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Structural diversity of phenoxy functionalized triazol-5-ylidene palladium(II) complexes and their application in C–N bond formation

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ABSTRACT

The preparation and isolation of a variety of mono-, bis-, and heteroleptic mesoionic triazol-5-ylidene palladium(II) complexes is reported. Treatment of phenoxy functionalized triazolium salts [**Bn**-MIC(H)]$^{+}$I^{-} (**1**) and [**Mes**-MIC(H)]$^{+}$I^{-} (**2**) with half equivalent of palladium acetate, produced complexes **3** and **4** with a general structure of [(MIC)$_2$Pd(I)$_2$] as isomeric cis/trans mixtures. When the reaction of palladium acetate and the cationic precursors was carried out with equimolar amounts in presence of sodium iodide, the μ_2-I$_2$ bridged complexes **5** and **6** of the type [(MIC)PdI$_2$]$_2$ were obtained as unique products. Additionally, the preparation of the heteroleptic PEPPSI-type complexes ([Py(PdI$_2$)MIC]) **7** and **8** was readily achieved by the thermal treatment of the triazolium precursors with PdCl$_2$, K$_2$CO$_3$, and sodium iodide in pyridine. All complexes have been fully characterized by ^{1}H and ^{13}C NMR, FT-IR, elemental analysis, and in the case of **2**, **3**$_{trans}$, **6**, and **7** single crystal X-ray diffraction. Preliminary catalytic results with the palladium series established the enhanced performance of PEPPSI complexes **7** and **8** in the Buchwald-Hartwing catalyzed formation of C–N bonds between aryl halides and primary/secondary amines under mild reaction conditions.

1. Introduction

The enormous impact of N-heterocyclic carbenes (NHCs) as spectator ligands for transition metal complexes has stimulated the research for the directed tuning of their structural and electronic properties [1]. The design and preparation of improved homogeneous catalyst based in NHCs is now envisaged as a useful alternative to facilitate synthetic procedures not accessible by classical methods [2]. In recent years, NHCs were the carbene center is not flanked by heteroatoms (nitrogen, sulphur, oxygen) in both sides of their structures, have attracted a big deal of attention as they have shown stronger σ-donation capacity towards the metal center when compared to classical analogues [3]. These ligands often referred as abnormal (aNHCs) or mesoionic carbenes (MICs) owe this description due to the fact that their structures can only be represented as zwitter ions and not in the neutral canonical form [4]. Despite that a handful of abnormal/mesoionic carbene complexes supported by pyrazol-4-ylidenes (A) [5], imidazol-5-ylidenes (B) [6], thiazol-5-ylidenes (C) [7], oxazol-4-ylidene (D) are available [8](Scheme 1), the easy access to 1,2,3-triazoles by the copper catalysed cycloaddition of azides and alkynes (CuAAC) and their readily N3-quaternarization has resulted in the exponential growth of the 1,2,3-triazol-5-ylidenes (E) efficient in several catalytic processes [9]. Particularly, palladium based MIC complexes are of great interest due to their potential as homogeneous catalysts in processes such as carbon-carbon cross coupling or carbon-heteroatom bond formation; however their structural diversity is noticeably less developed when compared to classical NHC analogues [10].

Our group is interested in the design and preparation of palladium-MIC complexes for synthetic applications, in particular the efficient catalysed formation of carbon-heteroatom bonds. We have foreseen that the 1,2,3-triazol-5-ylidenes enhanced electron

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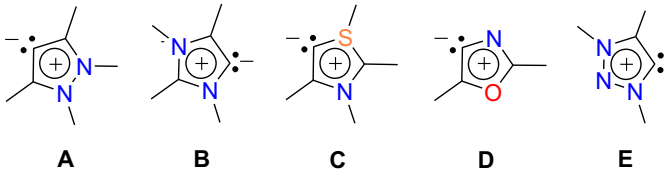
donor capacities together with the presence of hemilabile donor atoms at the 4-position could lead to increased reactivity and stability versus previously reported NHC systems. With this purpose, we report herein the directed synthesis of a series of mono-, bis-, and heteroleptic phenoxy functionalized mesoionic triazol-5-ylidene palladium(II) complexes. The treatment of triazolium salts **1** and **2** with equimolar amounts of palladium acetate in presence of sodium iodide generates selectively the dimeric carbenes of the type $[(MIC)PdI_2]_2$. If the reaction of the cationic precursors is carried out with half equivalent of palladium acetate, biscarbenes of the type $[(MIC)_2Pd(I)_2]$ are obtained as cis/trans mixtures in good yields. Additionally, the preparation of the heteroleptic PEPPSI (Pyridine Enhanced Precatalyst Preparation and Initiation) type complexes $[Py(PdI_2)MIC]$ **7** and **8** was readily achieved by the thermal treatment of the triazolium precursors with $PdCl_2$, and sodium iodide in pyridine. The full series of palladium(II) complexes have been synthesized under aerobic atmosphere and fully characterized in solution and solid state. Preliminary catalytic trials established the enhanced performance of **7** and **8** in the catalyzed coupling between aryl bromides and amines.

2. Results and discussion

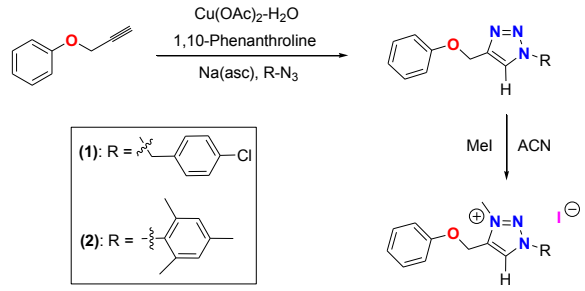
2.1. Synthesis and characterization

The 1,2,3-triazolium precursors [**Bn**-MIC(H)]$^+$I$^-$ (**1**) and [**Mes**-MIC(H)]$^+$I$^-$ (**2**) are readily prepared following the route displayed in Scheme 2. The initial triazoles are obtained in a one-pot reaction from the treatment of the corresponding alkyne with the organic azide (*in situ* generated in case of the *p*-chlorbenzyl derivative) [11] through click process (75–90% yields). N-alkylation with methyl iodide affords the corresponding cationic precursors in good yields (81–86%) after recrystallization from acetonitrile/diethyl ether. The formation of the triazolium salts was confirmed in ^{1}H NMR spectroscopy by the characteristic chemical shift values of the triazolyl hydrogens (singlets) between 9.02 and 9.11 ppm, and the *N*-bound methyl groups displayed as single peaks in the range of 4.38–4.64 ppm. Unambiguous characterization of **2** was performed by an X-ray diffraction study [12] and the molecular structure is depicted in Fig. 1. Triazolium **2** crystallized in the triclinic system with the *P-1* space group. The asymmetric unit contains two triazolium iodide entities with C–C and C–N bond distances, and CCN angles, similar to other cationic analogues.

