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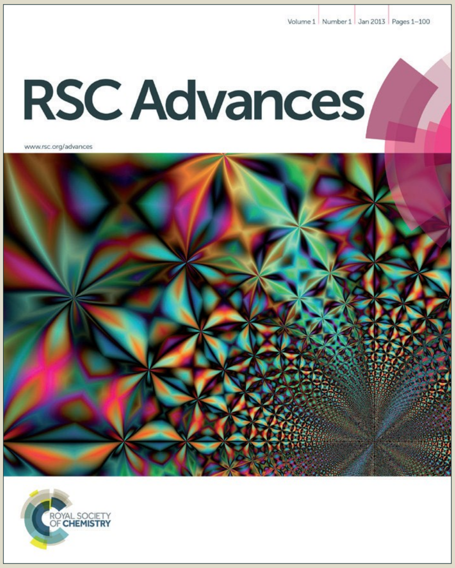

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ARTICLE

Synthesis and characterization of trinuclear *N*-heterocyclic carbene-palladium(II) complexes and their applications in the Suzuki-Miyaura cross-coupling reaction

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Five novel trinuclear *N*-heterocyclic carbene-palladium(II) complexes **5a-e** were conveniently synthesized through one-pot reactions of imidazolium salts, tridentate *N*-heterocycles {tris(4-(pyridin-4-yl)phenyl)amine or tris(4-(pyridin-3-yl)phenyl)amine} and palladium chloride in one step. All of the new complexes have been fully characterized by elemental analysis, ^{1}H, ^{13}C NMR, and IR spectra. Among them, the molecular structures of complex **5d** have been determined by X-ray single-crystal diffraction. Moreover, the obtained trinuclear palladium(II) complexes were the effective catalyst precursors for the Suzuki-Miyaura coupling of aryl as well as benzyl chlorides with arylboronic acids. Under the optimal reaction conditions, the expected biaryl products were obtained in good to almost quantitative yields.

Introduction

Since the pioneering work of Arduengo in the 1990s,[1] a wide variety of NHC-Pd complexes have been synthesized and applied in catalytic reactions such as Buchwald-Hartwig amination reactions, direct C-H bond arylation reactions, as well as cross-coupling reactions including Heck, Hiyama, Stille, Negishi, Suzuki-Miyaura, and Kumada-Tamao-Corriu(KTC) reactions.[2] In these transformations, it was found that the electronic properties and steric encumbrance of the NHC ligands were crucial. During the past few years, a number of modified carbene ligands such as IPr, IXy, IMes, SIPr, SIXy, SIMes and the corresponding palladium complexes have been successively designed and applied in organic reactions. In addition to the NHC moieties, another strategy is to introduce an ancillary ligand into the metal center, thereby enhancing the potential for hemilability and heterometallation of the carbene ligands. The ancillary ligands attached to the metal core also played important roles in tuning the electronic and steric properties of the coordination sphere. For example, The groups of Organ,[3] Tu,[4] Thiel[5] and Brenner[6] reported the pyridine type ligands modified carbene palladium complexes as active catalysts for a series of catalytic reactions. Strassner and co-workers[7] explored the applications of the NHC-Pd(II)-2-phenylimidazole complexes in Suzuki-Miyaura cross-coupling reaction of aryl chlorides, providing the desired products in excellent yields with low catalyst loading. Recently, Shao and Lu have developed well-defined NHC-Pd(II)-1-methylimidazole complexes,[8] which can be easily prepared from commercially available imidazolium salts, 1-methylimidazole, and $PdCl_2$ from a one-step process in good yields, and found them to be efficient catalysts for the Suzuki-Miyaura coupling, arylation of symmetric dialkyl ketones, direct C-H bond arylation reactions. In our previous work, we reported the mononuclear *N*-heterocyclic carbene-palladium(II) complexes with benzoxazole or benzothiazole ligands, which were used as effective catalysts for the Suzuki-Miyaura coupling of aryl as well as benzyl chlorides with arylboronic acids.[9] Very recently, the obtained NHC-Pd complexes also applied to the Buchwald-Hartwig amination of aryl chlorides with secondary or primary amines under the same reaction conditions.[10] While a series of tertiary phosphine modified carbene palladium complexes were used as effective catalysts for Suzuki cross-coupling and other reactions.[11] Besides mononuclear *N*-heterocyclic carbene palladium complexes, the dinuclear *N*-heterocyclic carbene complexes containing various bridging ligands have attracted increasing attention in recent years. *N*-heterocycles such as DABCO, pyrazine, and 4,4′-bipyridine have been the most widely used bridging ligands in this field.[12] Dinuclear NHC-palladium complexes containing phosphine spacers have also been reported to be active catalyst precursors for C-C and C-N coupling reactions.[13] Despite the impressive progress

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Electronic supplementary information (ESI) available: ^{1}H NMR and ^{13}C NMR spectra of the trinuclear palladium(II) complexes **5a-e**, the catalysis products **8** and **10**, characterization data of the catalysis products **8** and **10**, and CIF files for the Pd complex **5d**. See DOI: 10.1039/x0xx00000x

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made so far in the *N*-heterocyclic carbene-palladium complexes as catalysts, very little research has been reported on trinuclear or multinuclear carbene-palladium complexes bearing tridentate or multidentate bridging ligands. Encouraged by the results mentioned above and also in continuation of our interest in the construction of functionalized complexes for organic synthesis, herein we would like to report the facile synthesis and structural characterization of five novel trinuclear *N*-heterocyclic carbene-palladium(II) complexes bridged by tridentate *N*-heterocycles (Scheme 1). Furthermore, as their preliminary application, the resulting trinuclear NHC-palladium complexes were used in the Suzuki-Miyaura coupling of aryl and benzyl chlorides with arylboronic acids.

