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Bulky α-diimine palladium complexes: highly efficient for direct C–H bond arylation of heteroarenes under aerobic conditions†

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Through the strategy to enhance the bulkiness on both the backbone and the *N*-aryl moieties, we designed and synthesized a type of bulky α-diimine palladium complex (*i.e.*, {[Ar–N=C(R)–C(R)=N–Ar]$PdCl_2$, (Ar = 2-benzhydryl-4,6-dimethylphenyl)}, **C1**, R = H; **C2**, R = An; **C3**, R = Ph). The structures of these palladium complexes were well characterized, while **C1** and **C3** were further characterized by X-ray diffraction. The catalytic performances of the precatalysts were screened for direct C–H bond arylation of heteroarenes. The bidentate *N*,*N*-palladium complex **C3** with both a backbone and *N*-aryl bulkiness was found to be a highly efficient precatalyst under aerobic conditions. With a low palladium loading of 0.5–0.1 mol%, a variety of heteroarenes with challenging bulky steric aryl bromides as well as heteroaryl bromides are all applicable for this cross-coupling reaction.

Introduction

Arylated heteroarenes are important structural motifs widely found in many natural products, pharmaceuticals, and functional materials.[1] Consequently, much effort has been made in the development of more efficient and versatile methods for the construction of arylated heteroarenes.[2] Since the pioneering work of Ohta on direct arylation of indoles with chloropyrazines,[3] the palladium-catalyzed direct C–H bond arylation of heteroarenes has become an alternative approach to traditional cross-coupling, as there is no need for the preparation of organometallic reagents avoiding the generation of stoichiometric metal wastes.[4] In the past few decades, great efforts have been devoted to ligand design to improve the palladium-catalyzed reaction efficiency.[5,6]

Previously reported ligands for the direct arylation of heteroarenes are mostly electron-rich and sterically bulky phosphine compounds, which turned out to be very effective toward aryl halides to install a variety of arylated heteroarenes.[5] However, these phosphine-based ligands suffer from tedious preparation procedures and toxic reagents. From the viewpoint of economy and environmental friendliness, the development of phosphine-free ligands is highly desired, as they would provide a more efficient and straightforward access to bi(hetero)arenes.[6] In this context, nitrogen-based ligands, such as 1,10-phenanthroline,[7] 2,2′-bipyridyl[8] and others,[9] were found to catalyze the direct C–H arylation of heteroarenes with aryl halides to yield regioselective products. Very recently, Wu's group successfully established the *N*,*O*-based bis(alkoxo) palladium-catalyzed direct arylation of thiophenes.[10] Although remarkable advances have been achieved, some fundamental challenges still remain. The cleavage of the C–H bond is thermodynamically unfavorable due to its high bond-dissociation energy.[11] Generally, the catalytic process was performed in the temperature range of 100–150 °C, while the palladium catalytic species tend to decompose under these conditions. To ensure a satisfactory yield of the desired product, a loading of 5–10 mol% palladium as well as an air and moisture-free environment were required.[6] Obviously, the high cost of these catalytic systems and inconvenient manipulation greatly impeded their use in large-scale applications. Furthermore, although such an approach is attractive, the cross-coupling reaction of sterically hindered aryl/heteroaryl bromides is another challenge to overcome (Chart 1).

To achieve a highly efficient phosphine-free palladium catalyst system under aerobic reaction conditions with low palladium loading, we have recently reported a type of nitrogen-based α-hydroxyimine palladium complex.[12] We found that the key to ensure excellent catalytic activities is to incorporate

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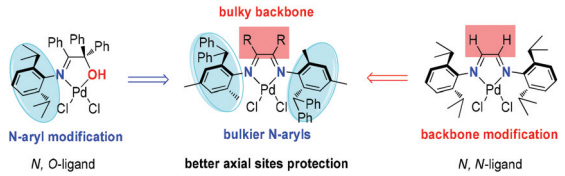


Chart 1 The design of the nitrogen-based palladium precatalyst.

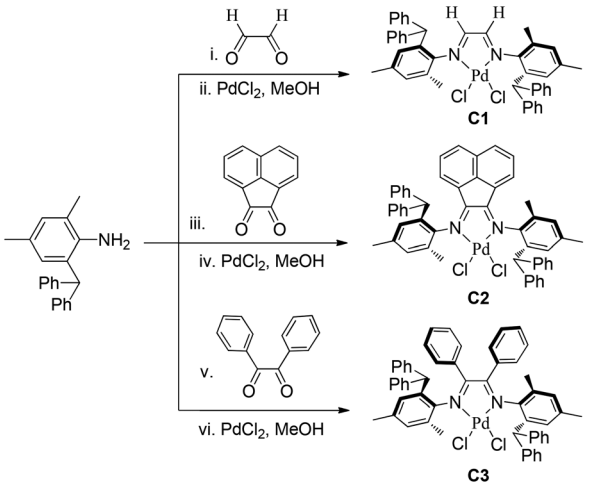
ortho substituents on the *N*-aryl moiety which positions the steric bulk at the axial sites lying above and below the coordination plane. Moreover, the backbone of the ligand also played an important role, as its bulky steric hindrance derived from the backbone could retard the C_{Ar}–N rotation further.[13] Considering the nature of the oxygen in the hydroxyl group that has been coordinated to the palladium in α-hydroxyimines, one side of the coordination plane is less protected. Hence, we envisioned that bulkier α-diimine ligands bearing two *N*-aryl moieties in the structural motifs would better shield the axial site than that of the *N*,*O*-based palladium complexes.[14] Moreover, the steric properties of these ligands can be easily tuned with appropriate substituents. Realizing that the α-diimine ligands can enable new opportunities in cross-coupling[15] and olefin polymerization,[13,16] as part of our ongoing research interest in direct arylation using phosphine-free ligands, we report herein the use of bulky α-diimine compounds as ligands to evaluate the reactivity in the cross-coupling of a variety of heteroarenes with aryl bromides under aerobic conditions.