According to literature reports, the most common pathways for the preparation of [MIC]-Pd complexes includes a) the transmetallation of MIC-silver(I) precursors [13], b) the generation of free MICs followed by metallation [6a-b,14], and c) the thermal palladation with $Pd(OAc)_2$ [15]. Drawbacks of the silver carbene metallation method and the use of strong bases (for preparing free MICs) include low yields and the use of strictly anhydrous conditions. Concerning thermal methods, it was previously reported by Albrecht and coworkers that the palladation of triazolium precursors with $Pd(OAc)_2$ in DMSO at 120 °C was not selective, generating invariably a mixture of mono- and dinuclear complexes in 1:1 ratio [16]. Further investigations by Sankararaman and



Scheme 1. Examples of *a*NHC/MIC ligands reported in the literature.



Scheme 2. Synthesis of [**Bn**-MIC(H)]$^+$I$^-$ (**1**) and [**Mes**-MIC(H)]$^+$I$^-$ (**2**) salts.

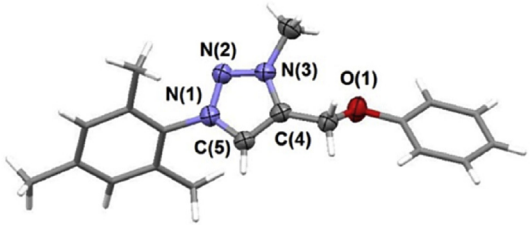
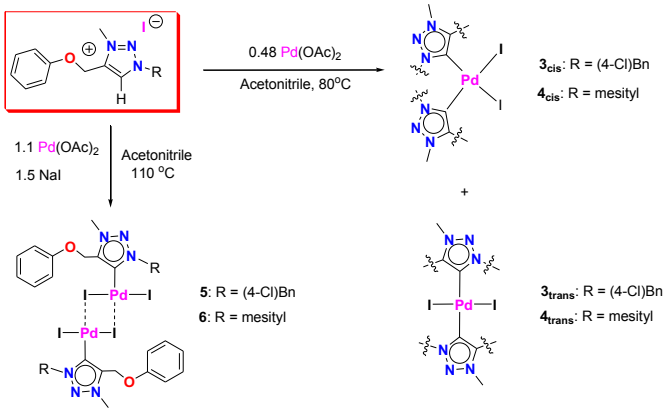


Fig. 1. Molecular structure of triazolium salt **2**. Iodine counterion has been omitted for clarity. Ellipsoids are shown at 30% probability.

coworkers demonstrated that treatment of triazolium salts with $Pd(OAc)_2$ in chloroform at 30 °C provided selectively mononuclear *trans* biscarbene palladium complexes; however long reaction times were required for optimal conversions (36–72 h) [17].

With the cationic precursors **1** and **2** in hand, we decided to proceed to the palladation process following the thermal method developed by Albrecht (120 °C in DMSO). Under those conditions, a mixture of at least three compounds was observed in the reaction crude reflecting the poor selectivity of the process. Further attempts to improve the synthesis were carried out by treatment of **1** and **2** with $Pd(OAc)_2$ in DCM at 30 °C for three days. Despite that a single metal complex was observed, a large amount of unreacted triazolium salt (~65%) was present in the mixture. As no efficient conversions were achieved, we tested several reaction conditions and found that the treatment of **1** and **2** with 0.48 equivalents of $Pd(OAc)_2$ in acetonitrile at 80 °C was successful in the selective generation of complexes **3** and **4** (Scheme 3) with a general structure of $[(MIC)_2Pd(I)_2]$ as isomeric cis/trans mixtures. The products are easily purified by column chromatography in good yields (77–81%) and according to the crude reaction mixture analysis no



Scheme 3. Synthesis of mono- and bis-MIC palladium complexes **3**–**6.**

presence of dimeric carbene complexes was noticed.

In solution, the ^{13}C NMR spectra for the cis/trans mixtures display the Pd=C peaks at 157.48 and 157.56 ppm for complex **3**, and at 157.5 and 158.7 ppm for complex **4**. These chemical shifts are similar to previously reported complexes with the general structure $[(MIC)_2Pd(I)_2]$ [16,17]. Interestingly, the bulkiness of the substituent at the 4-position in complexes **3** and **4** affects the ratio of the cis/trans mixtures. For instance, the presence of a flexible benzylic moiety in **3** allows for the mixture to be present in 1:1 ratio whilst, the bulkier mesityl group in complex **4** forces the steric congestion around the metal center to be lessened, increasing the presence of the *trans* isomer in a 4:1 ratio. Single crystals of complex $\mathbf{3_{trans}}$ were obtained by hexanes diffusion into a concentrated acetonitrile sample of **3** and the molecular structure is depicted in Fig. 2.

Complex $\mathbf{3_{trans}}$ crystallized in the monoclinic system with the C2/c space group. The molecular structure of $\mathbf{3_{trans}}$ confirms the biscarbenic nature of the palladium center which is located in a distorted square planar environment completed by the coordination of two iodine atoms. The Pd(1)-C(5)/C(10) (2.036(4)/2.038(4) Å) and Pd(1)-I(1)/I(2) (2.6051(4)/2.6198(4) Å) bond distances are in the typical range of such bonds in analogue *trans* complexes [16,17]. Interestingly, the phenoxy and benzylic moieties are located in the same side of the structure allowing for a C_2 axis to be drawn along the I(1)-Pd(1)-I(2) atoms.