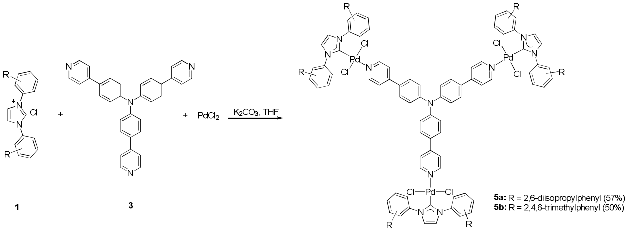
Results and discussion

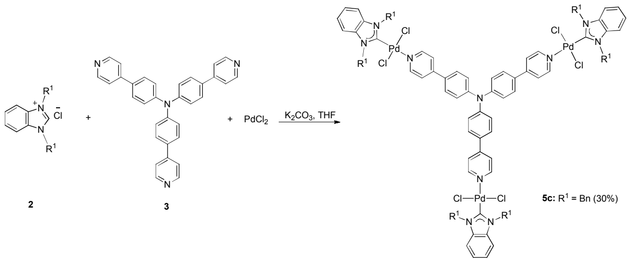
Synthesis and characterization of the trinuclear *N*-heterocyclic carbene-palladium(II) complexes

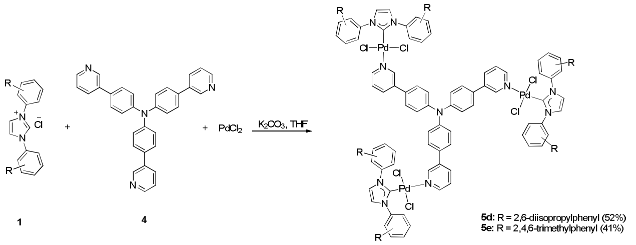
According to our previous report,[9] the trinuclear *N*-heterocyclic carbene-palladium(II) complexes **5** were conveniently prepared through one-pot reactions of imidazolium salts, tridentate *N*-heterocycles {tris(4-(pyridin-4-yl)phenyl)amine or tris(4-(pyridin-3-yl)phenyl)amine} and palladium chloride in one step as shown in Scheme 1. The expected palladium(II) complexes **5** were isolated in good yields (30-57%) and fully characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, and IR spectra. In addition, the trinuclear *N*-heterocyclic carbene-palladium(II) complexes are bench stable.

The molecular structures of Pd complex **5d** was further investigated by X-ray single crystal analysis. The molecules are illustrated in Figures 1. The crystal structure of **5d** showed a trinuclear framework with tridentate *N*-heterocycle ligands bridging across three square planar Pd(II) units. Each palladium center in complex **5d** is surrounded by an imidazolylidene, a pyridine, and two chloro ligands in an almost squareplanar fashion. The values of bond lengths and angles also compare well to those of the related NHC-Pd(II) complexes with *N*-containing compounds.[9, 14] The Pd(1)-C$_{\text{carbene}}$ bond lengths (around 1.986 Å) in complex **5d** are slightly shorter than that of Pd(1)-N(2) (around 2.106 Å). The angles of C$_{\text{carbene}}$-Pd(1)-N(2) and Cl(1)-Pd(1)-Cl(2) are almost close to 180°, while the C$_{\text{carbene}}$-Pd(1)-Cl(1) angles, C$_{\text{carbene}}$-Pd(1)-Cl(2) angles, N(2)-Pd(1)-Cl(1) angles and N(2)-Pd(1)-Cl(2) angles are almost close to 90°.

Scheme 1 Synthesis of trinuclear *N*-heterocyclic carbene-palladium(II) complexes **5a-e**.







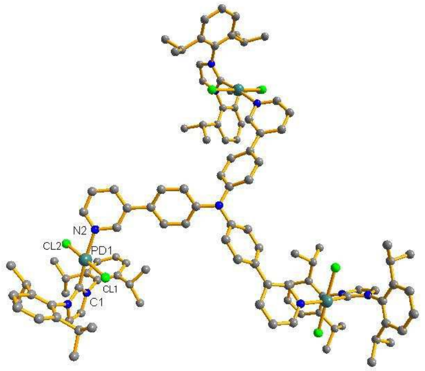


Fig.1 Molecular structures of the trinuclear *N*-heterocyclic carbene-palladium(II) complex **5d**. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg) in complex **5d** : Pd1-C1 1.986(5), Pd1-N2 2.106(4), Pd1-Cl1 2.2784(15), Pd1-Cl2 2.3078(15); C1-Pd1-Cl1 90.96(15), N2-Pd1-Cl1 89.56(12), C1-Pd1-Cl2 88.52(15), N2-Pd1-Cl2 91.09(12), C1-Pd1-N2 173.95(19), Cl1-Pd1-Cl2 178.65(6).