Results and discussion

Synthesis and characterization of α-diimine palladium complexes

The α-diimine ligands in this study were synthesized using a similar method reported previously,[17] and the corresponding α-diimine palladium complexes (Scheme 1) were readily prepared by the reaction of the ligands with palladium dichloride in methanol. These complexes are air and moisture stable, and can be stored on the shelf in solid form for more than six months without noticeable decomposition in NMR determination. These complexes are well soluble in CH_2Cl_2, $CHCl_3$, DMF and DMAc, while they are poorly soluble in hexane, MeOH and EtOH. Their chemical structures were characterized by NMR spectroscopy and elemental analysis. Although the potential existence of isomers was derived from the unsymmetric nature of the *N*-aryl moieties, the NMR analysis demonstrated one sole isomer in solution at ambient temperature.

To further reveal the structures of these complexes, a single crystal of complex **C1**, suitable for X-ray crystallographic analysis, was grown from methanol and DMF, while a single crystal of **C3** was grown from hexane and dichloromethane solution. ORTEP diagrams are given in Fig. 1 and 2, respectively, along with selected bond lengths and angles. In the solid structure, complex **C1** with the backbone of hydrogen



Scheme 1 Synthetic route for the α-diimine palladium complexes.

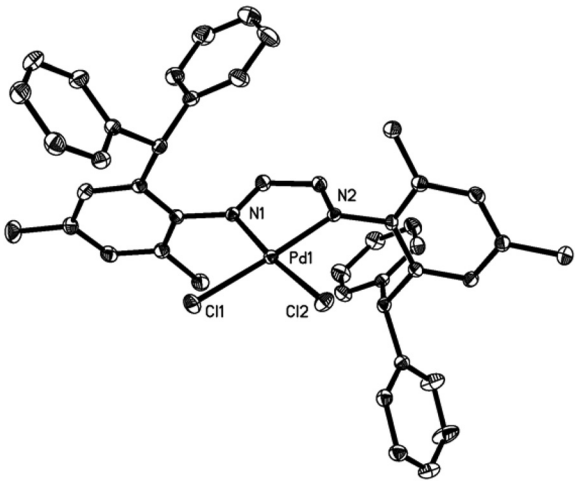


Fig. 1 Molecular structure of **C1**·DMF depicted with 30% thermal ellipsoids. Hydrogen atoms and DMF solvent have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–N(1) 2.0198(17), Pd(1)–N(2) 2.0278(16), Pd(1)–Cl(1) 2.2635(5), Pd(1)–Cl(2) 2.2778(5), N(1)–Pd(1)–N(2) 79.70(7), N(1)–Pd(1)–Cl(1) 94.25(5), N(2)–Pd(1)–Cl(1) 173.55(5), N(1)–Pd(1)–Cl(2) 174.11(5), N(2)–Pd(1)–Cl(2) 94.95(5), Cl(1)–Pd(1)–Cl(2) 91.18(2).

exhibits a slightly distorted square-planar coordination geometry. The 2-benzhydryl groups on *N*-aryl moieties were located as the *anti*-form lying above and below the coordination plane. Bearing the bulky steric substituents, the *N*-aryl moieties are nearly perpendicular to the five-membered chelate ring with a dihedral angle of 83.96 and 77.64°, respectively, which suggests that the axial sites of the palladium center would be blocked tightly. Nevertheless, the Pd–N and Pd–Cl bond distances as well as N(1)–Pd–N(2) bond angles in **C1** are in accordance with the values of other α-diimine palladium complexes.[18] In contrast, with the diphenyl backbone framework, the bond lengths of Pd–N(1) and Pd–N(2) in **C3** are 2.033(2) and 2.044(2) Å, respectively, which are longer than those of **C1**

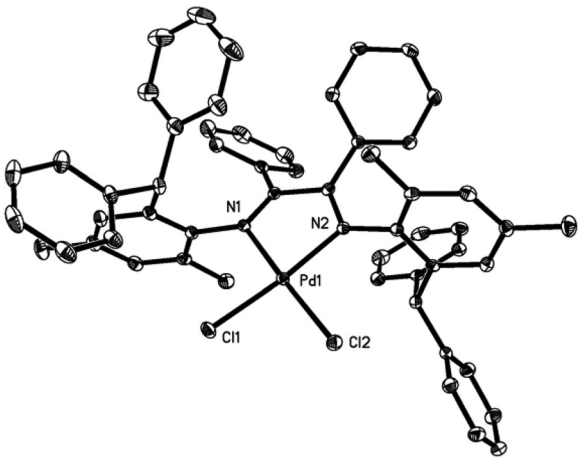
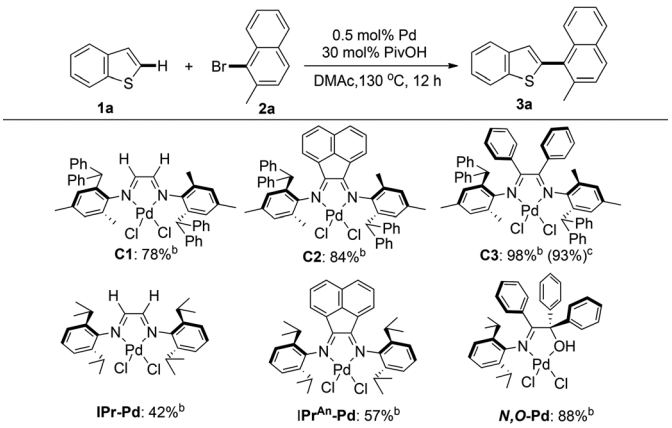