With the successful preparation of mononuclear biscarbene complexes **3** and **4**, we then moved to the quest for the selective synthesis of dinuclear $[(MIC)PdX_2]_2$ palladium complexes. As starting point, it was clear that the reaction of the triazolium salts and $Pd(OAc)_2$ required of stoichiometric amounts to favour the MIC/Pd 1:1 ratio. Indeed, the treatment of salts **1** and **2** with equimolar amounts of $Pd(OAc)_2$ in acetonitrile (110 °C) provided the expected dinuclear complexes **5** and **6** as major products but regrettably in mixture with mononuclear complexes **3** and **4**, respectively. Attempts to improve the selectivity towards the complexes **5** and **6** by increasing the amount of $Pd(OAc)_2$ to 1.5 or 2.0 equivalents proved unsuccessful as the mono- and biscarbenic mixtures were observed in all cases. Rationalizing that each palladium center in complexes **5** and **6** required of two iodine atoms, and that each triazolium cation could only provide one, we were prompted to seek for an external iodine source. We found that upon the addition of excess of sodium iodide (1.5 eq) to the equimolar reaction of salts **1** and **2** and $Pd(OAc)_2$, the selective preparation of **5** and **6** was achieved with the presence of only traces of **3** and **4** (Scheme 2). The products were easily isolated as orange solids in high yields (83–89%) by column chromatography using DCM/acetone (95:5) as eluent. In solution, the ^1H NMR spectra for **5** and **6** display only one set of resonances for the *N*-methyl, methylene, and aromatic groups, as it was expected for the symmetric dimers. ^{13}C NMR spectroscopy displays single palladium-carbene peaks for **5** and **6** located at 129.6 and 129.8 ppm respectively, which is substantially in higher field when compared with biscarbenes **3** and **4** (~157 ppm), but relatively close to analogous dimeric $[MIC\text{-}PdI_2]_2$ complexes [17,18].

Unambiguous evidence for the formation of the dimeric complexes was provided by an X-Ray diffraction analysis of complex **6**. The molecular structure displayed in Fig. 3 comprises a set of two palladium centers, two bridging iodine atoms, and the square planar coordination sphere around the metal center is completed by a MIC ligand and a second iodine atom. Due to the formation of a central Pd_2I_2 square, the mesityl and phenoxy moieties in **6** adopt a mutual *anti* conformation, while the triazolylidene ring is oriented perpendicular to the palladium square plane. The palladium-carbene (1.989(9) Å) and palladium-iodine (~2.59(7) Å) bond distances in **6** are similar to previously reported dimeric palladium complexes [17,18] and as expected, the bond distance of the palladium centers with the bridging iodine are elongated to 2.665(8) Å.

The benefits of catalysts that consist on one NHC-ligand and a second more labile moiety have been previously demonstrated by experimental and computational data [19]. In this subclass of heteroleptic metal complexes, the tightly bonded NHC ligand stabilizes the metal center while the more labile counterpart favour the presence of vacant coordination sites necessary for catalytic processes. With this background, we turned our attention to PEPPSI (Pyridine Enhanced Precatalyst Preparation Stabilization and Initiation) palladium catalysts as they can accelerate various amination and cross-coupling reactions [20]. This type of palladium complexes offers among other advantages, a facile synthesis and air and moisture stability when compared to traditional palladium catalysts. The preparation of PEPPSI complexes **7** and **8** was carried out by the one-pot reaction of the triazolium precursors **1** and **2** with K_2CO_3 and $PdCl_2$ in pyridine at 100 °C. Despite that the PEPPSI complexes were obtained using this initial methodology, the yields were lower than 40% after purification by column chromatography. Intrigued by the poor conversions, we performed various structural analyses of the heteroleptic complexes and observed that the data was not consistent with palladium centers containing chlorine atoms. Further product analysis revealed that a Cl/I halogen exchange took place likely favoured by the presence of *in situ* generated potassium iodide salt and the heating process. With this information, we modified the reaction conditions by adding an excess of NaI (2 equiv) to the mixture and prolonged the stirring for 24 h (Scheme 4). The optimized conditions allowed for the isolation of **7** and **8** in high yields (79–89%) as microcrystalline yellow solids.

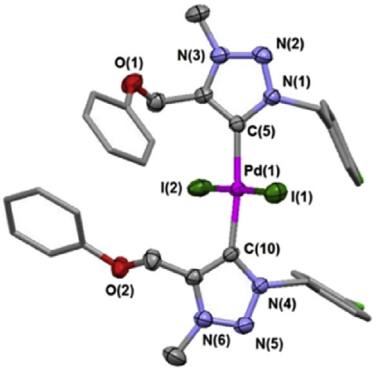


Fig. 2. Molecular structure of $\mathbf{3_{trans}}$. Hydrogen atoms have been omitted for clarity. Ellipsoids are shown at 30% probability.

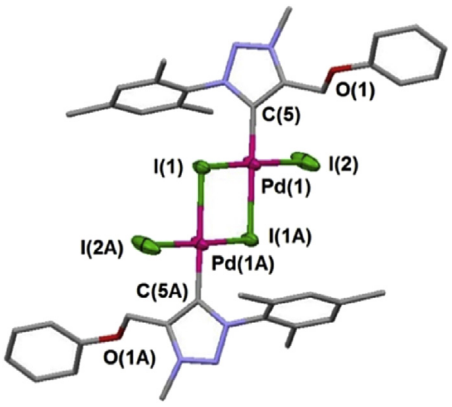
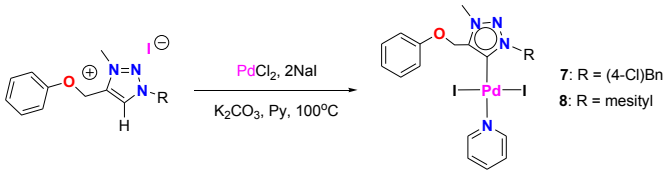


Fig. 3. Molecular structure of **6**. Hydrogen atoms have been omitted for clarity. Ellipsoids are shown at 30% probability.



Scheme 4. Synthesis of PEPPSI complexes **7** and **8**.