Catalytic study

The cross-coupling of organic halides and organoboron reagents, known as the Suzuki-Miyaura coupling has greatly progressed, especially inspired by 2010 Nobel Prize in chemistry. It has standed out as one of the most powerful and convenient carbon-carbon bond-forming process in natural products, advanced materials and organic synthesis.[15] Although aryl chloridesare less reactive than aryl bromides and aryl iodides, they are very desirable substrates for the coupling reaction because of their economic reason of low cost, availability and stability. As a result, the development of known or new catalysts with excellent catalytic reactivity is in great demand to allow the conversion of challenging aryl chlorides. In the present study, we found that the obtained trinuclear *N*-heterocyclic carbene-palladium(II) complexes could exhibit high catalytic activities in the reaction. In the

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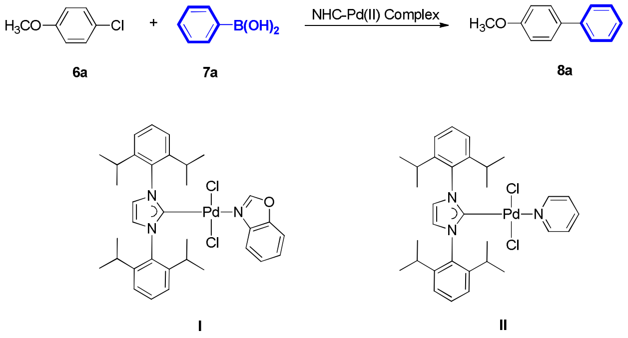
beginning the coupling of 1-chloro-4-methoxybenzene with phenylboronic acid was chosen as a model to evaluate the catalytic properties of complexes **5** in the mixed solvent of ^{i}PrOH (0.4 mL) and H_2O (0.8 mL) (Table 1). When 1.0 mol % of complex **5a** was used as catalyst, KO^{t}Bu, K_3PO_4, Cs_2CO_3 or NaOH as the base, the corresponding biaryl product **8a** was isolated in excellent yield (up to 99%) after 6 h (entries 1-4). KOH was proved to be inferior base affording product in 75% yield (entry 5). Other bases such as Na_2CO_3, NaO^{t}Bu or Na_2HCO_3 afforded the product in low yield (entries 6-8). In a word, base plays crucial role for the yield of the reaction.[16] Product **8a** was obtained in 90% yield when the reaction time was reduced to 4 h (entry 9). When the mixed solvent of EtOH and water was tested, the yield of the product decreased to 73% (entry 10). And increasing the amount of water from 0.8 mL to 0.9 mL led to decreased yield (entry 11). Then the other four trinuclear *N*-heterocyclic carbene-palladium(II) complexes **5b-e** were examined, and excellent yields were still achieved (90-95% yield, entries 12–15). Thus, the optimized conditions include using complex **5a** as the catalyst with K_3PO_4 base and ^{i}PrOH mixed with two equal volume of water as the solvent at 80 °C for 6 h. Fortunately, in our system, the trinuclear *N*-heterocyclic carbene-palladium(II) complexes were found to exhibit better catalytic activity than a related mononuclear NHC-Pd(II) complex in the Suzuki-Miyaura coupling reaction. For example, in the presence of 1 mol % of the mononuclear *N*-heterocyclic carbene-palladium(II) complexes **I** (containing palladium 0.0025 mmol), very low yield of the corresponding product **8a** was obtained (entry 16). While the amount of palladium complexes **I** was further increased to 3 mol% (containing palladium 0.0075 mmol), the yield slightly increased to 71% (entry 18). Similar results were also observed when the Pd-PEPPSI complex **II** was used as the catalysts (Table 1, entries 17 and 19).

Table 1 Optimization of reaction conditions for the Suzuki-Miyaura reaction of 1-chloro-4-methoxybenzene with phenylboronic acid catalyzed by the trinuclear NHC-Pd(II) complexes **5**[a]



Entry	Cat.	Base	Solvent	Yield (%)[b]
1	**5a**	KO^{t}Bu	^{i}PrOH/H_2O (1/2)	94
2	**5a**	Cs_2CO_3	^{i}PrOH/H_2O (1/2)	97
3	**5a**	K_3PO_4	^{i}PrOH/H_2O (1/2)	>99
4	**5a**	NaOH	^{i}PrOH/H_2O (1/2)	96
5	**5a**	KOH	^{i}PrOH/H_2O (1/2)	75
6	**5a**	Na_2CO_3	^{i}PrOH/H_2O (1/2)	35
7	**5a**	NaO^{t}Bu	^{i}PrOH/H_2O (1/2)	41
8	**5a**	$NaHCO_3$	^{i}PrOH/H_2O (1/2)	31
9[c]	**5a**	K_3PO_4	^{i}PrOH/H_2O (1/2)	90
10	**5a**	K_3PO_4	EtOH/H_2O (1/2)	73
11	**5a**	K_3PO_4	^{i}PrOH/H_2O (1/3)	86
12	**5b**	K_3PO_4	^{i}PrOH/H_2O (1/2)	92
13	**5c**	K_3PO_4	^{i}PrOH/H_2O (1/2)	90
14	**5d**	K_3PO_4	^{i}PrOH/H_2O (1/2)	95
15	**5e**	K_3PO_4	^{i}PrOH/H_2O (1/2)	91
16	**I**	K_3PO_4	^{i}PrOH/H_2O (1/2)	35
17	**II**	K_3PO_4	^{i}PrOH/H_2O (1/2)	56
18[d]	**I**	K_3PO_4	^{i}PrOH/H_2O (1/2)	71
19[d]	**II**	K_3PO_4	^{i}PrOH/H_2O (1/2)	85