Fig. 2 Molecular structure of **C3**·2CH_2Cl_2 depicted with 30% thermal ellipsoids. Hydrogen atoms and CH_2Cl_2 solvent have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–N(1) 2.033(2), Pd(1)–N(2) 2.044(2), Pd(1)–Cl(1) 2.2682(7), Pd(1)–Cl(2) 2.2738(7), N(1)–Pd(1)–N(2) 79.79(8), N(1)–Pd(1)–Cl(1) 95.07(6), N(2)–Pd(1)–Cl(1) 174.47(6), N(1)–Pd(1)–Cl(2) 175.00(6), N(2)–Pd(1)–Cl(2) 97.13(6), Cl(1)–Pd(1)–Cl(2) 88.14(3).

Table 1 Screening of palladium complexes for the direct arylation reaction of benzo[*b*]thiophene with 1-bromo-2-methylnaphthalene[a]



[a] Reaction conditions: benzo[*b*]thiophene (2 mmol), 1-bromo-2-methylnaphthalene (1 mmol), palladium complex (0.005 mmol), PivOH (0.3 mmol), K_2CO_3 (2 mmol) and DMAc (3 mL) in an aerobic environment. [b] Cross-coupling product determined by GC-FID using (trifluoromethyl)benzene as an internal standard. Cross-coupling was performed in two parallel reactions and the yield is given in average. [c] Isolated yields in parentheses.

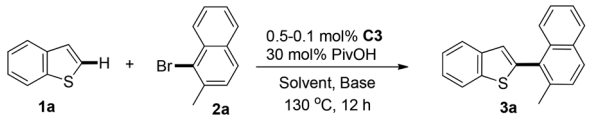
(2.020(2) and 2.028(2) Å, respectively), indicating a more constrained structure. Moreover, the dihedral angles between the *N*-aryl moieties and the chelate ring turned out to be 84.95 and 78.44°, respectively. Therefore, axial steric hindrance around the palladium center could further hinder the rotation of the C_{Ar}–N bond, which will play a significant role in the catalytic performances.[13,19]

The palladium-catalyzed direct C–H arylation reaction under aerobic conditions

The direct C–H arylation between sterically hindered 1-bromo-2-methylnaphthalene and benzo[*b*]thiophene was studied as the model reaction. Initially, all the palladium complexes **C1–C3** were screened under the same reaction conditions. The cross-coupling reactions were performed in DMAc under aerobic conditions at 130 °C for 12 h, in the presence of 0.5 mol% palladium loading with K_2CO_3 as the base and PivOH (pivalic acid) as the acid additive. As shown in Table 1, the precatalysts with 2-benzhydryl-4,6-dimethyl on *N*-aryl moieties showed superior activities. **C1** with two hydrogen atoms on the backbone gave the desired product **3a** in 78% GC yield, while a higher yield of 84% was observed when acenaphthyl was used as the backbone. To our delight, bearing a bulky diphenyl backbone, **C3** was identified as the most effective precatalyst with almost quantitative GC yield (98%), and a satisfactory isolated yield of 93% was obtained. As expected, our designed *N*,*N*-based ligand with more steric hindrance on the backbone could retard the rotation of the C_{Ar}–N bonds, enhancing the steric hindrance of the *ortho*-substituents on *N*-aryl moieties to block the axial positions of the palladium center, and therefore suppressing the related catalytic decomposition at high temperatures under aerobic reaction conditions. Besides the backbone, the effect of the *N*-aryl moieties on catalytic properties was further evaluated and *N*,*N*-based palladium complexes bearing 2,6-diisopropyls were further tested for comparison. It was shown that IPr-Pd with two hydrogen atoms and IPr^{An}-Pd with acenaphthyl as backbones gave **3a** in a much lower product yield of 42% and 57%, respectively. Moreover, our previously reported bulky *N*,*O*-Pd afforded a satisfactory yield of 88% under the present reaction conditions.[12] Nevertheless, it was also inferior to that of **C3**. Obviously, the bulky steric hindrance of 2-benzhydryl-4,6-dimethyl on *N*-aryl moieties played a profound role in the excellent catalytic performance of **C3**, which is consistent with the reductive elimination process as the rate-determining step in the direct C–H arylation.[12,20]

