gave a value of 68.3 kcal/mol (**1c**) and 69.0 kcal/mol (**2c**) for these palladium complexes (Supplementary material Table S7). The bond dissociation energy (D_e) values of 68.3 kcal/mol (**1c**) and 69.0 kcal/mol (**2c**) are similar to that estimated for other related palladium complexes namely, *trans*-[4-benzyl-1-*i*-propyl-1,2,4-triazol-5-ylidene]$PdBr_2$(NC_5H_5) (56.3 kcal/mol) [17], *trans*-[4-benzyl-1-(*t*-butylaminocarbonylmethyl)-1,2,4-triazol-5-ylidene]$PdBr_2$(NC_5H_5) (58.1 kcal/mol) [17], *trans*-[1-benzyl-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene]$_2PdBr_2$ (74.8 kcal/mol) [15], *cis*-[1-benzyl-3-(*N*-*t*-butylacetamido)imidazol-2-ylidene]$_2PdCl_2$ (75.1 kcal/mol) [15] and *trans*-[1-(benzyl)-3-(*N*-*t*-butylacetamido)imidazol-2-ylidene]$PdCl_2$-(NC_5H_5) (81.9 kcal/mol) [16].

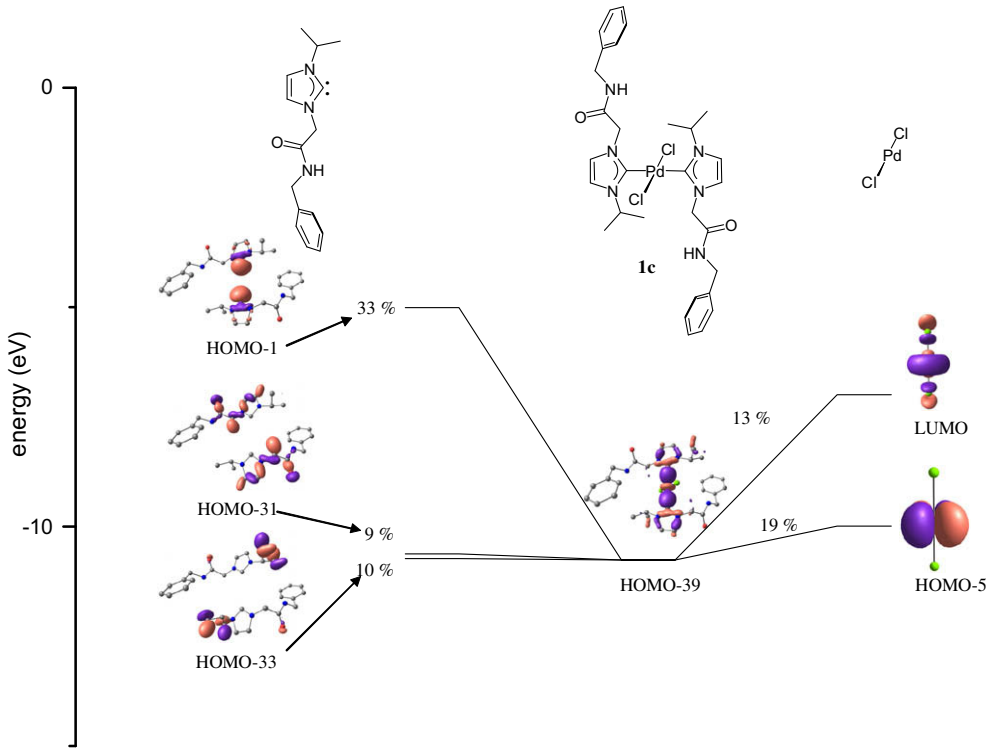


Fig. 4. Simplified orbital interaction diagram showing the major contribution of NHC–Pd bond in **1c**.