[a] All reactions were carried out using **6a** (0.25 mmol), **7a** (0.375 mmol), base (2.0 equiv), Cat. (1.0 mol%) in solvent (1.2 mL) at 80 °C for 6 h. [b] Isolated yields. [c] Reaction time was 4 h. [d] Cat. (3.0 mol%).

With optimized conditions in hand, the generality and limitation of the reactions between a variety of aryl chlorides and aryl boronic acids was first tested. The results are shown in Table 2. Gratifyingly, most of the coupling reaction proceeded rapidly and efficiently to provide the corresponding biaryl products in good to almost quantitative yields. Diverse electronic and stericallyhindered substituents in the phenyl ring of aryl chlorides were all tolerated in such transformation and good results were obtained (entries 1-10). For instance, electron-donating groups such as methoxy and methyl group and electron-withdrawing group such as NO_2 group are all tolerated to give the corresponding products in good to almost quantitative yields. It seems that the relative position of the same substituents on the phenyl groups of aryl chlorides did not affect the product yields apparently. For example, the reaction was quite feasible with ortho-substituted aryl chlorides when the phenylboronic acid was used (entries 3 and 6). To our pleasure, heteroaromatic aryl chlorides such as 2-chloropyridine and 3-chloropyridine were also good substrates, giving corresponding products **8i-j** in good to high yields (entries 9-10). Based on the above satisfactory results, kinds of arylboronic acids were also subjected to the optimal conditions to test the generality and limitations (entries 11-18). In most cases, the reaction worked well and approached to corresponding products in good to almost quantitative yields under identical conditions. For instance, electron-rich

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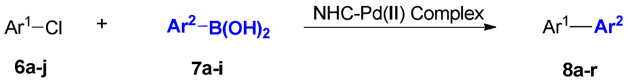
and electron-poor groups substituted boronic acids are all tolerated to give the corresponding products in high yields. However, sterically hindered boronic acid such as 2,6-dimethylphenylboronic acid resulted in a significant decrease in yield (entry 14). In fact, in the case of 3-pyridinylboronic acid or 4-pyridinylboronic acid gave trace amounts of product under the present reaction conditions (data not shown in Table 2). The possible reason for the failure of cross-coupling of pyridinylboronic acid was attributable to their susceptibility to hydrolysis.

Inspired by these successful results, we then turned our interest to such transformations using the benzyl chlorides as the substrates. To our pleasure, the optimal reaction conditions are also suitable for benzyl chlorides. As shown in Table 3, all reactions proceed smoothly to afford diarylmethanes in good to almost quantitative yields under identical conditions. Particularly, when sterically hindered boronic acids such as 2,6-dimethylphenylboronic acid were used as the substrates, high yield of the corresponding product was always observed (99% yield, entry 4). In these reactions, electron-rich, and -neutral substituents on both substrates had a detrimental effect on the catalytic activity instead. Overview, the above results confirm that the present trinuclear *N*-heterocyclic carbene-palladium(II) complexes are highly efficient catalysts for the Suzuki-Miyaura coupling of aryl as well as benzyl chlorides with arylboronic acids.

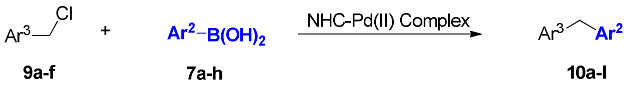
Table 2 Substrate scope for the catalytic Suzuki-Miyaura reaction of aryl chlorides using the NHC-Pd(II) complex **5a** as the catalyst[a]



Entry	**6** (Ar^1)	**7** (Ar^2)	Product	Yield (%)[b]
1	**6a** (4-MeO-C_6H_4)	**7a** (Ph)	**8a**	> 99
2	**6b** (3-MeO-C_6H_4)	**7a** (Ph)	**8b**	> 99
3	**6c** (2-MeO-C_6H_4)	**7a** (Ph)	**8c**	98
4	**6d** (4-Me-C_6H_4)	**7a** (Ph)	**8d**	99
5	**6e** (3-Me-C_6H_4)	**7a** (Ph)	**8e**	99
6	**6f** (2-Me-C_6H_4)	**7a** (Ph)	**8f**	94
7	**6g** (4-CH_3CO-C_6H_4)	**7a** (Ph)	**8g**	99
8	**6h** (4-NO_2-C_6H_4)	**7a** (Ph)	**8h**	87
9	**6i** (2-Pyridyl)	**7a** (Ph)	**8i**	84
10	**6j** (3-Pyridyl)	**7a** (Ph)	**8j**	99
11	**6a** (4-OMe-C_6H_4)	**7b** (4-Me-C_6H_4)	**8k**	> 99
12	**6a** (4-OMe-C_6H_4)	**7c** (3-Me-C_6H_4)	**8l**	99
13	**6a** (4-OMe-C_6H_4)	**7d** (2-Me-C_6H_4)	**8m**	99
14	**6a** (4-OMe-C_6H_4)	**7e** (2,6-Me_2-C_6H_3)	**8n**	57
15	**6a** (4-OMe-C_6H_4)	**7f** (4-F-C_6H_4)	**8o**	99
16	**6a** (4-OMe-C_6H_4)	**7g** (4-CF_3-C_6H_4)	**8p**	98
17	**6a** (4-OMe-C_6H_4)	**7h** (1-Naphthyl)	**8q**	99
18	**6a** (4-OMe-C_6H_4)	**7i** (2-Naphthyl)	**8r**	98