Having identified the most effective precatalyst, the optimization of the reaction conditions was investigated. First, the reaction was conducted in the absence of PivOH and the product **3a** was obtained in only 56% GC yield (Table 1, run 1), thus confirming the important role of the acid additive in the direct C–H arylation reaction. We next performed a systematic screening of the bases and a significant acceleration was observed on introducing the carboxylate salts into the reaction. K_2CO_3 was proved to be the most efficient and gave the desired product in 98% GC yield. It is noteworthy that only KOPiv worked well and gave a satisfactory yield of 96%. Moreover, KOPiv associated with PivOH was also investigated, and it afforded a yield of 97% (run 3, Table 2). Other carboxylate bases such as Na_2CO_3, $NaHCO_3$, KOAc, and NaOAc were also efficient and moderate to high yields were obtained, whereas other bases provided low yields for this transformation. The indispensability of PivOH and the key role of the carboxylate base suggest a concerted metalation–deprotonation (CMD) pathway involved in the direct C–H arylation.[11,21] Moreover,

Table 2 Screening of reaction conditions for the direct arylation reaction of benzo[*b*]thiophene with 1-bromo-2-methylnaphthalene[a]



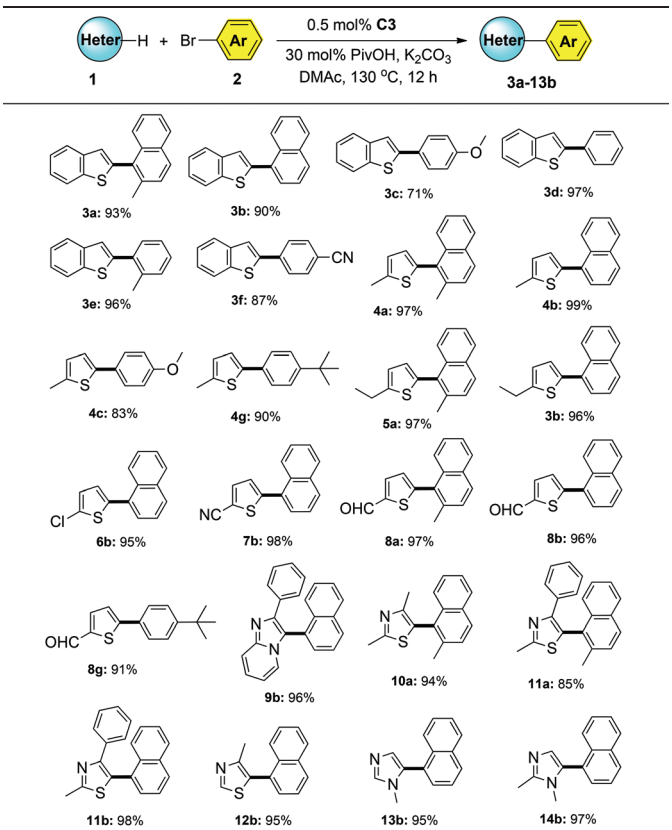
Run	Pd loading	Solvent	Base	*T* (°C)	Yield[b] (%)
1[c]	0.5	DMAc	K_2CO_3	130	56
2	0.5	DMAc	K_2CO_3	130	98
3	0.5	DMAc	PivOK	130	97
4[c]	0.5	DMAc	PivOK	130	96
5	0.5	DMAc	KOAc	130	67
6	0.5	DMAc	Na_2CO_3	130	76
7	0.5	DMAc	$NaHCO_3$	130	82
8	0.5	DMAc	NaOAc	130	65
9	0.5	DMAc	KF	130	36
10	0.5	DMAc	K_3PO_4	130	49
11	0.5	DMAc	LiOH	130	39
12	0.5	DMAc	KOH	130	31
13	0.5	DMAc	Na^tOBu	130	35
14	0.5	DMAc	K^tOBu	130	33
15	0.5	DMF	K_2CO_3	130	96
16	0.5	NMP	K_2CO_3	130	79
17	0.5	Toluene	K_2CO_3	130	33
18	0.5	Xylene	K_2CO_3	130	11
19	0.5	Dioxane	K_2CO_3	130	NR
20	0.5	DMSO	K_2CO_3	130	NR
21	0.5	DMAc	K_2CO_3	100	38
22	0.5	DMAc	K_2CO_3	110	55
23	0.5	DMAc	K_2CO_3	120	83
24	0.1	DMAc	K_2CO_3	130	61

[a] Reaction conditions: benzo[*b*]thiophene (2 mmol), 1-bromo-2-methylnaphthalene (1 mmol), palladium complex **C3** (0.005 or 0.001 mmol), PivOH (0.3 mmol), K_2CO_3 (2 mmol) and DMAc (3 mL) in an aerobic environment. [b] Cross-coupling product determined by GC-FID using (trifluoromethyl)benzene as an internal standard. Cross-coupling was performed in two parallel reactions and the yield is given in average. [c] In the absence of PivOH.

a profound influence of the solvent has been found, with toluene and xylene affording poor yields. Moreover, it was observed that DMF and NMP gave **3a** in moderate to excellent yields, whereas DMAc afforded the best yield (Table 2). Other reaction conditions were tested further. However, the decrease in palladium loading to 0.1 mol% or lowering the reaction temperature to 100 °C all impeded the efficiency. Thus, the optimized reaction conditions were obtained by using a mixture of benzo[*b*]thiophene (2.0 equiv.), 1-bromo-2-methylnaphthalene (1.0 equiv.), **C3** as the precatalyst, a palladium loading of 0.5 mol%, K_2CO_3 as a base and PivOH (30 mol%) as an acid additive and DMAc as a solvent in an aerobic environment.