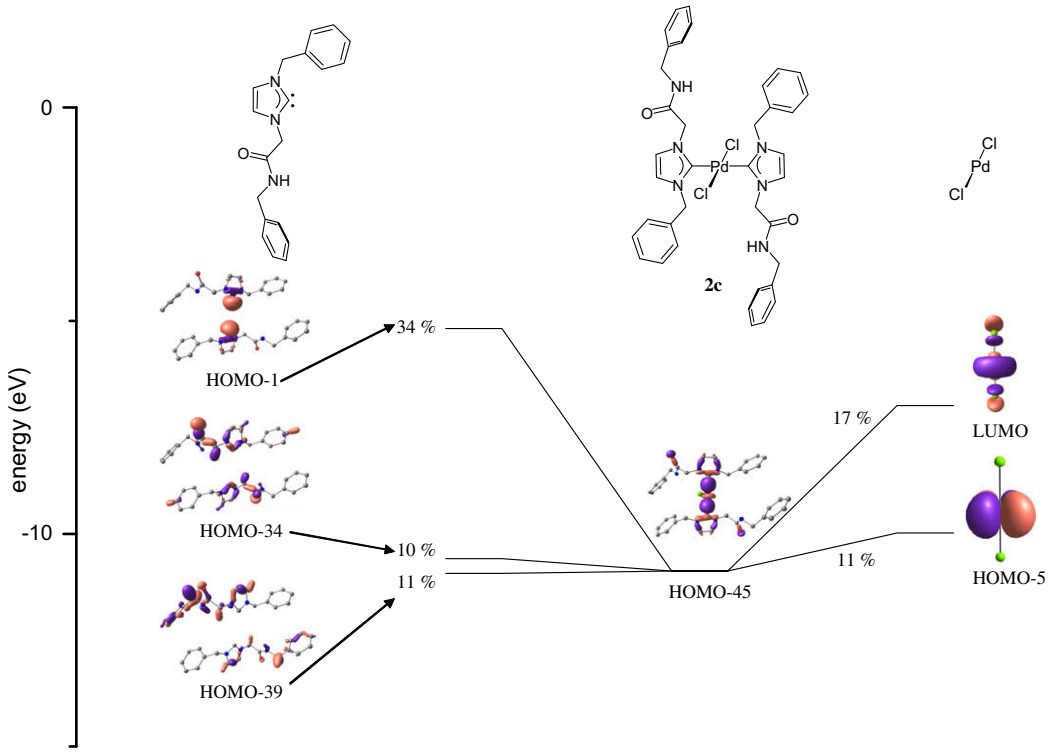
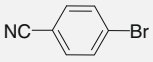
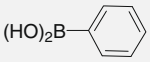
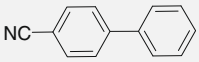
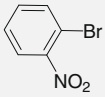
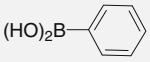
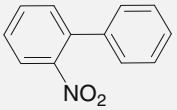
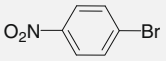
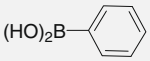
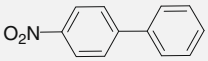
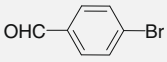
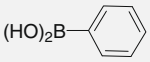
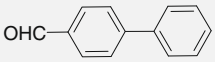
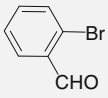
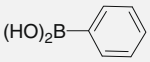
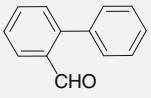
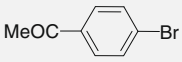
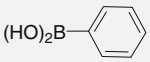
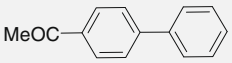
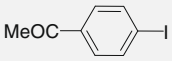
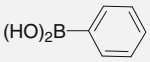
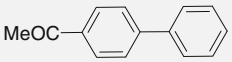
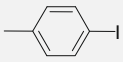
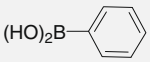
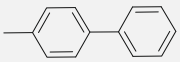
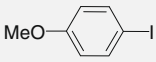
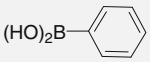
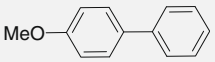


Fig. 5. Simplified orbital interaction diagram showing the major contribution of NHC–Pd bond in **2c**.