[a]All reactions were carried out using **6** (0.25 mmol), **7** (0.375 mmol), K_3PO_4 (2.0 equiv), Cat. **5a** (1.0 mol%) in ^{i}PrOH/H_2O (V:V = 1:2, 1.2 mL) at 80 °C for 6 h. [b]Isolated yields.

Table 3 Substrate scope for the catalytic Suzuki-Miyaura reaction of benzyl chlorides using the NHC-Pd(II) complex **5a** as the catalyst[a]



Entry	**9** (Ar^3)	**7** (Ar^2)	Product	Yield (%)[b]
1	**9a** (Ph)	**7b** (4-Me-C_6H_4)	**10a**	> 99
2	**9a** (Ph)	**7c** (3-Me-C_6H_4)	**10b**	99
3	**9a** (Ph)	**7d** (2-Me-C_6H_4)	**10c**	99
4	**9a** (Ph)	**7e** (2,6-Me_2-C_6H_3)	**10d**	99
5	**9a** (Ph)	**7f** (4-F-C_6H_4)	**10e**	75
6	**9a** (Ph)	**7g** (4-CF_3-C_6H_4)	**10f**	81
7	**9a** (Ph)	**7h** (1-Naphthyl)	**10g**	99
8	**9b** (4-^{t}Bu-C_6H_4)	**7a** (Ph)	**10h**	87
9	**9c** (4-Me-C_6H_4)	**7a** (Ph)	**10i**	99
10	**9d** (3-Me-C_6H_4)	**7a** (Ph)	**10j**	96
11	**9e** (2-Me-C_6H_4)	**7a** (Ph)	**10k**	72
12	**9f** (4-F-C_6H_4)	**7a** (Ph)	**10l**	66

[a]All reactions were carried out using **9** (0.25 mmol), **7** (0.375 mmol), K_3PO_4 (2.0 equiv), Cat. **5a** (1.0 mol%) in ^{i}PrOH/H_2O (V:V = 1:2, 1.2 mL) at 80 °C for 6 h. [b]Isolated yields.

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Conclusions

In summary, a new class of trinuclear *N*-heterocyclic carbene-palladium(II) complexes as catalysts has been developed successfully. These complexes are easy to prepare and their structures can be readily modified as well. Furthermore, they have revealed high activity in the catalytic Suzuki-Miyaura coupling reaction. With a typical catalyst loading of 1.0 mol%, a variety of electronically and structurally diverse aryl chlorides as well as benzyl chlorides reacted effectively with arylboronic acids, thus providing a convenient and alternative method for the synthesis of biaryl products. Further modification of the trinuclear *N*-heterocyclic carbene-palladium(II) complexes and their applications in other reactions are in progress.

Experimental

General procedures

Reactions for the preparation of trinuclear *N*-heterocyclic carbene-palladium(II) complexes as well as all the catalytic reactions were carried out under nitrogen atmosphere. Solvents were dried with standard methods and freshly distilled prior to use if needed. Tris(4-(pyridin-4-yl)phenyl)amine **3** and tris(4-(pyridin-3-yl)phenyl)amine **4** were prepared according to the literature methods.[17] All other chemicals were used as purchased. Melting points were measured on an XT4A melting point apparatus and are uncorrected. IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 instrument using TMS as an internal standard. Elemental analyses were measured on a Thermo Flash EA 1112 elemental analyzer.

Table 4 Summary of crystallographic details for complex **5d**

	Complex 5d
Empirical formula	$C_{114}H_{135}Cl_6N_{10}Pd_3$
Mr	2177.3367
temperature (K)	173(2)
wavelength (Å)	0.71073
crystal system	trigonal
cryst size (mm)	0.28 x 0.22 x 0.15
a (Å)	24.2624(8)
b (Å)	24.2624(8)
c (Å)	13.1013(4)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	6679.0(4)
Z	2
space group	P-3
D_{calcd} (g cm^{-3})	1.213
μ (mm^{-1})	0.572
ϑ range (°)	2.91-22.97
F(000)	2540
no. of data collected	104000
no. of unique data	6182
R(int)	0.0832
final R indices	$R_1 = 0.0524$
($I > 2\sigma(I)$)	$wR_2 = 0.1336$
R indices (all data)	$R_1 = 0.0700$
	$wR_2 = 0.1471$
Largest diff peak and hole (e·Å^{-3})	1.029 and -0.694

General procedure for the synthesis of trinuclear N-heterocyclic carbene-palladium(II) complexes 5a-e

Under an N_2 atmosphere, the mixture of imidazolium salts (0.33 mmol), tridentate N-heterocycles (0.1 mmol), $PdCl_2$ (58.5 mg, 0.33 mmol) and K_2CO_3 (45.6 mg, 0.33 mmol) was stirred in anhydrous THF (5 mL) under reflux for 12 h. After cooling, filtration and evaporation, the residue was purified by preparative TLC on silica gel plates eluting with CH_2Cl_2 to afford the corresponding trinuclear N-heterocyclic carbene-palladium(II) complexes 5a-e.