Having established the optimal reaction conditions, the coupling reactions between benzo[*b*]thiophene and a variety of aryl bromides were screened. It is noteworthy that the bulky hindrance of the electrophile substrates showed little effect on the transformation. The *ortho*-substituted aryl bromides such as 1-bromo-2-methylbenzene, 1-bromonaphthalene, and 1-bromo-2-methylnaphthalene, which are challenging coupling partners and generally afforded much lower yields than their *meta*- and *para*-substituted analogues in previous studies,[22] were successfully coupled with benzo[*b*]thiophene to give the heterocyclic product **3a**, **3b**, and **3e** in 90–96% yields under the optimal reaction conditions. Moreover, it was found that the cross-couplings with the aryl bromide partners bearing electron-withdrawing, -neutral and -donating groups and bulky groups could all take place efficiently to afford the corresponding products in good to excellent yields (**3c–3f**, Table 3). For example, substrates with an electron-withdrawing group such as 4-bromobenzonitrile afforded **3f** in a yield of 87%, while the substrate with an electron-donating group, 4-bromoanisole, afforded **3c** in 71% yield. To further evaluate the potential breadth of the substrate scope, a variety of five-membered heteroarenes bearing C-2 electron-donating and electron-withdrawing functional groups were also successfully coupled with bulky aryl bromides in excellent yields (**4a–13b**, Table 3). Heteroarenes, such as 2-methylthiophene, 2-ethylthiophene, 2-chlorothiophene, thiophene-2-carbonitrile, thiophene-2-carbaldehyde, imidazo[1,2-*a*]pyridine, 2,4-dimethylthiazole, 2-methyl-4-phenylthiazole and 4-methylthiazole gave the desired arylated products **4a–11b** in 83–99% yields under the optimized conditions. To our delight, the

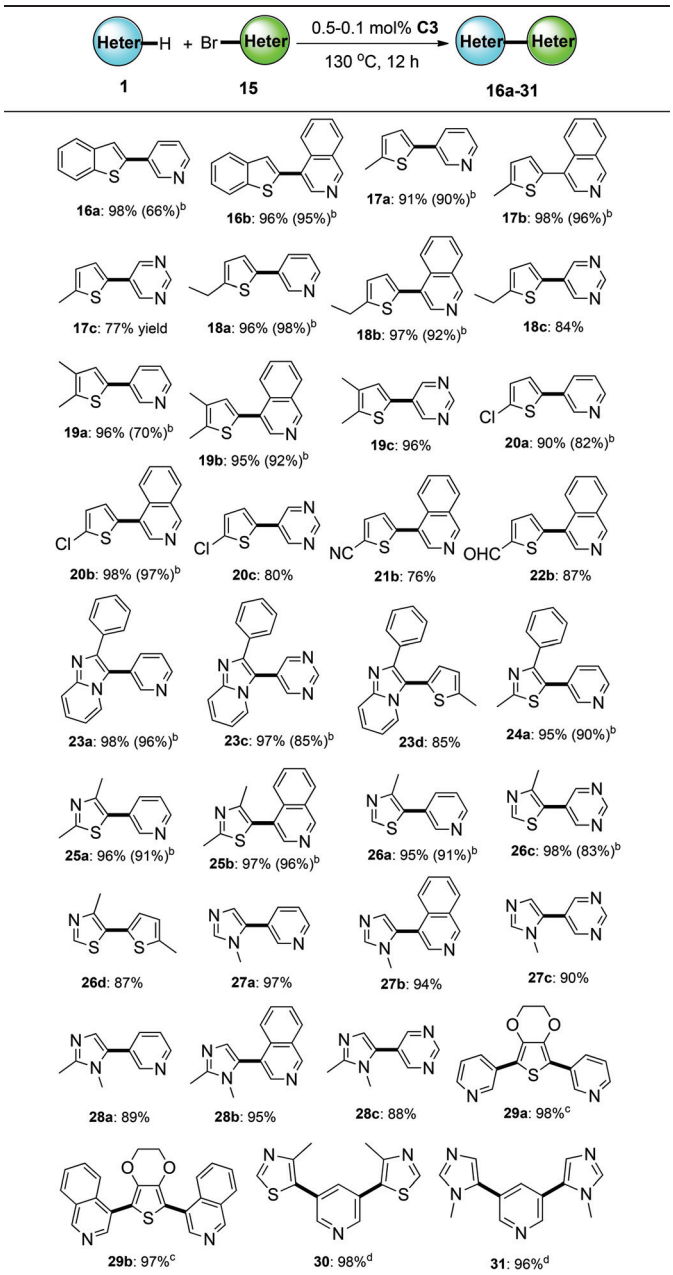
Table 3 The palladium-catalyzed direct arylation of heteroarenes with aryl bromides[a]



[a] Reaction conditions: heteroarene (2 mmol), aryl bromide (1 mmol), palladium complex **C3** (0.5 mol%), PivOH (0.3 mmol), K_2CO_3 (2 mmol) and DMAc (3 mL), 130 °C for 12 h in an aerobic environment. Cross-coupling was performed in two parallel reactions and the isolated yields are given in average.

much less reactive imidazoles[23] such as 1-methyl-1*H*-imidazole and 1,2-dimethyl-1*H*-imidazole also successfully coupled to provide **12b** and **13b** in nearly quantitative yield. It seems that the electronic nature and steric hindrance of the aryl bromides, such as *p*-cyano, methoxy, *tert*-butyl and *ortho*-methyl were well tolerated, leading to excellent yields.