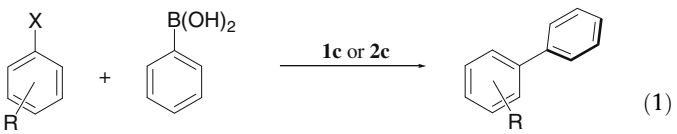
Significantly enough, the palladium complexes **1c** and **2c** efficiently carried out the Suzuki–Miyaura C–C cross-coupling reactions of aryl bromides and iodides with phenyl boronic acid at 0.35 mol% of the catalyst loading in good to excellent yields in air after 12 h at 90 °C (Table 1 and Eq. (1)). Notably, effective conversions were observed for activated aryl bromides containing electron withdrawing substrates while for the aryl iodides substrates the same could be seen for both the electron withdrawing as well as electron donating substrates. Quite interestingly, the palladium **1c** precatalyst, containing a *i*-propyl N1-substituent, was found to be more efficient that the **2c** precatalyst containing a benzyl N1-substituent presumably due to the greater steric demand of

Table 1
Selected results of Suzuki–Miyaura cross coupling reaction catalyzed by **1c** and **2c**.

Entry	Reagent[a]	Reagent[a]	Product	Yield[b] (%)	
				1c	**2c**
1				99	99
2				99	99
3				99	87
4				85	99
5				78	74
6				94	67
7				96	24
8				74	48
9				42	26

[a] *Reaction conditions*: 0.50 mmol of aryl halide, 0.60 mmol of phenyl boronic acid, 0.75 mmol of K_2CO_3, 0.35 mol% of **1c** or **2c**, diethyleneglycol-di-*n*-butyl ether (0.50 mmol, internal standard) and 10 mL of CH_3CN were taken for each run at 90 °C temperature (12 h).
[b] GC yields.

the *i*-propyl group over the benzyl moiety. A comparison of the catalysis results of **1c** and **2c** with blank as well as the control experiments performed with $PdCl_2$ clearly highlight the so-called "ligand influence" present in these palladium based **1c** and **2c** pre-catalysts. Specifically, amplifications of up to 68% were observed with respect to the control experiments in case of the catalysis by **1c** and **2c** (Supplementary material Table S10). The homogeneous nature of the Suzuki–Miyaura coupling reaction was further confirmed by performing the classical Hg(0) drop experiment [30,31] for a representative precatalyst **2c** that showed no significant reduction in the reaction yield in presence or absence of mercury under analogous conditions (Supplementary material Table S11).



(1)

X= Br, I
R= CN, NO_2, CHO, COMe, Me, OMe

Important is the comparison of reactivity of **1c** and **2c** complexes with the other related N-heterocyclic carbene based analogs. For example, the PEPPSI themed precatalysts namely, the *trans*-[1-(benzyl)-3-(*N*-*t*-butylacetamido)imidazol-2-ylidene]$PdCl_2(NC_5H_5)$, [16] *trans*-[1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazol-2-ylidene]$PdCl_2(NC_5H_5)$ [16] and *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]$PdBr_2(NC_5H_5)$, [16] complexes carried out Suzuki–Miyaura coupling of aryl bromide and iodide substrates with phenyl boronic acid at 85 °C exhibiting a conversion of 30–99%. However, the *trans*-$(NHC)_2PdX_2$ (X = halide) type complexes namely, [1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]$_2PdCl_2$, containing two N-heterocyclic carbene ligands, exhibited ultra high turn over numbers for Suzuki–Miyaura cross-coupling of aryl bromides with phenyl boronic acid at 85 °C. In this backdrop, the complexes **1c** and **2c** also show considerable activity by virtue of belonging to the class of more electron rich *trans*-$(NHC)_2PdX_2$ (X = halide) type catalysts.