Complex **5a**: Pale yellow solid (124.1 mg, 57%). M.p.: 221-223 °C. IR (KBr): ν 2963, 2917, 2866, 1595, 1521, 1489, 1466, 1410, 1329, 1224, 944, 819, 803, 758, 703 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, J = 6.5 Hz, 2H, ArH), 7.49 (t, J = 7.7 Hz, 2H, ArH), 7.37-7.34 (m, 6H, ArH), 7.24 (d, J = 6.6 Hz, 2H, ArH), 7.13-7.09 (m, 4H, ArH), 3.22-3.15 (m, 4H, $CH(CH_3)_2$), 1.49 (d, J = 6.5 Hz, 12H, $CH(CH_3)_2$), 1.12 (d, J = 6.8 Hz, 12H, $CH(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 151.4, 148.8, 148.0, 146.7, 135.1, 130.2, 128.1, 125.0, 124.7, 124.0, 121.2, 28.7, 26.3, 23.3. Anal. Calcd for $C_{114}H_{135}Cl_6N_{10}Pd_3$ (2177.34): C, 62.89; H, 6.25; N, 6.43. Found: C, 62.59; H, 6.74; N, 6.38.

Complex **5b**: Pale yellow solid (96.2 mg, 50%). M.p.: 224-227 °C. IR (KBr): ν 2954, 2919, 2856, 1597, 1519, 1488, 1434, 1408, 1376, 1331, 1292, 1227, 927, 853, 819, 761, 730, 699 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, J = 6.4 Hz, 2H, ArH), 7.39 (d, J = 8.6 Hz, 2H, ArH), 7.24 (d, J = 6.6 Hz, 2H, ArH), 7.12-7.05 (m, 8H, ArH), 2.37 (s, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 151.5, 148.8, 148.0, 139.2, 136.4, 135.1, 129.3, 128.2, 124.7, 124.2, 121.1, 21.2, 19.2. Anal. Calcd for $C_{96}H_{99}Cl_6N_{10}Pd_3$ (1924.86): C, 59.90; H, 5.18; N, 7.28. Found: C, 59.43; H, 5.65; N, 7.22.

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Complex **5c**: Pale yellow solid (57.2 mg, 30%). M.p.: 168-171 °C. IR (KBr): ν 3031, 2922, 2851, 1611, 1594, 1519, 1488, 1448, 1414, 1327, 1290, 1222, 1187, 1027, 817, 740, 711 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.99 (d, J = 5.3 Hz, 2H, ArH), 7.64-7.51 (m, 8H, ArH), 7.40-7.24 (m, 8H, ArH), 7.10-7.08 (m, 4H, ArH), 6.28 (s, 4H, CH$_2$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 165.0, 151.3, 149.4, 148.3, 135.1, 134.6, 131.7, 128.9, 128.4, 128.2, 128.0, 124.9, 123.3, 121.6, 111.5, 53.2. Anal. Calcd for $C_{96}H_{81}Cl_6N_{10}Pd_3$ (1906.72): C, 60.47; H, 4.28; N, 7.35. Found: C, 60.13; H, 4.66; N, 7.30.

Complex **5d**: Pale yellow solid (113.2 mg, 52%). M.p.: 228-231 °C. IR (KBr): ν 2965, 2913, 2862, 1585, 1520, 1484, 1465, 1408, 1320, 1219, 943, 817, 803, 756, 703 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.78 (s, 1H, ArH), 8.50 (d, J = 4.6 Hz, 1H, ArH), 7.70 (d, J = 7.8 Hz, 1H, ArH), 7.49 (t, J = 7.7 Hz, 2H, ArH), 7.36 (d, J = 7.7 Hz, 4H, ArH), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.16-7.11 (m, 5H, ArH), 3.24-3.17 (m, 4H, C*H*(CH$_3$)$_2$), 1.51 (d, J = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 1.13 (d, J = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 154.9, 149.8, 149.4, 147.4, 146.7, 136.7, 135.1, 131.3, 130.3, 128.1, 125.0, 124.8, 124.1, 123.8, 28.8, 26.3, 23.3. Anal. Calcd for $C_{114}H_{135}Cl_6N_{10}Pd_3$ (2177.34): C, 62.89; H, 6.25; N, 6.43. Found: C, 62.62; H, 6.59; N, 6.41.