Table 4 The palladium-catalyzed direct arylation of heteroarenes with heteroaryl bromides[a]



[a] Reaction conditions: heteroarene (2 mmol), aryl bromide (1 mmol), palladium complex **C3** (0.5 mol%), PivOH (0.3 mmol), K_2CO_3 (2 mmol) and DMAc (3 mL), 130 °C for 12 h in an aerobic environment. Cross-coupling was performed in two parallel reactions and the isolated yields are given in average. [b] The reaction was performed at a palladium loading of 0.1 mol%. [c] Reaction conditions: 3,4-ethylenedioxythiophene (1 mmol), aryl bromide (3 mmol), other reaction conditions were the same as those in footnote 'a'. [d] Reaction conditions: heteroarene (3 mmol), 3,5-dibromopyridine (1 mmol), other reaction conditions were the same as those in footnote 'a'.

Biheteroaryls are well known as common substructures in natural and biologically active compounds.[24] The coupling of heteroaryl bromides with heteroarenes remains quite an important but challenging task due to the low reactivity of substrates and the poisoning of palladium species by heteroatoms.[20] Encouraged by the above results using highly sterically congested aryl bromides as the substrates, we then expanded it to reactions between heteroarenes (such as thiophenes, thiazole, imidazole, and imidazo[1,2-*a*]pyridine) and heteroaryl bromides under the optimal conditions. As can be seen from Table 4, the reaction proceeded in excellent yields in spite of the electronic nature of the heteroaryl bromides. Electron-poor and electron-rich aromatic systems underwent direct arylation in excellent yields irrespective of the substitution pattern. The functional groups, such as pyridyl, pyrimidine, isoquinoline and thiophene, were well tolerated. As a result, a variety of desired biheteroarenes **16a–28c** were obtained. Inspired by the outstanding performance of the pre-catalyst **C3**, we tested the possibility of a low palladium loading of 0.1 mol% further. To our delight, it was found that both electron-donating and -withdrawing substituents on the five-membered heteroarenes were compatible in these reactions to provide the respective products in high to excellent yields (Table 4).

Recently, the conjugated poly(hetero)arenes have been extensively investigated for the fabrication of functional materials, such as optoelectronic and electrochromic devices.[25] The highly efficient palladium complexes prompt us to explore the potential application in di-arylation reactions of heteroarenes. As can be seen in Table 4, **C3** was found to be useful for carrying out the di-arylation reaction. For example, 3,4-ethylenedioxythiophene (EDOT) reacts with 3 equiv. of 3-bromopyridine and 4-bromoisoquinoline to give the 2,5-arylated product of **29a** and **29b** in 98 and 97% yield, respectively. Moreover, we attempted another strategy of the diheteroarylation of heteroarenes with dibromoarene. It is a pleasure that 3,5-dibromopyridine successfully coupled with 4-methylthiazole and 1-methyl-1*H*-imidazole, affording the regioselective products **30** and **31** in excellent yields of 98 and 96%, respectively. Significantly, this straightforward and selective diarylation reaction provides a potential efficient method for the direct arylation polymerization for the construction of functional materials.[26]

Experimental

General procedures

2-Benzhydryl-4,6-dimethylaniline was prepared according to previous reports.[27] Heteroarenes and aryl bromides were purchased from Darui Chemical Reagent Factory. Oxalaldehyde aqueous (40%), acenaphthenequinone, benzil, and palladium chloride were purchased from Beijing HWEK Chem. Co., Ltd. Inorganic bases and solvents were purchased from Guangzhou

Chemical Reagent Factory and were used as received. IPr-Pd[28a,b] and IPrAn-Pd[29] compounds were synthesized according to literature methods.

The NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature with the decoupled nucleus, using TMS as an internal standard and $CDCl_3$ as a solvent. Elemental analysis was performed using a Flash EA1112 microanalyzer. The X-ray diffraction data of single crystals were collected with the ω–2θ scan mode on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 173 K for **C1** and **C3**. Cell parameters were obtained by global refinement of the positions of all the collected reflections. The intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All hydrogen atoms were placed in the calculated positions. Structure solution and refinement were carried out by using the SHELXL-97 package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in the calculated positions with the displacement factors of the host carbon atoms. CCDC 1486526 (**C1**) and 1486527 (**C3**) contain the supplementary crystallographic data for this paper.