3. Conclusions

In summary, a series of air-stable, robust and highly efficient precatalysts **1c** and **2c** supported over new amido-functionalized N-heterocyclic carbene ligands for the Suzuki–Miyaura C–C cross-coupling reaction of aryl bromides and iodides with phenyl boronic acids have been designed. More interestingly, the sterically demanding *i*-propyl derivative **1c** exhibited superior activity compared to the benzyl derivative **2c**. The density functional theory studies of the **1c** and **2c** complexes indicated the greater stability of the Pd–NHC interaction as the molecular orbitals representing

these σ-interactions in these palladium complexes were found to be low lying and consequently are less susceptible to nucleophilic or electrophilic attacks.

4. Experimental

4.1. General procedures

All manipulations were carried out using a combination of a glovebox and standard Schlenk techniques. Solvents were purified and degassed by standard procedures. 1-*i*-propylimidazole [32], 1-benzylimidazole [33] and (COD)$PdCl_2$ [34] were prepared according to the reported literature procedures. ^1H and ^{13}C {^1H} NMR spectra were recorded on a Varian 400 MHz NMR spectrometer. ^1H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), and septet (sept). Infrared spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were done on a Micromass Q-Tof spectrometer. Elemental Analysis was carried out on Thermo Quest FLASH 1112 SERIES (CHNS) Elemental Analyzer. X-ray diffraction data for compounds **1c** and **2c** were collected on an Oxford Diffraction Excaliber-S diffractometer and crystal data collection and refinement parameters are summarized in Table S1. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.10) [35,36]. GC spectra were obtained on a Perkin–Elmer Clarus 600 equipped with a FID. GCMS spectra were obtained on a Perkin–Elmer Clarus 600 T equipped with an EI source.

4.2. Synthesis of 1-(i-propyl)-3-N-(benzylacetamido)imidazolium chloride (**1a**)

A mixture of *N*-benzyl-2-chloro-acetamide (3.20 g, 17.5 mmol) and 1-*i*-propylimidazole (2.51 g, 22.7 mmol) was dissolved in toluene (*ca.* 10 mL), and refluxed at 110 °C for 12 h, at which point a solid separated out. The solid was isolated by decanting off the solvent and washed with hot hexane (3 × *ca.* 15 mL) to obtain the product **1a** as an off-white solid (4.31 g, 84%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 10.05 (s, 1H, NC*H*N), 9.73 (s, 1H, N*H*), 7.57 (br, 1H, NC*H*CHN), 7.34 (d, 2H, $^3J_{HH}$ = 8 Hz, *o*-C_6H_5), 7.26 (t, 2H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_5), 7.21 (m, 2H, *p*-C_6H_5 & NCHC*H*N), 5.37 (s, 2H, CH_2), 4.65 (sept, 1H, $^3J_{HH}$ = 7 Hz, C*H*(CH_3)$_2$), 4.40 (d, 2H, $^3J_{HH}$ = 6 Hz, CH_2), 1.58 (d, 6H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 165.2 (*C*O), 138.0 (*ipso*-C_6H_5), 135.5 (N*C*HN), 128.3 (*m*-C_6H_5), 127.4 (*o*-C_6H_5), 126.9 (*p*-C_6H_5), 123.8 (N*C*HCHN), 119.4 (NCH*C*HN), 52.9 (CH_2), 51.2 (*C*H(CH_3)$_2$), 43.1 (CH_2), 22.6 (CH(*C*H$_3$)$_2$). IR (KBr pellet cm^{-1}): 1684 (ν_{CO}). HRMS (ES): *m*/*z* 258.1614 [(NHC−H)]$^+$, calcd 258.1606.