Complex **5e**: Pale yellow solid (78.9 mg, 41%). M.p.: 184-187 °C. IR (KBr): ν 2955, 2916, 2848, 1596, 1512, 1480, 1438, 1408, 1387, 1331, 1294, 1223, 927, 855, 819, 767, 729, 696 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.72 (s, 1H, ArH), 8.49 (d, J = 3.4 Hz, 1H, ArH), 7.71 (d, J = 6.0 Hz, 1H, ArH), 7.33 (d, J = 6.8 Hz, 2H, ArH), 7.15-7.13 (m, 3H, ArH), 7.06 (s, 7H, ArH), 2.38 (s, 18H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 152.6, 149.8, 149.6, 147.4, 139.2, 136.4, 135.1, 129.3, 128.4, 124.7, 124.2, 123.7, 21.3, 19.2. Anal. Calcd for $C_{96}H_{99}Cl_6N_{10}Pd_3$ (1924.86): C, 59.90; H, 5.18; N, 7.28. Found: C, 59.55; H, 5.63; N, 7.19.

General procedure for the catalytic Suzuki-Miyaura coupling reaction

A Schlenk flask was charged with aryl chlorides (0.25 mmol), arylboronic acids (0.375 mmol), trinuclear *N*-heterocyclic carbene-palladium(II) complex **5** (1 mol %), K$_3$PO$_4$ (2.0 equiv), ^{i}PrOH (0.4 mL) and H$_2$O (0.8 mL). The mixture was stirred at 80 °C for 6 h under N$_2$. After cooling, the reaction mixture was evaporated and the product was isolated by preparative TLC on silica gel plates.

X-ray diffraction studies

Crystal of **5d** (CCDC 1472981) was obtained by recrystallization from CH$_2$Cl$_2$/n-hexane at ambient temperature. Their data were collected on an Oxford diffraction Gemini E diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71073 Å). The structures were solved by direct methods using the SHELXS-97 program, and all non-hydrogen atoms were refined anisotropically on F2 by the full-matrix least-squares technique, which used the SHELXL-97 crystallographic software package.[18] The hydrogen atoms were included but not refined. Squeeze indicates a total solvent accessible area volume of 124 Å^3, corresponding to about 12 electrons per cell or approximately 1 water molecules per formula. Details of the crystal structure determination of the Pd(II) complex **5d** was summarized in Table 4.

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Notes and references

1 A. J. Arduengo III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc*., 1991, **113**, 361.

2 (a) F. E. Hahn and M. C. Jahnke, *Angew. Chem. Int. Ed*., 2008, **47**, 3122; (b) V. Nair, S. Vellalath and B. P. Babu, *Chem. Soc. Rev*., 2008, **37**, 2691; (c) S. Diez-Gonzalez, N. Marion and Steven P. Nolan, *Chem. Rev*., 2009, **109**, 3612; (d) T. Droge and F. Glorius, *Angew. Chem. Int. Ed*., 2010, **49**, 6940; (e) G. C. Fortman and S. P. Nolan, *Chem. Soc. Rev*.; 2011, **40**, 5151; (f) D. Yuan and H. V. Huynh, *Molecules*, 2012, **17**, 2491; (g) S. Budagumpi, R. A. Haque and A. W. Salman, Coordin. *Chem. Rev*.; 2012, **256**, 1787; (h) R. S. Menon, A. T. Biju and V. Nair, *Chem. Soc. Rev*.; 2015, **44**, 5040.

3 For selected examples, see: (a) C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A.Chass, A. Lough, A. C. Hopkinson and M. G. Organ, *Chem.-Eur. J*., 2006, **12**, 4743; (b) M. G. Organ, S. Avola, I. Dubovyk, N. Hadei, E. A. B. Kantchev, C. J. O'Brien and C. Valente, *Chem.-Eur. J*., 2006, **12**, 4749; (c) E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, *Angew. Chem., Int. Ed*., 2007, **46**, 2768; (d) C. Valente, S. Baglione, D. Candito, C. J. O'Brien and M. G. Organ, *Chem. Commun*., 2008, 735; (e) G. Shore, S. Morin, D. Mallik and M. G. Organ, *Chem.-Eur. J*., 2008, **14**, 1351; (f) M. G. Organ, M. Abdel-Hadi, S. Avola, I. Dubovyk, N. Hadei, E. A. B. Kantchev, C. J. O'Brien, M. Sayah and C. Valente, *Chem.-Eur. J*., 2008, **14**, 2443; (g) J. Nasielski, N. Hadei, G. Achonduh, E. A. B. Kantchev, C. J. O. Brien, A. Lough and M. G. Organ, *Chem. Eur. J*., 2010, **16**, 10844; (h) J. L. Farmer, M. Pompeo, A. J. Lough and M. G. Organ, *Chem. Eur. J*., 2014, **20**, 15790.

4 (a) T. Tu, W. Fang and J. Jiang, *Chem. Commun*., 2011, **47**, 12358; (b) T. Tu, Z. Sun, W. Fang, M. Xu, Y. Zhou, *Org. Lett*., 2012, **14**, 4250; (c) W. Fang, Q. Deng, M. Xu and T. Tu, *Org. Lett*., 2013, **15**, 3678; (d) Z. Liu, N. Dong, M. Xu, Z. Sun and T. Tu, *J. Org. Chem*., 2013, **78**, 7436; (e) S. Liu, Q. Deng, W. Fang, J. -F. Gong, M. -P. Song, M. Xu and T. Tu, *Org. Chem. Front*., 2014, **1**, 1261.