The formation of the PEPPSI complexes was evident by the loss of the C–H peak of the cationic precursors (around 9.1 ppm) and the presence of new aromatic peaks belonging to the pyridine ligand. The ^{13}C NMR spectra show the MIC-Pd signals at 135.9 and 135.4 ppm for **7** and **8** respectively, which are at much lower field compared to the mono- and dinuclear complexes **3**–**6**. This behaviour has been previously observed in analogue PEPPSI complexes and is related to the weak Pd-MIC bonding which may have important contribution to catalytic applications. Single crystals of complex **7** were obtained by slow diffusion of hexanes into a concentrated THF solution and the molecular structure is displayed in Fig. 4.

Complex **7** displays a slightly distorted square planar palladium center with the pyridine and MIC ligands located *trans* to each other. The C(5)-Pd(1)-N(4) and I(1)-Pd(1)-I(2) angles of 175.8(4) and 177.37(3)° are close to the expected 180° for a square plane. The Pd(1)-C(5) bond distance of 1.955(6) Å is slightly shorter than in complexes **3**–**6,** and the Pd(1)-N(4) bond distance of 2.093(5) Å is similar to analogous PEPPSI complexes reported in the literature [13c,21]. The triazolylidene ring in **7** is planar with negligible deviations denoted by the C(5)N(1)N(2)N(3) (1.52°) and C(4)N(3)N(2)N(1) (0.50°) torsion angles. Interestingly, to diminish the steric constrains, the phenoxy and benzylic moieties adopt a mutual *anti* conformation with respect to the triazol-5-ylidene plane.

2.2. Catalysis

Since the seminal work by Buchwald and Hartwig [22], palladium catalysed N-aryl amination has attracted increased attention due to its significance in natural product synthesis. Currently, a vast amount of synthetic routes leading to biologically valued compounds now employ these methods in both academia and industry [23]. Initially limited to aryl bromides and iodides, the use of bulky, electron-rich ancillary ligands such as trialkylphosphines, biarylphosphines, proazaphosphathrane, have enlarged the scope of these reactions [24]. More recently, the use of N-heterocyclic carbenes (NHCs) as ligands in Pd-catalyzed aminations has shown much promise [10]. Initially accessed by the *in situ* generation of the free carbene in presence of Pd^{II} or Pd^{0} sources, NHC-based protocols for Buchwald-Hartwig amination processes now rely on the preparation of well-defined NHC-palladium precatalysts. With scarce reports on the use of MIC-Pd based catalysts for aryl amination, we decided to preliminary test the efficiencies of our newly synthesized palladium triazol-5-ylidenes in the Buchwald-Hartwig process. We began our investigation by testing precatalysts **3**–**8** in the *N*-aryl amination of morpholine with bromobenzene. Initial reaction conditions included loading 3 mol% of the appropriate catalyst, KO^{t}Bu as the base, and 1,4-dioxane as solvent (entries 1–6). As observed in Table 1, the process performed at room temperature for 6h, revealed that PEPPSI-type complexes **7** and **8** are the most active precatalysts for the amination process. Interestingly, despite the larger amount of metal available in the dimeric palladium complexes **5** and **6**, they displayed the lowest conversions of the series. Optimization of the reaction conditions for our system shown that the use of DME as solvent and raising the temperature to 50 °C provided the highest conversions, reaching up to 94% of isolated yield when employing catalyst **8**. Encouragingly, no observation of palladium black was observed at 50 °C in contrast to the performance of analogue PEPPSI catalysts in processes performed at similar temperatures [13c,20c].

With the presence of a phenoxy moiety in complexes **7** and **8**, it was pertinent to argue that the latent coordination of the oxygen atom to the metal center could stabilize low valent catalytic species. As a proof of concept, we decided to compare the catalytic performance of **7** and **8** with complex **9** which represents the non-phenoxy PEPPSI version [15]. As observed in Table 2, the coupling of bromobenzene with morpholine under various reaction conditions unveils that complexes **7** and **8** are better precatalysts for the amination process than complex **9**. This could be related within some other aspects, to the availability of a hemilabile phenoxy moiety for coordination to palladium.

With optimized reaction conditions, we then proceeded to investigate the scope of the reaction using complexes **7** and **8** as precatalysts. Results of the coupling reaction of several amines with aryl halides are summarized in Table 3.

Overall, the catalytic performance of **7** and **8** displayed good efficiency toward cyclic dialkylamines with activated (entries 1, 4), neutral (entry 2), and unactivated aryl bromides (entry 3).

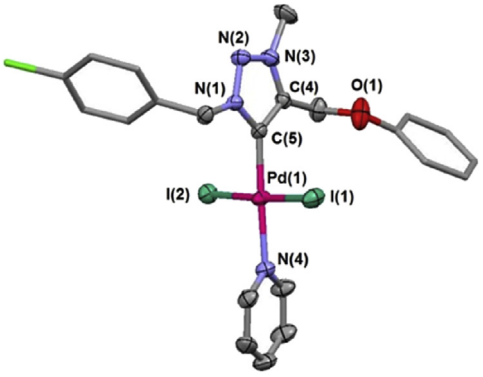
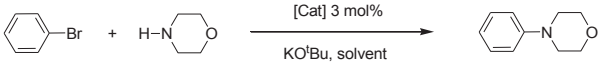


Fig. 4. Molecular structure of **7**. Hydrogen atoms have been omitted for clarity. Ellipsoids are shown at 30% probability.

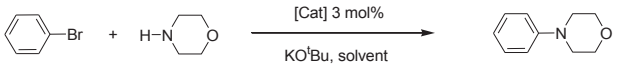
Table 1
Optimization results in the *N*-Aryl amination of morpholine with bromobenzene.

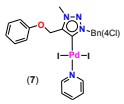
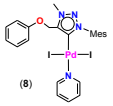
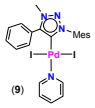


Entry	Cat	Temp (°C)	Solvent	Conv(%)[a]
1	**3**	25	Dioxane	46
2	**4**	25	Dioxane	42
3	**5**	25	Dioxane	27
4	**6**	25	Dioxane	23
5	**7**	25	Dioxane	60
6	**8**	25	Dioxane	67
7	**3**	25	DME	44
8	**4**	25	DME	49
9	**7**	25	DME	77
10	**8**	25	DME	79
11	**7**	35	DME	83
12	**8**	35	DME	85
13	**7**	50	DME	86
14	**8**	50	DME	94

Reaction conditions: 3 mol% catalyst loading, 1 mmol of bromobenzene, 1.1 mmol of morpholine, 1.5 mmol KO^{t}Bu, 2 mL solvent, 6h.
[a] Isolated yields, average of two runs.