The syntheses of *N*,*N*-bis-(2-benzhydryl-4,6-dimethyl) ethanediimine (L1)

2-Benzhydryl-4,6-dimethylaniline (10 mmol) and CH_3COOH (4 mL) were added in ethanol (30 mL). To this solution, 40 wt% glyoxal in H_2O (5 mmol) was added slowly, while the yellow suspension emerged immediately. The mixture was stirred for 8 h at 80 °C. When reaching the schedule time, the reaction was stopped and the precipitation was filtered. The residue was recrystallized in dichloromethane/ethanol (15 mL/20 mL) to give a light yellow solid (2.4 g, 80% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, Ar–H, 2H), 7.26 (t, J = 7.3 Hz, Ar–H, 8H), 7.20 (t, J = 6.9 Hz, Ar–H, 4H), 7.04 (d, J = 7.5 Hz, Ar–H, 8H), 6.97 (s, Ar–H, 2H), 6.58 (s, Ar–H, 2H), 5.47 (s, Ar_2C–H, 2H), 2.24 (s, CH3, 6H), 2.03 (s, CH3, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 147.2, 143.5, 133.7, 133.4, 129.8, 129.5, 128.2, 128.0, 126.2, 125.0, 51.8, 21.0, 18.3. Anal. Calcd for: $C_{44}H_{40}N_2$: C, 88.55; H, 6.76; N, 4.69. Found: C, 88.34; H, 6.80; N, 4.61.

General procedures for the synthesis of α-diimine compounds L2 and L3

2-Benzhydryl-4,6-dimethylaniline (12 mmol) was dissolved in 30 mL of anhydrous toluene under a nitrogen atmosphere, trimethylaluminum (5 mL, 1.0 M in hexane) was added slowly through a syringe at room temperature and the reaction mixture was heated to reflux for 2 h. After cooling to room temperature, the 1,2-diketone (5 mmol) was added, and then the mixture was stirred for 8 h at 110 °C under a nitrogen atmosphere. When the determined time was reached, the reaction mixture was carefully hydrolyzed with 5% iced aqueous NaOH solution. The organic product was extracted with toluene and dried over $MgSO_4$ and the solvent was evaporated, the crude material was purified by column chromatography (hexane/EtOAc = 20/1) as the desired product.

Bis[*N*,*N*-(2-benzhyldryl-4,6-dimethyl)imino]acenaphthene (**L2**) was obtained as orange crystals (3.0 g, 85% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.2 Hz, Ar–H, 2H), 7.30–7.23 (m, Ar–H, 4H), 7.22–7.17 (m, Ar–H, 2H), 7.14–6.99 (m, Ar–H, 7H), 6.88 (d, J = 7.3 Hz, Ar–H, 4H), 6.72 (s, Ar–H, 2H), 6.34 (dd, J = 16.1, 7.6 Hz, Ar–H, 6H), 6.11 (t, J = 7.4 Hz, Ar–H, 2H), 5.74 (s, Ar–H, 1H), 5.32 (s, Ar_2C–H, 2H), 2.35 (s, CH_3, 6H), 2.28 (s, CH_3, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 146.4, 143.6, 141.7, 139.8, 133.0, 132.7, 129.8, 129.6, 129.5, 129.2, 128.9, 128.0, 128.0, 127.7, 127.1, 126.9, 125.9, 125.0, 124.8, 122.4, 52.5, 21.2, 17.8. Anal. Calcd for: $C_{54}H_{44}N_2$: C, 89.96; H, 6.15; N, 3.89. Found: C, 89.85; H, 6.21; N, 3.82.

N,*N*-(1,2-Diphenylethane-1,2-diylidene)bis(2-benzhydryl-4,6-dimthylaniline) (**L3**) was obtained as light yellow crystals (3.0 g, 82% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (t, J = 72.4 Hz, Ar–H, 22H), 6.78 (d, J = 30.6 Hz, Ar–H, 8H), 6.44 (d, J = 58.4 Hz, Ar–H, 2H), 5.55 (d, J = 19.2 Hz, Ar–H, 2H), 5.30 (s, Ar_2C–H, 2H), 2.14 (s, CH_3, 6H), 1.90 (s, CH_3, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 144.9, 144.1, 143.1, 135.5, 135.2, 132.3, 131.6, 129.9, 129.5, 129.4, 128.9, 128.7, 128.0, 127.6, 126.0, 125.9, 125.0, 124.8, 51.4, 21.0, 18.9. Anal. Calcd for: $C_{56}H_{48}N_2$: C, 89.80; H, 6.46; N, 3.74. Found: C, 89.74; H, 6.35; N, 3.68.

General procedures for the synthesis of α-diimine Pd compounds

The α-diimine ligand (1.0 mol) and palladium dichloride (0.177 g, 1.0 mmol) were mixed in 10 mL of methanol at room temperature. After the reaction mixture was heated to reflux overnight, the methanol was removed under reduced pressure. The residue was dissolved in 5 mL of dichloromethane, and 20 mL hexane was added. The precipitate of the palladium complex was collected by filtration and washed with hexane. Drying in vacuum produced the desired palladium complex.

{*N*,*N*-Bis-(2-benzhydryl-4,6-dimethyl)ethanediimine}dichloropalladium **C1** was obtained as an orange solid (0.69 g, 90% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, J = 5.0 Hz, Ar–H, 6H), 7.23 (d, J = 7.3 Hz, Ar–H, 8H), 7.19 (t, J = 6.8 Hz, Ar–H, 2H), 7.12 (d, J = 7.4 Hz, Ar–H, 4H), 7.02 (s, Ar–H, 2H), 6.55 (s, Ar–H, 2H), 6.41 (s, Ar–H, 2H), 6.20 (s, Ar_2C–H, 2H), 2.34 (s, CH_3, 6H), 2.23 (s, CH_3, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 143.1, 142.8, 141.8, 138.5, 136.4, 130.0, 129.8, 129.7, 129.0, 128.7, 128.3, 128.2, 127.0, 126.7, 52.6, 21.4, 18.7. Anal. Calcd for: $C_{44}H_{40}Cl_2N_2Pd$: C, 68.27; H, 5.21; N, 3.62. Found: C, 68.05; H, 5.14; N, 3.52.