5 F. Rajabi and W. R. Thiel, *Adv. Synth. Catal*., 2014, **356**, 1873.

6 M. Teci, E. Brenner, D. Matt and L. Toupet, *Eur. J. Inorg. Chem*.; 2013, 2841.

7 M. Micksch, M. Tenne and T. Strassner, *Organometallics*, 2014, **33**, 3966.

8 (a) H. -Y. Yin, M. -Y. Liu and L. -X. Shao, *Org. Lett*., 2013, **15**, 6042; (b) H. Lv, L. Zhu, Y. -Q.Tang and J. -M. Lu, *Appl. Organometal. Chem*., 2014, **28**, 27; (c) Z.- K. Xiao, H. -Y. Yin and J. -M. Lu, *Inorg. Chim. Acta*., 2014, **423**, 106; (d) X. -B. Shen, Y. Zhang, W. -X. Chen, Z. -K. Xiao, T. -T. Hu and L. -X. Shao, *Org. Lett*., 2014, **16**, 1984; (e) Z. -S. Gu, W. -X.Chen and L. -X. Shao, *J. Org. Chem*., 2014, **79**, 5806; (f) Y. Zhang, S. -C. Yin and J. -M. Lu, *Tetrahedron*, 2015, **71**, 544.

9 T. Wang, H. Xie, L. Liu and W - X. Zhao, *J. Organomet. Chem*., 2016, **804**, 73.

View Article Online
DOI: 10.1039/C6RA20852E

10 T.Wang, K. Xu, L. Liu, H. Xie, Y. Li and W - X. Zhao, *Transition Met Chem*., 2016, **41**, 525.

11 For selected examples, see: (a) V. Jurcik, S. P. Nolan and C. S. J. Cazin, *Chem.-Eur. J.*, 2009, **15**, 2509; (b) O. Diebolt, V. Jurcik, R. Correa da Costa, P. Braunstein, L. Cavallo, S. P. Nolan, A. M. Z. Slawin and C. S. J. Cazin, *Organometallics*, 2010, **29**, 1443; (c) X. Cai, S. Majumdar, G. C. Fortman, C. S. J. Cazin, A. M. Z. Slawin, C. Lhermitte, R. Prabhakar, M. E. Germain, T. Palluccio, S. P. Nolan, E. V. Rybak-Akimova, M. Temprado, B. Captain and C. D. Hoff, *J. Am. Chem. Soc*., 2011, **133**, 1290; (d) V. Jurčík, T. E. Schmid, Q. Dumont, A. M. Z. Slawin and C. S. J. Cazin, *Dalton Trans*., 2012, **41**, 12619; (e) J. Broggi, V. Jurcik, O. Songis, A. Poater, L. Cavallo, A. M. Z. Slawin and C. S. J. Cazin, *J. Am. Chem. Soc*., 2013, **135**, 4588; (f) T. E. Schmid, D. C. Jones, O. Songis, O. Diebolt, M. R. L. Furst, A. M. Z. Slawin and C. S. J. Cazin, *Dalton Trans*., 2013, **42**, 7345; (g) C. E. Hartmann, V. Jurčík, O. Songis and C. S. J. Cazin, *Chem. Commun*., 2013, **49**, 1005.

12 (a) Y. Han, H. V. Huynh and G. K. Tan, *Organometallics*, 2007, **26**, 6447; (b) J. Yang and L.Wang, *Dalton Trans*., 2012, **41**, 12031.

13 (a) J. Yang, P. Li, Y. Zhang and L. Wang, *J. Organomet. Chem*., 2014, **766**, 73; (b) J. Yang, P. Li, Y. Zhang and L. Wang, *Dalton Trans*., 2014, **43**, 7166.

14 (a) M.-T. Chen, D. A. Vicic, M. L. Turner and O. Navarro, *Organometallics*, 2011, **30**, 5052; (b) L. Zhu, T.-T. Gao and L.-X. Shao, *Tetrahedron*, 2011, **67**, 5150; (c) P. Huang, Y. -X. Wang, H. - F. Yu and J. -M. Lu, *Organometallics*, 2014, **33**, 1587.

15 (a) N. Miyaura and A. Suzuki, *Chem. Rev*., 1995, **95**, 2457; (b) A. Suzuki, *J. Organomet. Chem*., 1999, **576**, 147; (c) J.-P. Corbet and G. Mignani, *Chem. Rev*., 2006, **106**, 2651; (d) N. Marion and S. P. Nolan, *Acc. Chem. Res*., 2008, **41**, 1440; (e) G. C. Fu, *Acc. Chem. Res*., 2008, **41**, 1555; (f) C. Valente, S. Calimsiz, K.-H. Hoi, D. Mallik, M. Sayah and M. G. Organ, *Angew. Chem. Int. Ed*., 2012, **51**, 3314.

16 K. Ouyang and Z. Xi, *Acta Chim. Sinica*, 2013, **71**, 13.

17 C. Hua, P. Turner and D. M. D'Alessandro, *Dalton Trans*., 2013, **42**, 6310.

18 (a) G. M.Sheldrick, SHELXS-97, Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, 1997. (b) G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

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