4.3. Synthesis of {[1-(i-propyl)-3-N-(benzylacetamido)imidazol-2-ylidene]$_2$Ag}$^+Cl^-$ (**1b**)

A mixture of 1-(*i*-propyl)-3-*N*-(benzylacetamido)imidazolium chloride (4.37 g, 14.9 mmol) and Ag_2O (1.72 g, 7.45 mmol) in dichloromethane (*ca.* 40 mL) was stirred at room temperature for 4 h. The reaction mixture was filtered, and the solvent was removed under vacuum to give the product **1b** as a white solid (3.28 g, 67%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 9.12 (br, 2H, N*H*), 7.31 (t, 4H, $^3J_{HH}$ = 3 Hz, *m*-C_6H_5), 7.28 (br, 4H, *o*-C_6H_5), 7.19 (br, 2H, *p*-C_6H_5), 7.17 (br, 2H, NC*H*CHN), 7.02 (br, 2H, NCHC*H*N), 5.00 (s, 4H, CH_2), 4.64 (sept, 2H, $^3J_{HH}$ = 7 Hz, C*H*(CH_3)$_2$), 4.38 (s, 4H, CH_2), 1.48 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 179.8 (Ag–N*C*N), 166.8 (*C*O), 138.1 (*ipso*-C_6H_5), 128.2 (*m*-C_6H_5), 127.5 (*o*-C_6H_5), 126.8 (*p*-C_6H_5), 123.0 (N*C*HCHN), 116.8 (NCH*C*HN), 53.9 (CH_2), 53.9 (*C*H(CH_3)$_2$), 42.9 (CH_2), 23.6 (CH(*C*H$_3$)$_2$). IR (KBr pellet cm^{-1}): 1676 (ν_{CO}). Anal. Calc. for $C_{30}H_{38}ClAgN_6O_2{\cdot}0.5CH_2Cl_2$: C, 52.30; H, 5.61; N, 12.00. Found: C, 52.60; H, 6.36; N, 11.99%.

4.4. Synthesis of [1-(i-propyl)-3-{N-(benzylacetamido)imidazol-2-ylidene}]$_2PdCl_2$ (**1c**)

A mixture of {[1-(*i*-propyl)-3-{*N*-(benzylacetamido)imidazol-2-ylidene}]$_2$Ag}$^+Cl^-$ (0.304 g, 0.462 mmol) and (COD)$PdCl_2$ (0.132 g, 0.462 mmol) was dissolved in CH_2Cl_2 (*ca.* 40 mL) and was stirred at room temperature for 6 h, at which the point the formation of an off-white AgCl precipitate was observed. The reaction mixture was filtered, and the solvent was removed under vacuum to get the crude product. The crude product was purified by column chromatography on silica gel, using a $CHCl_3/CH_3OH$ mixture (50:1) as an eluent to obtain the product **1c** as a yellow solid (0.167 g, 52%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.50 (s, 1H, NC*H*CHN), 7.42 (s, 1H, NC*H*CHN), 7.24–7.21 (m, 9H, C_6H_5), 7.04 (d, 1H, $^3J_{HH}$ = 8 Hz, *o*-C_6H_5), 6.98 (s, 2H, NCHC*H*N), 6.97 (br, 2H, N*H*), 5.59 (sept, 1H, $^3J_{HH}$ = 7 Hz, C*H*(CH_3)$_2$), 5.50 (sept, 1H, $^3J_{HH}$ = 7 Hz, C*H*(CH_3)$_2$), 5.25 (s, 2H, CH_2), 5.07 (s, 2H, CH_2), 4.41 (d, 2H, $^3J_{HH}$ = 6 Hz, CH_2), 4.39 (d, 2H, $^3J_{HH}$ = 6 Hz, CH_2), 1.61 (d, 6H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.51 (d, 6H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 169.3 (Pd–N*C*N), 169.2 (Pd–N*C*N), 167.1 (*C*O), 167.0 (*C*O), 138.2 (*ipso*-C_6H_5), 138.1 (*ipso*-C_6H_5), 128.5 (*m*-C_6H_5), 128.4 (*m*-C_6H_5), 127.8 (*o*-C_6H_5), 127.7 (*o*-C_6H_5), 127.2 (*p*-C_6H_5), 127.2 (*p*-C_6H_5), 121.9 (N*C*HCHN), 121.7 (N*C*HCHN), 118.1 (NCH*C*HN), 117.6 (NCH*C*HN), 54.4 (CH_2), 54.0 (CH_2), 52.8 (*C*H(CH_3)$_2$), 52.5 (*C*H(CH_3)$_2$), 43.5 (CH_2), 43.4 (CH_2), 23.3 (CH(*C*H$_3$)$_2$), 23.2 (CH(*C*H$_3$)$_2$). IR (KBr pellet cm^{-1}): 1683 (ν_{CO}). Anal. Calc. for $C_{30}H_{38}PdCl_2N_6O_2{\cdot}CH_2Cl_2$: C, 47.92; H, 5.19; N, 10.82. Found: C, 47.91; H, 5.87; N, 11.28%.