Table 2
N-Aryl amination of morpholine with bromobenzene using complexes **7**–**9**.



Entry	Catalyst	Temp(°C)	Solvent	Yield(%)[a]
1		25	Dioxane	80
2		25	Dioxane	81
3		25	Dioxane	57
4	**7**	50	DME	89
5	**8**	50	DME	91
6	**9**	50	DME	71

Reaction conditions: 3 mol% catalyst loading, 1 mmol of bromobenzene, 1.1 mmol of morpholine, 1.5 mmol KO^{t}Bu, 2 mL solvent, 6h.
[a] Isolated yields, average of two runs.

Challenging the tolerance of **7** and **8** to sterically encumbered substrates was explored by the reactions of bromobenzene with N-methylaniline, 2,6-diisopropilaniline, and 2,4,6-trimethylaniline. We were pleased to find that the respective hindered diarylamines (entries 5–7) were obtained in good yields after column chromatography purification.

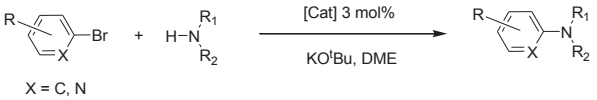
With the premise that heterocyclic moieties are widely represented in biologically active molecules, the coupling of heterocyclic halides with amines are of great interest. With this in mind, we carried out the treatment 2-bromopyridine with morpholine, piperidine, and N-methylaniline (entries 8–10). To our delight, the coupling of these substrates proceeds smoothly under our catalytic protocol providing the expected heterocyclic substrates in good conversions. Finally, to test the catalysts performance with cheaper chloride substrates, we carried out the coupling of benzylchloride, *p*-cyano benzylchloride and 2-chloropyridine with morpholine. As observed in Table 1 (entries 11–13), the conversion to products is successful but the yields are lower when compared to the analogue bromide couplings.

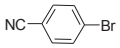
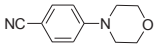
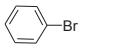
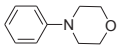
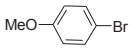
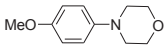
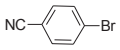
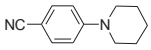
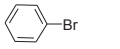
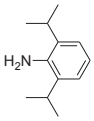
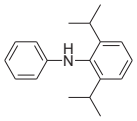
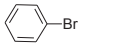
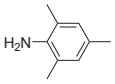
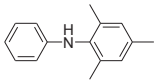
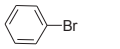
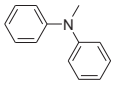
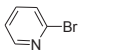
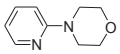
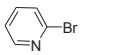
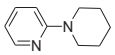
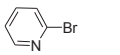
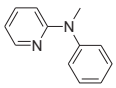
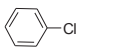
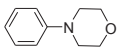
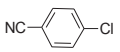
To further investigate the performance of **7** and **8**, a direct comparison between these precatalysts was performed by GC analysis in the process of *N*-Aryl amination of morpholine with bromobenzene. As expected from the comparable product yields and according to Fig. 5, both complexes display similar catalytic behaviour. A short induction period was present for **8** relative to **7** which may be related to the steric effect of the mesityl moiety which may facilitate the reductive elimination step in the catalytic cycle of the amination process.

3. Conclusions

In conclusion we have described the selective preparation and isolation a variety of mono-, bis-, and heteroleptic mesoionic triazol-5-ylidene palladium(II) complexes. The selective preparation of mono- and biscarbene complexes relies in the stoichiometry of palladium acetate used in the reaction. Heteroleptic PEPPSI type complexes are obtained as single products and the yields can be

Table 3
N-Aryl amination of aryl/heterocyclic halides.



Entry	Aryl halide	Amine	Product	Cat: Yield(%)[a]
1				**7**:90 **8**:94
2				**7**:89 **8**:91
3				**7**:83 **8**:89
4				**7**:93 **8**:96
5				**7**:87 **8**:88
6				**7**:91 **8**:95
7				**7**:94 **8**:93
8				**7**:79 **8**:83
9				**7**:85 **8**:87
10				**7**:76 **8**:81
11				**7**:75 **8**:78
12				**7**:80 **8**:82
13				**7**:70 **8**:67

Reaction conditions: 3 mol% catalyst loading, 1 mmol arylhalide, 1.2 mmol amine, 1.5 mmol KO^{t}Bu, 1 mL of DME, 50 °C, 6h.
[a] Isolated yields, average of two runs.

Fig. 5. Comparison of catalytic activity of **7** and **8** in the N-aryl amination of morpholine with bromobenzene.

improved after the addition of an external iodine source. All complexes have been synthesized under aerobic conditions and fully characterized by ^{1}H and ^{13}C NMR, FT-IR, elemental analysis, and in the case of **2**, $\mathbf{3}_{trans}$, **6**, and **7** by single crystal X-ray diffraction. All crystal structures contain square planar palladium centers and no coordination through the phenoxy moiety is observed. Preliminary catalytic trials established the enhanced performance of PEPPSI complexes **7** and **8** in the Buckwald-Hartwig amination under low catalyst loadings and mild reaction conditions using aryl bromides/chlorides as substrates. Further study of the catalytic applications of these triazol-5-ylidene palladium complexes is subject of investigation in our research group.

4. Material and methods

4.1. General methods

Commercially available reagents and solvents were used as received. 1-(ethynyloxy)benzene [11], 1(4-chlorobenzyl)-4-(phenoxymethyl)-1*H*-1,2,3-triazole [11], triazolium **1** [9i], and mesityl azide [25], were synthesized as reported in the literature. All manipulations related to the synthesis of triazolium salts and metal complexes were performed under air. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. IR spectra were recorded on a Bruker Alpha FT-IR/ATR spectrometer. NMR spectra were obtained with a Bruker Ascend (400 MHz) spectrometer. GC-MS analyses were performed in an Agilent GC model HP 5890 coupled with a mass detector model 5973. Elemental analyses were obtained with a Perkin Elmer Series II CHNS/O 2400 instruments. X-Ray diffraction analyses were collected in an Agilent Gemini Diffractometer using Mo Kα radiation (l = 0.71073 Å). Data were integrated, scaled, sorted, and averaged using the CrysAlisPro software package. The structures we solved using direct methods, using SHELX 97 and refined by full matrix least squares against F^2 [26]. All non hydrogen atoms were refined anisotropically. The position of the hydrogen atoms were kept fixed with common isotropic display parameters. The crystallographic data and some details of the data collection and refinement are given in Table 4. In the crystal structure of $\mathbf{3}_{trans}$ two highly disordered acetonitrile molecules were treated with the program SQUEEZE [27]. Corrections of the X-ray data for $\mathbf{3}_{trans}$ by SQUEEZE (47 electron cell) were close to the required values (44 electron cell). The programs ORTEP [28] and POV-Ray [29] were used to generate the X-ray structural diagrams pictured in this article.