{Bis[*N*,*N*-(2-benzhyldryl-4,6-dimethyl)imino]acenaphthene} dichloropalladium **C2** was obtained as an orange solid (0.79 g, 88% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.3 Hz, Ar–H, 2H), 7.33 (d, J = 7.5 Hz, Ar–H, 4H), 7.25 (dd, J = 16.6, 8.4 Hz, Ar–H, 8H), 7.11 (d, J = 8.3 Hz, Ar–H, 6H), 6.76 (s, Ar–H, 2H), 6.63 (s, Ar–H, 2H), 6.38 (t, J = 7.4 Hz, Ar–H, 4H), 6.07 (t, J = 7.4 Hz, Ar–H, 2H), 5.32 (s, Ar_2C–H, 2H), 2.54 (s, CH_3, 6H), 2.34 (s, CH_3, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 146.2, 142.2, 140.9, 140.2, 138.2, 137.7, 131.4, 130.0, 129.9, 129.8, 129.6, 129.3, 128.8, 128.0, 127.9, 127.7, 126.4, 125.3, 125.1, 123.7,

52.8, 21.6, 18.4. Anal. Calcd for: $C_{54}H_{44}Cl_2N_2Pd$: C, 72.20; H, 4.94; N, 3.12. Found: C, 71.98; H, 4.83; N, 3.17.

{*N*,*N*-(1,2-Diphenylethane-1,2-diylidene)bis(2-benzhydryl-4,6-dimthylaniline)}dichloropalladium **C3** was obtained as an orange solid (0.80 g, 87% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 13.9, 8.3 Hz, Ar–H, 3H), 7.85 (d, J = 7.3 Hz, Ar–H, 1H), 7.71 (d, J = 6.1 Hz, Ar–H, 5H), 7.48 (dd, J = 16.9, 9.0 Hz, Ar–H, 3H), 7.28–7.19 (m, Ar–H, 11H), 7.16 (d, J = 8.1 Hz, Ar–H, 3H), 7.17–7.06 (m, Ar–H, 4H), 6.66 (d, J = 7.2 Hz, Ar–H, 3H), 6.56 (d, J = 7.2 Hz, Ar–H, 1H), 5.30 (s, Ar_2C–H, 2H), 2.52 (s, CH_3, 6H), 2.41 (s, CH_3, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 146.6, 139.6, 138.6, 137.9, 134.8, 131.3, 131.0, 130.0, 129.7, 129.6, 129.1, 129.0, 128.5, 128.0, 127.3, 125.2, 124.7, 60.2, 21.3, 19.1. Anal. Calcd for: $C_{56}H_{48}Cl_2N_2Pd$: C, 72.61; H, 5.22; N, 3.02. Found: C, 72.49; H, 5.28; N, 2.96.

General procedure for direct arylation promoted by palladium complexes

Unless otherwise noted, the direct C–H arylation reactions were carried out under aerobic conditions. The reaction temperatures are reported as the temperature of the heating vessel unless otherwise stated. All solvents were used as received and no further purification was needed. A parallel reactor containing a stirring bar was charged with Pd complexes (0.005–0.001 mmol, extracted from a constant volume in the standard stock solution of DMAc), heteroarene (2.0 mmol), aryl bromide (1.0 mmol), base (2.0 mmol), and 3 mL of solvent. The reaction was carried out at 130 °C for 12 h. After completion of the reaction, the reaction mixture was cooled to ambient temperature and 20 mL of water was added. The mixture was diluted with dichloromethane (5 mL), followed by extraction three times (3 × 5 mL) with dichloromethane. The organic layer was dried with anhydrous magnesium sulfate, filtered and evaporated under reduced pressure. When 3,4-ethylenedioxythiophene was selected as the substrate, the direct diheteroarylation reactions were performed using 3,4-ethylenedioxythiophene (1 mmol) and aryl bromide (3 mmol) as substrates, while other reaction conditions were the same as mono-arylation described above. When 3,5-dibromopyridine was used as substrates, the direct arylation reactions were carried out using heteroarene (3 mmol) and 3,5-dibromopyridine (1 mmol) as substrates, while other reaction conditions were the same as mono-arylation described above. The crude cross-coupling products were purified by silica-gel column chromatography using petroleum ether–dichloromethane (20/1) as an eluent. The isolated cross-coupling products were characterized by ^{1}H NMR and ^{13}C NMR, and the spectra can be found in the ESI.†

Conclusions

We have developed a type of bulky α-diimine palladium complex for direct C–H arylation under aerobic conditions. The catalytic performances of the precatalysts were screened. It was found that both the bulky backbone and the *N*-aryl moiety were crucial to promote the efficiency of the cross-coupling reaction. Under the optimized conditions, an array of sterically hindered as well as heteroaryl bromides have been successfully coupled with various heteroarenes at a 0.5–0.1 mol% palladium loading. The results highlight a new type of nitrogen-based phosphine-free catalytic system to enhance catalytic activities under mild reaction conditions.

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