4.5. Synthesis of 1-(benzyl)-3-N-(benzylacetamido)imidazolium chloride (**2a**)

A mixture of *N*-benzyl-2-chloro-acetamide (3.15 g, 17.2 mmol) and 1-benzylimidazole (2.72 g, 17.2 mmol) was dissolved in toluene (*ca.* 10 mL), and refluxed at 110 °C for 12 h, at which point a solid separated out. The solid was isolated by decanting off the solvent and washed with hot hexane (3 × *ca.* 15 mL) to obtain the product **2a** as an off-white solid (4.75 g, 81%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 9.97 (s, 1H, NC*H*N), 9.73 (br, 1H, N*H*), 7.50 (s, 1H, NC*H*CHN), 7.36 (br, 2H, *o*-C_6H_5), 7.34 (br, 1H, *o*-C_6H_5), 7.31 (br, 1H, *o*-C_6H_5), 7.29 (br, 1H, *m*-C_6H_5), 7.20 (t, 3H, $^3J_{HH}$ = 7 Hz, *m*-C_6H_5), 7.13 (d, 2H, $^3J_{HH}$ = 7 Hz, *p*-C_6H_5), 7.05 (s, 1H, NCHC*H*N), 5.36 (s, 2H, CH_2), 5.32 (s, 2H, CH_2), 4.36 (d, 2H, $^3J_{HH}$ = 6 Hz, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 164.9 (*C*O), 138.2 (*ipso*-C_6H_5), 137.6 (*ipso*-C_6H_5), 132.6 (N*C*HN), 129.8 (*m*-C_6H_5), 129.7 (*m*-C_6H_5), 128.8 (*o*-C_6H_5), 128.6 (*o*-C_6H_5), 127.9 (*p*-C_6H_5), 127.3 (*p*-C_6H_5), 124.0 (N*C*HCHN), 120.9 (NCH*C*HN), 53.6 (CH_2), 51.8 (CH_2), 43.6 (CH_2). IR (KBr pellet cm^{-1}): 1689 (ν_{CO}). HRMS (ES): *m*/*z* 306.1620 [(NHC−H)]$^+$, calcd 306.1606.

4.6. Synthesis of {[1-(benzyl)-3-N-(benzylacetamido)imidazol-2-ylidene]$_2$Ag}$^+Cl^-$ (**2b**)

A mixture of 1-(benzyl)-3-*N*-(benzylacetamido)imidazolium chloride (4.37 g, 12.8 mmol) and Ag_2O (1.48 g, 6.41 mmol) in dichloromethane (*ca.* 40 mL) was stirred at room temperature for 4 h. The reaction mixture was filtered, and the solvent was removed under vacuum to give the product **2b** as a white solid (2.89 g, 61%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 9.36 (br, 2H, N*H*), 7.30 (br, 2H, NC*H*CHN), 7.28 (br, 4H, *o*-C_6H_5), 7.27–7.25 (br, 4H, *m*-C_6H_5), 7.17 (br, 2H, *o*-C_6H_5), 7.15 (br, 4H, *m*-C_6H_5), 7.07–