Table 4
Crystallographic Data and Summary of data Collection and Structure Refinement.

	3_{trans}·2MeCN	6	7
Formula	$C_{38}H_{38}Cl_2I_2N_8O_2Pd$	$C_{19}H_{21}I_2N_3OPd$	$C_{22}H_{21}ClI_2N_4OPd$
Fw	1069.89	667.59	753.08
cryst syst	Monoclinic	Triclinic	Orthorhombic
Space group	C2/c	P-1	P212121
T, K	293(2)	293(2)	293(2)
a, Å	29.5993(8)	9.7170(5)	10.5447(7)
b, Å	9.6929(3)	10.1580(4)	13.1626(9)
c, Å	29.2241(11)	11.9574(4)	18.3505(10)
α, deg	90	87.444(3)	90
β, deg	108.263(4)	70.382(4)	90
γ, deg	90	81.858(4)	90
V, Å^3	7963.4 (4)	1100.54(8)	2547.0(3)
Z	8	2	4
d_{calc} g.cm^{-3}	1.648	2.015	1.964
μ, mm^{-1}	2.187	3.661	3.278
refl collected	51563	13642	29675
T_{min}/T_{max}	0.822	0.887	0.867
N_{measd}	5900	3868	4483
[R_{int}]	0.0309	0.0311	0.0546
R [*I*> 2sigma(*I*)]	0.0358	0.0469	0.0328
R (all data)	0.0446	0.0754	0.0441
R_w[*I*> 2sigma(*I*)]	0.0788	0.1479	0.0709
R_w (all data)	0.0821	0.1667	0.0788
GOF	1.115	1.075	1.034

4.1.1. Synthesis of 1-mesytil-4-(phenoxymethyl)-1H-1,2,3-triazole

To a 20 mL round-bottomed flask equipped with a magnetic stirrer, were charged 7 mg (0.035 mmol, 5 mol%) of $Cu(OAc)_2 \bullet H_2O$, 7 mg (0.035 mmol, 5 mol%) of 1,10-phenanthroline monohydrate, and 139 mg (0.70 mmol) of sodium L-ascorbate. After addition of 5 mL of a mixture EtOH-H_2O (4:1 *v*/*v*), the resulting suspension was stirred for five minutes at room temperature. Subsequently, 93 mg (0.70 mmol) of 1-(ethynyloxy)benzene and 124 mg (0.77 mmol) of mesityl azide, were added to the reaction mixture, which was stirred during 16 h at room temperature. The resulting suspension was extracted with dichloromethane (2 × 20 mL), washed with brine, and dried over magnesium sulphate. After solvent removal under vacuum, the crude product was purified by column chromatography (CH_2Cl_2-MeOH 99:1 *v*/*v*) providing the title product as a white solid in 90% yield (0.63 mmol, 185 mg). m.p. = 108–110 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.97 (s, 6H, CH_3), 2.37 (s, 3H, CH_3), 5.35 (s, 2H, ArOCH_2), 6.98–7.02 (m, 3H, CH_{ar}), 7.04 (d, *J* = 7.7 Hz, 2H, CH_{ar}), 7.28–7.34 (m, 2H, CH_{ar}), 7.66 (s, 1H, $CH_{triazole}$). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 17.3, 21.1, 62.3, 115.0, 121.3, 124.6, 129.1, 129.5, 133.4, 135.1, 140.1, 144.2, 158.2. FT-IR/ATR ν_{max} cm^{-1}: 3121, 3094, 3040, 3016, 2937, 2876, 1602, 1585, 1496, 1483, 1469. Found: C, 73.81; H, 6.24; N, 14.00; Calc for: $C_{18}H_{19}N_3O$ C, 73.69; H, 6.53; N, 14.32.

4.1.2. Synthesis of 1,2,3-triazolium 2

Methyl iodide (2.26 g, 15.9 mmol) was added to a 6 mL acetonitrile solution of 1-mesytil-4-(phenoxymethyl)-1H-1,2,3-triazole (467 mg, 1.59 mmol) and the resulting clear solution was refluxed for 16 h. After reaching room temperature, the solvent was reduced to 2/3 of the original volume and diethyl ether was added until a precipitate is formed. The residue was washed thoroughly with cold diethyl ether (3 × 20 mL) and dried under vacuum. Pure product as colourless crystals in 86% yield (595 mg, 1.37 mmol) was obtained after recrystallization with acetonitrile/diethyl ether (1:3). m.p. = 145–147 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.11 (s, 6H, CH_3), 2.38 (s, 3H, CH_3), 4.64 (s, 3H, NCH_3), 5.90 (s, 2H, ArCH_2O), 7.02–7.06 (m, 3H, CH_{ar}), 7.13 (d, *J* = 7.8 Hz, 2H, CH_{ar}), 7.29–7.34 (m, 2H, CH_{ar}), 9.11 (s, 1H, $CH_{triazolium}$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 18.0, 21.2, 40.9, 59.7, 115.3, 122.7, 129.93, 129.94, 131.0, 132.7, 134.4, 141.2, 142.7, 156.7. FT-IR/ATR ν_{max} cm^{-1}: 3069, 3012, 2986, 2954, 2920, 1769, 1599, 1586, 1487, 1470, 1302, 1172, 868, 838, 762. Found: C, 54.47.; H, 4.95; N, 9.42; Calc for: $C_{19}H_{22}N_3OI$ C, 54.42; H, 5.09; N, 9.65.