7.05 (br, 4H, *p*-C_6H_5), 6.87 (br, 2H, $^3J_{HH}$ = 2 Hz, NCHC*H*N), 5.07 (s, 4H, CH_2), 5.04 (s, 4H, CH_2), 4.36 (d, 4H, $^3J_{HH}$ = 6 Hz, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 182.2 (Ag–N*C*N), 167.0 (*C*O), 138.5 (*ipso*-C_6H_5), 137.5 (*ipso*-C_6H_5), 129.1 (*m*-C_6H_5), 128.6 (*m*-C_6H_5), 128.5 (*o*-C_6H_5), 127.9 (*o*-C_6H_5), 127.5 (*p*-C_6H_5), 127.1 (*p*-C_6H_5), 123.6 (NC*H*CHN), 120.8 (NCH*C*HN), 55.5 (*C*H_2), 54.1 (*C*H_2), 43.4 (*C*H_2). IR (KBr pellet cm^{-1}): 1659 (ν_{CO}). Anal. Calc. for $C_{38}H_{38}AgN_6O_2Cl{\cdot}CH_2Cl_2$: C 55.83; H, 4.81; N, 10.02. Found: C, 55.93; H, 4.47; N, 9.94%.

4.7. Synthesis of [1-(benzyl)-3-N-(benzylacetamido)imidazol -2-ylidene]$_2$PdCl$_2$ (**2c**)

A mixture of {[1-(benzyl)-3-{*N*-(benzylacetamido)imidazol-2-ylidene}]$_2$Ag}$^+Cl^-$ (0.471 g, 0.625 mmol) and (COD)$PdCl_2$ (0.178 g, 0.625 mmol) was dissolved in CH_2Cl_2 (*ca.* 40 mL) and was stirred at room temperature for 6 h, at which the point the formation of an off-white AgCl precipitate was observed. The reaction mixture was filtered, and the solvent was removed under vacuum to get the crude product. The crude product was purified by column chromatography on silica gel, using a $CHCl_3/CH_3OH$ mixture (50:1) as an eluent to obtain the product **2c** as a yellow solid (0.315 g, 64%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.11 (br, 2H, N*H*), 7.48-7.38 (m, 10H, *o*/*m*-C_6H_5), 7.25-7.19 (m, 10H, *m*/*p*-C_6H_5), 7.02 (br, 1H, NC*H*CHN), 6.97 (br, 1H, NC*H*CHN), 6.82-6.77 (br, 1H, NCHC*H*N), 6.76–6.74 (br, 1H, NCHC*H*N), 5.84 (s, 1H, CH_2), 5.60 (d, 2H, $^3J_{HH}$ = 6 Hz, CH_2), 5.36 (s, 1H, CH_2), 5.30 (s, 2H, CH_2), 5.12 (s, 1H, CH_2), 5.07 (d, 2H, $^3J_{HH}$ = 6 Hz, CH_2), 4.44 (d, 1H, $^3J_{HH}$ = 6 Hz, CH_2), 4.41 (d, 1H, $^3J_{HH}$ = 6 Hz, CH_2), 4.30 (d, 1H, $^3J_{HH}$ = 6 Hz, CH_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz, 25 °C): δ 166.2 (*C*O), 166.1 (*C*O), 159.0 (Pd–N*C*N), 156.8 (Pd–N*C*N), 138.4 (*ipso*-C_6H_5), 138.2 (*ipso*-C_6H_5), 135.6 (*ipso*-C_6H_5), 135.4 (*ipso*-C_6H_5), 128.4 (*m*-C_6H_5), 128.3 (*m*-C_6H_5), 128.3(*m*-C_6H_5), 128.2(*m*-C_6H_5), 128.2(*m*-C_6H_5), 128.1 (*m*-C_6H_5), 128.0 (*m*-C_6H_5), 127.8 (*m*-C_6H_5), 127.7 (*o*-C_6H_5), 127.6 (*o*-C_6H_5), 127.5 (*o*-C_6H_5), 127.4 (*o*-C_6H_5), 127.4 (*o*-C_6H_5), 127.3 (*o*-C_6H_5), 126.7 (*o*-C_6H_5), 126.6 (*o*-C_6H_5), 125.1 (*p*-C_6H_5), 124.8 (*p*-C_6H_5), 124.2 (*p*-C_6H_5), 122.6 (*p*-C_6H_5), 121.9 (NCHCHN), 121.4 (N*C*HCHN), 121.2 (NCH*C*HN), 120.2 (NCH*C*HN), 53.2 (*C*H_2), 52.6 (*C*H_2), 52.2 (*C*H_2), 52.6 (*C*H_2), 42.5 (*C*H_2), 42.3 (*C*H_2). IR (KBr pellet cm^{-1}): 1635 (ν_{CO}). Anal. Calc. for $C_{38}H_{38}PdN_6O_2Cl_2{\cdot}0.5\,CH_2Cl_2$: C 55.68; H, 4.73; N, 10.12. Found: C, 55.87; H, 4.79; N, 10.35%.