4.1.3. Synthesis of complexes 3 and 4

Complex 3. The triazolium salt **1** (88.3 mg, 0.20 mmol) and palladium acetate (22.0 mg, 0.098 mmol) were charged in a 20 mL pressure tube. Dry acetonitrile was added (5 mL) and the reaction mixture was heated at 80 °C for 16 h. After reaching room temperature, the solvent was removed under reduced pressure and the residue was extracted with 15 mL of DCM. After filtration over celite and vacuum drying the crude product was purified by column chromatography using a mixture of DCM/acetone (99:1) giving **3** (80 mg, 81% yield) as an analytical pure *cis/trans* mixture (1:1 ratio).

Cis isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.05 (s, 6H, NCH_3), 5.44 (s, 4H, ArCH_2N), 5.81 (s, 4H, ArCH_2O), 6.97 (t, *J* = 7.7 Hz, 2H, CH_{ar}), 7.14–7.15 (m, 4H, CH_{ar}), 7.23–7.29 (m, 8H, CH_{ar}), 7.42 (d, *J* = 7.8 Hz, 4H, CH_{ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 37.3, 58.2, 61.9, 115.2, 121.7, 128.86, 129.81, 130.4, 132.7, 134.37, 140.9, 157.36, 157.48

(C=Pd).

Trans isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.07 (s, 6H, NCH_3), 5.55 (s, 4H, ArCH_2N), 5.95 (s, 4H, ArCH_2O), 7.01 (t, *J* = 7.7 Hz, 2H, CH_{ar}), 7.16–7.17 (m, 4H, CH_{ar}), 7.25–7.33 (m, 8H, CH_{ar}), 7.50 (d, *J* = 7.8 Hz, 4H, CH_{ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 37.4, 58.4, 62.1, 115.2, 121.9, 128.89, 129.83, 130.6, 132.8, 134.41, 141.0, 157.39, 157.56 (C=Pd).

FT-IR/ATR ν_{max} cm^{-1}: 3109, 3105, 3061, 3032, 2991, 2961, 2874, 2862, 2851, 1631, 1603, 1493, 1455, 1404, 1023, 1003, 895, 756. Found: C, 41.53.; H, 3.75; N, 8.02; Calc for: $C_{34}H_{32}Cl_2N_6O_2I_2Pd$ C, 41.34; H, 3.27; N, 8.51.

Complex 4. The triazolium salt **2** (87.0 mg, 0.20 mmol) and palladium acetate (22.0 mg, 0.098 mmol) were charged in a 20 mL pressure tube. Dry acetonitrile was added (5 mL) and the reaction mixture was heated at 80 °C for 16 h. After reaching room temperature, the solvent was removed under reduced pressure and the residue was extracted with 15 mL of DCM. After filtration over celite and vacuum drying the crude product was purified by column chromatography using DCM as eluent giving **4** (75 mg, 77% yield) as an analytical pure *cis/trans* mixture (1:4 ratio).

Cis isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.98 (s, 12H, CH_3), 2.26 (s, 6H, CH_3), 4.20 (s, 6H, NCH_3), 5.48 (s, 4H, ArCH_2O), 6.84 (s, 4H, CH_{ar}), 6.96–6.99 (m, 4H, CH_{ar}), 7.21–7.24 (m, 2H, CH_{ar}), 7.31–7.33 (m, 4H, CH_{ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.8, 21.1, 37.2, 62.7, 115.3, 122.1, 129.09, 129.83, 135.6, 136.1, 139.6, 141.3, 157.1 (C=Pd), 157.5.

Trans isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.01 (s, 12H, CH_3), 2.49 (s, 6H, CH_3), 4.15 (s, 6H, NCH_3), 5.69 (s, 4H, ArCH_2O), 6.93 (s, 4H, CH_{ar}), 6.99–7.04 (m, 4H, CH_{ar}), 7.12–7.14 (m, 2H, CH_{ar}), 7.39–7.43 (m, 4H, CH_{ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.5, 21.3, 37.5, 63.2, 115.5, 121.6, 129.13, 129.81, 135.5, 135.7, 139.1, 141.4, 157.5 (C=Pd), 158.7.

FT-IR/ATR ν_{max} cm^{-1}: 3056, 3029, 3010, 2951, 2922, 2854, 1596, 1493, 1454, 1398, 1374, 1246, 1033, 848, 752. Found: C, 47.15.; H, 3.99; N, 8.45; Calc for: $C_{38}H_{42}N_6O_2I_2Pd$ C, 46.81; H, 4.34; N, 8.62.

4.1.4. Synthesis of complexes *5* and *6*

Complex 5. The triazolium salt **1** (88.3 mg, 0.20 mmol), sodium iodide (45 mg, 0.30 mmol), and palladium acetate (47.0 mg, 0.21 mmol) were charged in a 20 mL pressure tube. Dry acetonitrile was added (5 mL) and the reaction mixture was heated at 110 °C for 24 h. After reaching room temperature, the solvent was removed under reduced pressure and the residue was extracted with 15 mL of DCM. After filtration over celite and vacuum drying the crude product was purified by column chromatography using a mixture of DCM/acetone (99:1) giving **5** (112 mg, 83% yield) as crystalline orange solid. m.p. = 248–250 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.08 (s, 6H, NCH_3), 5.49 (s, 4H, ArCH_2N), 5.93 (s, 4H, ArCH_2O), 7.04 (t, *J* = 7.7 Hz, 2H, CH_{ar}), 7.14 (d, *J* = 7.8 Hz, 4H, CH_{ar}), 7.34–7.40 (m, 8H, CH_{ar}), 7.62 (d, *J* = 7.8 Hz, 4H, CH_{ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 38.2, 58.9, 61.0, 115.1, 122.2, 129.2, 129.6 (C=Pd), 129.9, 131.5, 135.2, 139.9, 144.6, 157.0. FT-IR/ATR ν_{max} cm^{-1}: 3100, 3082, 3053, 2953, 2921, 2853, 1723, 1694, 1649, 1600, 1482, 1446, 1266, 1144, 1069, 848, 760, 690. Found: C, 30.70; H, 2.65; N, 6.32; Calc for: $C_{34}H_{32}Cl_2N_6O_2I_4Pd_2$ C, 30.29; H, 2.39; N, 6.23.