4.8. Computational methods

Density functional theory calculations were performed on **1c** and **2c** using GAUSSIAN 03 [37] suite of quantum chemical programs. The Becke three parameter exchange functional in conjunction with Lee–Yang–Parr correlation functional (B3LYP) has been employed in this study [38,39]. Sttutgart–Dresden effective core potential (ECP), representing 19 core electrons, along with valence basis sets (SDD) is used for palladium [40–42]. All other atoms are treated with 6-31G(d) basis set [43]. All stationary points are characterized as minima by evaluating Hessian indices on the respective potential energy surfaces. Tight SCF convergence (10^{-8} a.u.) was used for all calculations. Natural bond orbital (NBO) analysis was performed using the NBO 3.1 program implemented in the GAUSSIAN 03 package.

Inspection of the metal–ligand donor–acceptor interactions was carried out using the charge decomposition analysis (CDA) [44]. CDA is a valuable tool in analyzing the interactions between molecular fragments on a quantitative basis, with an emphasis on the electron donation [45,46]. The orbital contributions in the geometry optimized palladium complexes **1c**, and **2c** can be divided into three parts:

(i) σ-donation from the [NHC → $PdCl_2$] fragment,
(ii) π-back donation from [NHC ← $PdCl_2$] fragment and
(iii) Repulsive polarization (*r*).

The CDA calculations are performed using the program AOMIX [47], using the B3LYP/SDD, 6-31G(d) wave function. Molecular orbital (MO) compositions and the overlap populations were calculated using the AOMIX program [48]. The analysis of the MO compositions in terms of occupied and unoccupied fragment orbitals (OFOs and UFOs, respectively), construction of orbital interaction diagrams, the charge decomposition analysis (CDA) was performed using the *AOMix-CDA* [49].

4.9. General procedure for the Suzuki–Miyaura reaction

In a typical run, performed in air, a 25 mL vial was charged with a mixture of the aryl halide compound (0.50 mmol), phenyl boronic acid (0.60 mmol), K_2CO_3 (0.75 mmol) diethyleneglycol-di-*n*-butyl ether (0.50 mmol) (internal standard) in a molar ratio of 1:1.2:1.5 and precatalysts **1c** or **2c** (0.35 mol%) in CH_3CN (10 mL). The reaction mixture was refluxed for an appropriate period of time, after which it was filtered and the product was analyzed by GC and GCMS analysis using diethyleneglycol-di-*n*-butyl ether as an internal standard.

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Appendix A. Supplementary material

CCDC 679084 and 707910 contain the supplementary crystallographic data for **1c** and **2c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.09.011.

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