Complex 6. The triazolium salt **2** (87.0 mg, 0.20 mmol), sodium iodide (45 mg, 0.30 mmol), and palladium acetate (47.0 mg, 0.21 mmol) were charged in a 20 mL pressure tube. Dry acetonitrile was added (5 mL) and the reaction mixture was heated at 110 °C for 24 h. After reaching room temperature, the solvent was removed under reduced pressure and the residue was extracted with 15 mL of DCM. After filtration over celite and vacuum drying the crude product was purified by column chromatography using DCM as eluent giving **6** (119 mg, 89% yield) as a crystalline orange solid. m.p. = 227–229 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.99 (s, 12H, CH_3), 2.48 (s, 6H, CH_3), 4.16 (s, 6H, NCH_3), 5.68 (s, 4H, ArCH_2O), 6.92 (s, 4H, CH_{ar}), 7.23 (t, *J* = 7.7 Hz, 2H, CH_{ar}), 7.25–7.26 (m, 2H, CH_{ar}), 7.28–7.32 (m, 6H, CH_{ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.5, 21.3, 37.5, 63.2, 115.3, 121.5, 129.1, 129.8 (CHar + C=Pd), 135.5, 139.1, 141.3, 145.0, 157.5. FT-IR/ATR ν_{max} cm^{-1}: 3106, 3096, 3031, 2978, 2912, 2880, 1700, 1692, 1675, 1582, 1482, 1441, 1301, 1144, 1075, 853, 774, 657. Found: C, 34.03.; H, 3.51; N, 6.57; Calc for: $C_{38}H_{42}N_6O_2I_4Pd_2$ C, 34.18; H, 3.17; N, 6.29.

4.1.5. Synthesis of complexes *7* and *8*

Complex 7. The triazolium salt **1** (88.3 mg, 0.20 mmol), sodium iodide (60 mg, 0.40 mmol), anhydrous potassium carbonate (138 mg, 1 mmol), and palladium chloride (36.0 mg, 0.20 mmol) were charged in a 20 mL pressure tube. Dry pyridine was added (5 mL) and the reaction mixture was heated at 100 °C for 24 h. After reaching room temperature, the solvent was removed under reduced pressure and the residue was extracted with 15 mL of DCM. After filtration over celite and vacuum drying the crude product was purified by column chromatography using a mixture of DCM/acetone (98:2) giving **7** (119 mg, 79% yield) as crystalline yellow solid. m.p. = 187–189 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.07 (s, 3H, NCH_3), 5.54 (s, 2H, ArCH_2N), 5.98 (s, 2H, ArCH_2O), 7.06 (t, *J* = 7.4 Hz, 1H, CH_{ar}), 7.19 (d, *J* = 8.7 Hz, 2H, CH_{ar}), 7.32–7.38 (m, 4H, CH_{ar}), 7.41 (d, *J* = 7.4 Hz, 2H, CH_{ar}), 7.63 (d, *J* = 8.7 Hz, 2H, CH_{ar}), 7.74 (t, *J* = 7.7 Hz, 1H, CH_{ar}), 8.99 (d, *J* = 6.5 Hz, 2H, CH_{ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 38.0, 59.0, 61.8, 115.2, 122.0, 124.5, 129.0, 129.9, 131.5, 131.9, 135.0, 135.9 (C=Pd), 137.6, 139.8, 153.9, 157.3. FT-IR/ATR ν_{max} cm^{-1}: 3059, 3035, 3022, 2945, 2918, 2849, 1585, 1484, 1445, 1406, 1313, 1291, 1221, 1166, 1008, 848, 745, 693. Found: C, 35.21; H, 2.69; N, 7.08; Calc for: $C_{22}H_{21}ClN_4OI_2Pd$ C, 35.09; H, 2.81; N, 7.44.

Complex **8.** The triazolium salt **2** (87.0 mg, 0.20 mmol), sodium iodide (60 mg, 0.40 mmol), anhydrous potassium carbonate (138 mg, 1 mmol), and palladium chloride (36.0 mg, 0.20 mmol) were charged in a 20 mL pressure tube. Dry pyridine was added (5 mL) and the reaction mixture was heated at 100 °C for 24 h. After reaching room temperature, the solvent was removed under reduced pressure and the residue was extracted with 15 mL of DCM. After filtration over celite and vacuum drying the crude product was purified by column chromatography using DCM giving **8** (133 mg, 89% yield) as crystalline yellow solid m.p. = 201–203 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.34 (s, 6H, CH_3), 2.41 (s, 3H, CH_3), 4.22 (s, 3H, NCH_3), 5.76 (s, 2H, ArCH_2O), 7.06 (s, 2H, CH_{ar}), 7.24–7.29 (m, 3H, CH_{ar}), 7.39–7.43 (m, 4H, CH_{ar}), 7.65 (t, *J* = 7.7 Hz, 1H, CH_{ar}), 8.84 (d, *J* = 6.5 Hz, 2H, CH_{ar}).^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.2, 21.3, 38.1, 63.0, 115.3, 122.0, 124.2, 129.5, 129.9, 135.4 (C=Pd), 135.6, 137.2, 138.5, 140.6, 140.7, 153.8, 157.3. FT-IR/ATR ν_{max} cm^{-1}: 3067, 3041, 3012, 2945, 2918, 2856, 1604, 1591, 1484, 1445, 1406, 1327, 1243, 1192, 1023, 843, 756, 691. Found: C, 36.53.; H, 3.73; N, 7.84; Calc for: $C_{24}H_{26}N_4OI_2Pd$ C, 36.80; H, 3.51; N, 7.50.

4.1.5.1. General procedure for the Buchwald-Hartwig amination or aryl bromides (Table 2).

Potassium *tert*-butoxide (1.5 mmol), and the precatalyst (3 mol%), were charged into a 5 mL screw-cap vial that was sealed with a septum and purged with argon. The amine (1.2 mmol) was added via syringe, and the reaction was allowed to stir for 5 min at room temperature. DME (1 mL) was the injected via syringe followed by the aryl bromide (1.0 mmol). The reaction mixture was stirred at 50 °C for 6 h, filtered through a bed of celite and washed with ethyl acetate (2 × 3 mL). The filtrate was evaporated under vacuum and purified by column chromatography on silica gel using appropriate mixtures of hexanes/Et_2O as eluent.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.12.021.

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